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STEP-GROWTH PHOTOPOLYMERIZATIONS

Final Technical Report

by

W.J. Feast

January 1979

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EUROPEAN RESEARCH OFFICE
United States Army
London England

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SUMMARY

This report is divided into two parts.

The first part describes an attempt to extend earlier work on step-growth photopolymerization leading to polyoxetanes to the synthesis of fluorinated polyoxetanes. This work, which was the primary objective of the research, was unfruitful. A variety of olefin and carbonyl containing monomers were prepared but all polymerization attempts failed.

The second part of the report describes work undertaken in response to the difficulties encountered with the initial project, several topics involving the use of aromatic carbonyl compounds as components of potential step-growth photoreductive photopolymerizations were investigated. Some work was carried out on photoreductive polymerization leading to polypinacols, and the possibility of extending this approach to the synthesis of polymers with pentaphenylglycerol or tetraphenylethanol repeat units was also examined. This work led to the synthesis of some novel polymers and provided information on the limitations of some photochemical reactions, which were thought to be rather more general than now turns out to be the case. Finally, preliminary work on the use of aromatic aldehydes as monomers in step-growth photopolymerizations is reported.

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Preface

The work described in this report was funded on the basis of a proposal submitted to ERO in March 1974.[1] The proposal envisaged extending earlier work on step-growth photopolymerization leading to polyoxetanes[2,3,4] to the synthesis of fluorinated polyoxetanes. The primary objectives were the synthesis of monomers of the type shown in Figure 1 and their photopolymerization. The units A, B, D and E in Figure 1 could, in principle, be chosen from a very wide selection of possibilities but priority was to be given to fluorine or fluoroalkylene sequences.

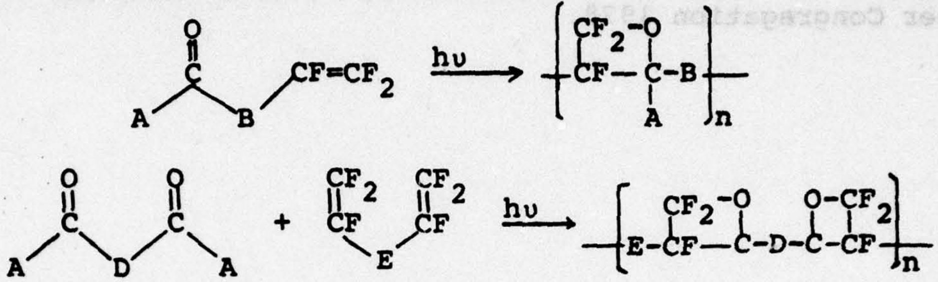


Figure 1. Schematic for proposed synthesis of fluorinated polyoxetanes.

Two research students, Mr. Constantine Spanomanolis and Mr. R. Bruce Tulloch commenced work on this project during the summer of 1975. The work was largely unsuccessful and is described in detail in Part 1 of this report. In the face of the difficulties encountered with the initial project a second line of work was undertaken in the same general research area of step-growth photopolymerization. This second line of research proved somewhat more fruitful and is described in Part 2 of this report. During the course of the investigation of the initial project both research students were required by the regulations of the University to write reports and pass oral examinations, these qualifying tests are taken at the end of the first year. Mr. Spanomanolis was successful at the first attempt but Mr. Tulloch did not reach the required standard of performance; however, due to extenuating personal circumstances, he was granted a further qualifying period in which to improve his performance, unfortunately he was unable to achieve the expected improvement and he left the University in the summer of 1977, the work he carried out forms a part of Part 1 of this report. Since the initial grant allowed for two research students for three years there remained one year's grant and accordingly Mr. Jonathan Batey started work on the project in October 1977 aiming to complete an M.Sc. in one year. Mr. Batey's work forms a part of Part 2 of this report.

Both Mr. Batey and Dr. Spanomanolis successfully completed all the requirements of their courses, including submission of theses [Batey (M.Sc.), Spanomanolis (Ph.D.)], and received their degrees at the December Congregation 1978.

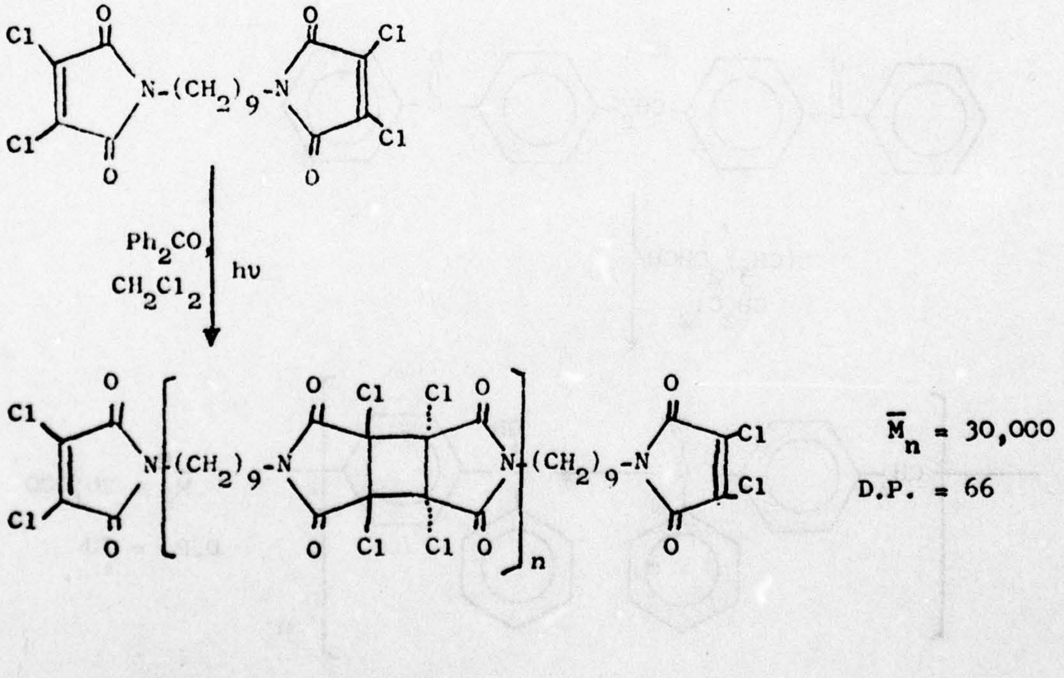
Part 1

1.1. Introduction and Background

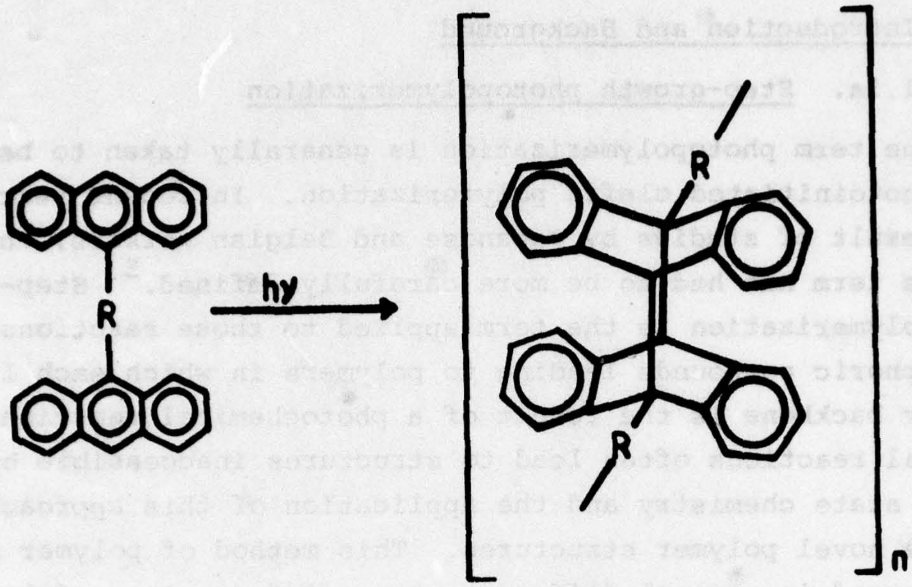
1.1a. Step-growth photopolymerization

The term photopolymerization is generally taken to be synonymous with photoinitiated olefin polymerization. In recent years, chiefly as a result of studies by Japanese and Belgian workers, the meaning of this term has had to be more carefully defined.[5] Step-growth photopolymerization is the term applied to those reactions of bis-chromophoric compounds leading to polymers in which each link in the polymer backbone is the result of a photochemical reaction. Photochemical reactions often lead to structures inaccessible by conventional ground state chemistry and the application of this approach has led to some novel polymer structures. This method of polymer synthesis can be used in several different ways and four successful cases are given below as illustrations:

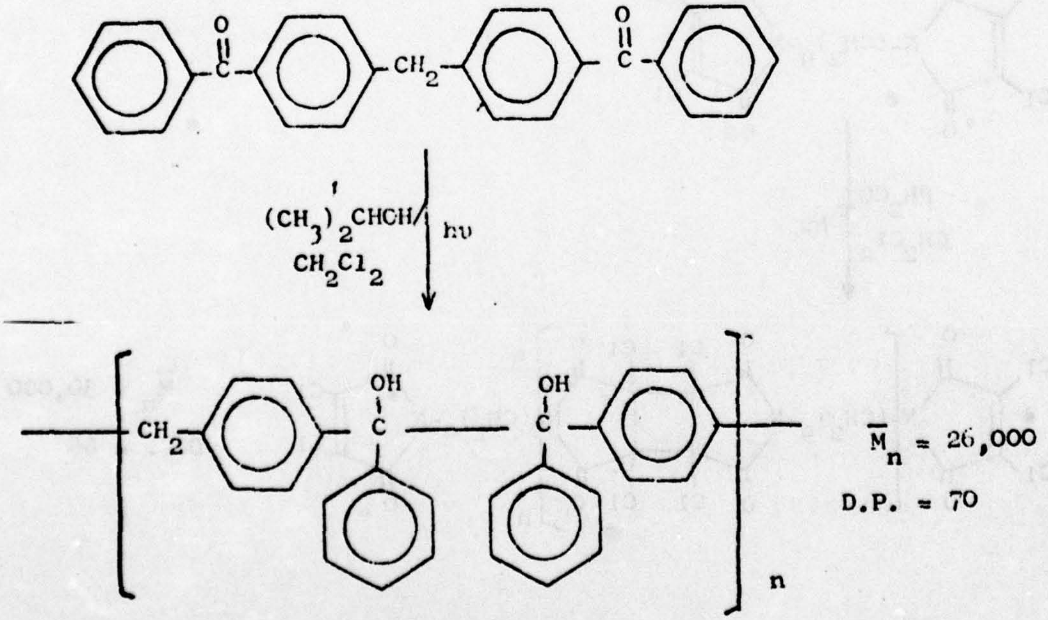
(i) Reaction via the triplet excited manifold:[6]



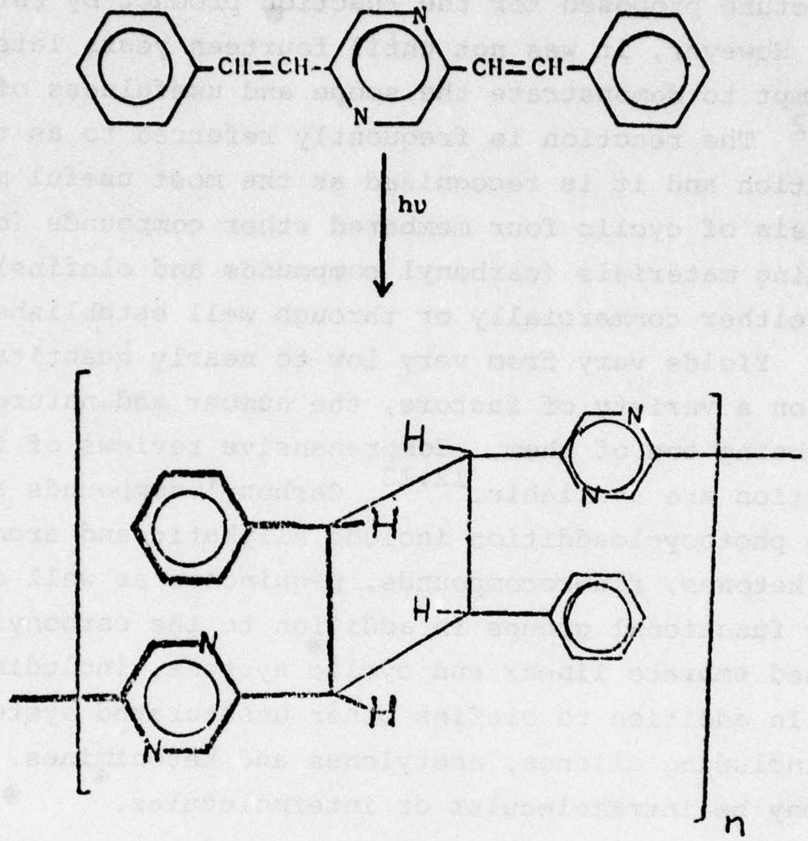
(ii) **Reaction via the singlet excited manifold:**[7]



(iii) **Reaction via species derived from a previous photochemical reaction,**[8] **in the example below via a pinacol radical.**



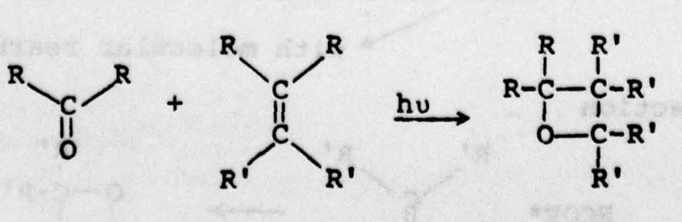
(iv) Solid phase photopolymerization:[9]



Although this approach to polymer synthesis clearly offers a potential route to a variety of polymers of novel structure relatively few reports of successful step-growth photopolymerizations have followed the examples published in the early years of this decade. Work in the author's laboratory[2-4] provided a start on the investigation of the application of the Paterno-Büchi reaction (see later) to polymer formation, the work described in this report was undertaken with the intention of extending this area of polymer synthesis.

1.1b. *The Paterno-Büchi reaction*

The photocycloaddition of carbonyl compounds to olefins leading to the formation of oxetanes (I) was first reported by Paterno and Chieffi at the beginning of the century.[10] Büchi reinvestigated the



reaction in 1954[11] and as a result of his work the cyclic four member ether structure proposed for the reaction product by Paterno was verified. However, it was not until fourteen years later that the first attempt to demonstrate the scope and usefulness of the reaction was made.[12] The reaction is frequently referred to as the Paterno-Büchi reaction and it is recognised as the most useful method for the synthesis of cyclic four membered ether compounds (oxetanes). Both starting materials (carbonyl compounds and olefins) are readily available either commercially or through well established laboratory syntheses. Yields vary from very low to nearly quantitative, depending on a variety of factors, the number and nature of side reactions being one of them. Comprehensive reviews of the Paterno-Büchi reaction are available.[12,13] Carbonyl compounds successfully undergoing photocycloaddition include aliphatic and aromatic aldehydes and ketones, fluorocompounds, p-quinones as well as compounds containing functional groups in addition to the carbonyl group. Olefins used embrace linear and cyclic systems, including fluoroolefins. In addition to olefins other unsaturated systems have been employed including allenes, acetylenes and ketenimines. The cycloaddition may be intramolecular or intermolecular.

Photoreduction and cycloaddition reactions are characteristic of the carbonyl $n \rightarrow \pi^*$ state and carbonyl compounds undergoing photocycloaddition generally undergo photoreduction in isopropanol. The important steps in the reaction for electron rich olefins may frequently be represented by the scheme shown in Figure 2.

i) Excitation

$$\text{RCOR} \xrightarrow{h\nu} \text{RCOR* (singlet)}$$

ii) Intersystem Crossing

$$\text{RCOR* (singlet)} \longrightarrow \text{RCOR* (triplet)}$$

iii) Deactivation

$$\begin{tikzcd}
 & \text{radiative or non-radiative} \arrow[dr] & \\
\text{RCOR*} \arrow[ur] \arrow[r] \arrow[dr] & \text{with or without quenchers} \arrow[r] & \text{RCOR (ground state)} \\
 & \text{with molecular rearrangement} \arrow[ur] &
\end{tikzcd}$$

iv) Reaction

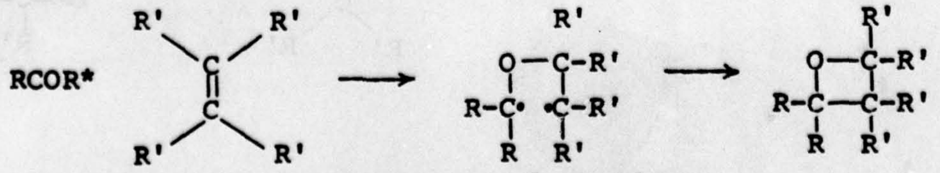
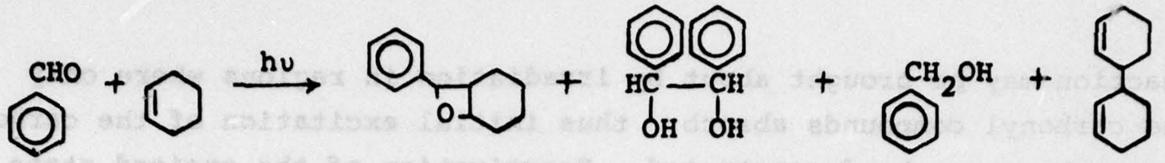


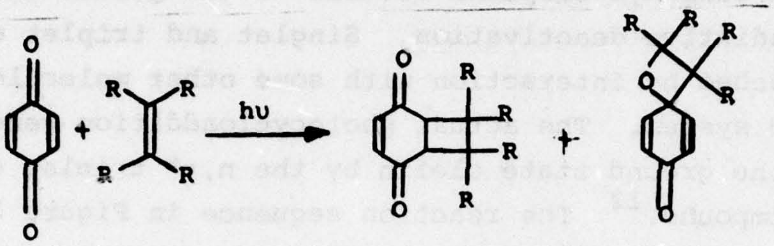
Figure 2. Reaction scheme for oxetane formation.

Reaction may be brought about by irradiation in regions where only the carbonyl compounds absorb; thus initial excitation of the carbonyl chromophore can be demonstrated. Deactivation of the excited state without oxetane formation may occur by a variety of competing processes, the n,π^* triplet existing in fluid solution for approximately 10^{-5} sec.[14] The rate of cycloaddition must be rapid enough to occur before the excited carbonyl compound returns to the ground state by, for example, radiative deactivation. Singlet and triplet excited states may be quenched by interaction with some other molecule such as an unsaturated system. The actual photocycloaddition generally involves attack on the ground state olefin by the n,π^* triplet excited carbonyl compound.[12] The reaction sequence in Figure 2 involves addition of the lone electron on the oxygen atom to an unsaturated system giving a 1,4-biradical intermediate which subsequently ring closes to form the oxetane. With unsymmetrical unsaturated olefins two isomers may be formed; the structure of the major adduct is predictable from considerations of which of the two possibilities corresponds to the most stable biradical intermediate. There is good evidence for the formation of the biradical intermediate during the reaction,[12] and a large amount of experimental data can be rationalized by the biradical mechanism. There are however alternative mechanisms proposed which include charge-transfer complex formation,[15] and exciplex formation.[16,17] For instance intramolecular cycloaddition in 5-hept-2-one is thought to proceed via singlet exciplex formation.[18] It has also been suggested that cycloaddition of benzophenone to 2,3-dimethyl-1,3-butadiene proceeds by addition of diene triplet to ground state benzophenone,[19] and there are several other reports of oxetane formation from excited olefins and ground state carbonyl compounds.[20,21,22]

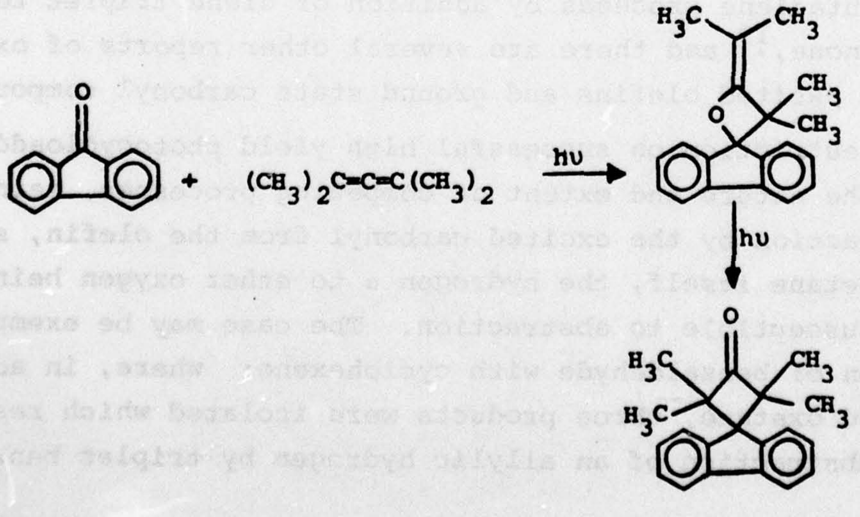
A major restriction on successful high yield photocycloaddition reactions is the nature and extent of competing processes, mainly hydrogen abstraction by the excited carbonyl from the olefin, solvent, or even the oxetane itself, the hydrogen α to ether oxygen being particularly susceptible to abstraction. The case may be exemplified by the reaction of benzaldehyde with cyclohexene; where, in addition to the expected oxetane, three products were isolated which result from initial abstraction of an allylic hydrogen by triplet benzaldehyde:-



Cyclobutane formation may be an alternative reaction to oxetane formation, as with 1,4-quinones such as chloranil.[23]



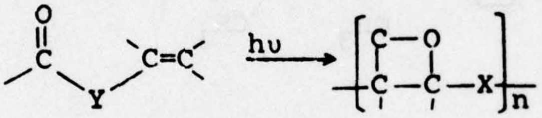
Norrish type I and type II processes may compete with oxetane formation. Norrish type I rupture of acyl-halide bonds of perfluoroacylchlorides and bromides competes with oxetane formation from these carbonyl compounds.[24] Products must be stable to the irradiation conditions used. Oxetanes are transparent in the long wavelength region but may ring open on irradiation at short wavelengths.[25] Photochemically active chromophores present in addition to the carbonyl group of the carbonyl compound may lead to complications, for example the irradiation of fluorenone and tetramethylallene proceeds via initial oxetane formation to the final product shown below.[26]

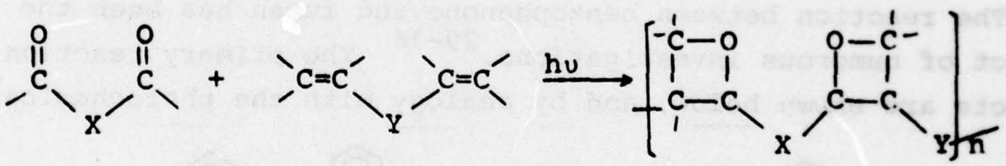


Oxetane products, though detectable and characterizable by infrared and n.m.r. spectroscopy, may be too unstable for purification; an example being the oxetane from 4,4'-dimethoxybenzophenone and isobutylene which fragments into formaldehyde and diarylethylene.[12,27]

1.1c. The application of the Paterno-Büchi reaction to polymer synthesis.

The photochemical reaction of a carbonyl group with an olefin yielding an oxetane has been used for crosslinking, chain extension and structural modification of polymers.[28] In principle, there are two possible ways in which the reaction can be used in the synthesis of linear polymers with oxetane units in the polymer chain; they are generalized below:





The lower route was examined by Andrews and Feast;[3,4] a variety of aromatic bisketones and two different diolefinic systems, tetramethylallene and furan were used as monomers. Their choice was based on several criteria:-

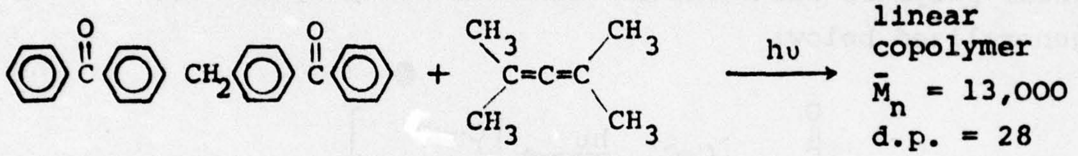
(i) the model reactions with monofunctional reagents were thoroughly studied and understood;[12]

(ii) the monomers and polymers were soluble in photostable solvents;

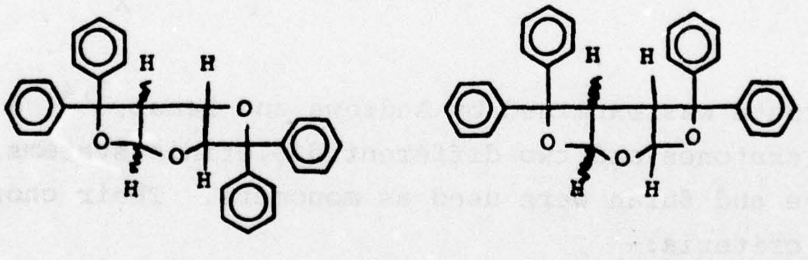
(iii) the reactions proceeded in high yield and conversion without chain terminating side reactions and both reactants and products were stable to radiation in the energy range required for photopolymerization.

These restrictions eliminated a large proportion of the documented Paterno-Büchi reactions as candidates for these initial photopolymerization studies.

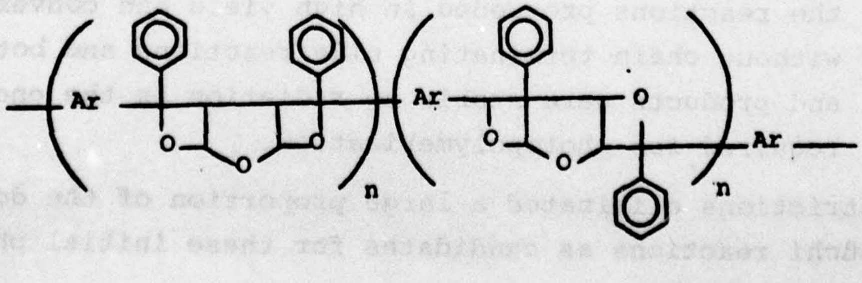
In the case of the bisketone-tetramethylallene photopolymerizations, the investigations carried out established that under appropriate conditions copolymers in which ca. 90% of the polymer chain links are oxetanes can be prepared by irradiation of equimolar solutions of aromatic diketones and tetramethylallene in benzene solution. In this respect, the behaviour of aromatic bisketones seem to be in line with the behaviour of their monofunctional analogue, benzophenone, which affords ca. 90% oxetanes upon irradiation in tetramethylallene, and 10% hydroxyl-containing products, arising presumably from radicals formed in an initial hydrogen abstraction reaction by the photoexcited carbonyl. For example:



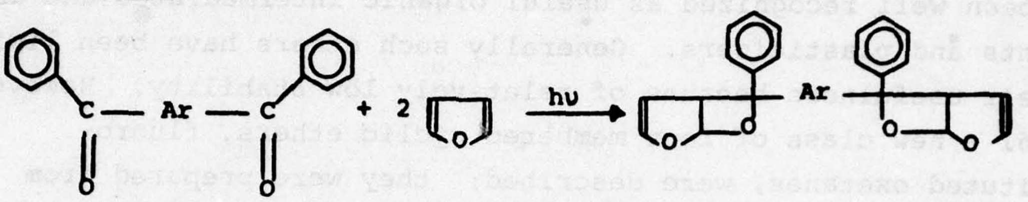
The reaction between benzophenone and furan has been the subject of numerous investigations.[29-36] The primary reaction products are shown below, and by analogy with the photochemical



behaviour of the bisketone-tetramethylallene system, irradiation of equimolar amounts of bisketones and furan in benzene were expected to yield polymers of structure:-



Several attempts to effect the expected reaction were largely unsuccessful, yielding only low molecular weight materials suggesting that the problems inherent in the quantitative manipulation of furan (b.p. 32°C) were preventing the preparation of precisely equimolar solutions. Finally this difficulty was overcome by preparing 2:1 adducts between the diketones and furan by the route shown below.



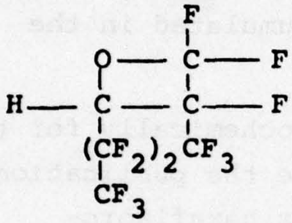
These adducts being solids could be quantitatively manipulated without difficulty, and consequently irradiation of equimolar solutions of 2:1 furan-diketone adducts and diketones in benzene gave rise to linear polymers. For example, irradiation of the 2:1 adduct of furan and meta-dibenzoylbenzene with an equimolar proportion of meta-dibenzoylbenzene gave a linear polymer with a $\bar{M}_n$ of 8,000 (d.p. 23).

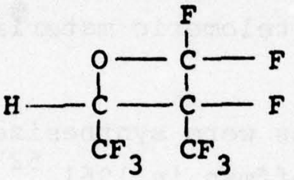
Spectroscopic examinations of these materials revealed both oxetane and hydroxyl bands in the infrared region. Previous studies of the reaction between benzophenone and furan had not revealed any tendency for hydrogen abstraction from furan by benzophenone triplets; indeed in the reactions of benzophenone with methylfurans, where abstraction from the allylic C-H bonds might be expected to be favourable, the authors specifically stated that oxetanes were the only products.[35] However, since the experimental details of the polymerizations and those of the model reactions were different in several respects (due to low monomer solubility and relatively slow oxetane formation), possible sources of the hydroxyl hydrogen could be postulated. For instance slow photoreaction of benzophenone with benzene is known to yield benzopinacol and diphenyl;[37-43] also, all polymers contain a C-H bond α to two ether oxygens and such hydrogens are known to be particularly susceptible to abstraction.[44] Such abstractions could lead to crosslinking and precipitation.

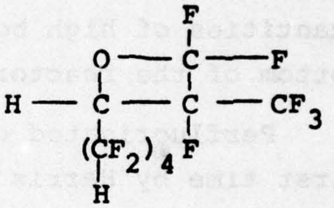
It is thus apparent that application of the Paterno-Büchi reaction to polymer synthesis in the systems investigated was only partly successful, mainly due to competing processes (especially hydrogen abstraction and crosslinking), relatively low monomer solubility and the requirement for prolonged irradiation times.

1.1d. The Paterno-Büchi reactions of fluorinated compounds

Cyclic ethers as a class have been known for a long time and have been well recognized as useful organic intermediates and as solvents and plasticizers. Generally such ethers have been limited in their usefulness because of relatively low stability. However, in 1961 a new class of four membered cyclic ethers, fluoro-substituted oxetanes, were described; they were prepared from fluoro-olefins and fluoroaldehydes via the Paterno-Büchi reaction.[45] More specifically this new class of polyfluorocyclic ethers carried one hydrogen atom on the ring carbon adjacent to ether oxygen; their outstanding chemical and physical stability was emphasized by the author. The new 2-hydropolyfluoro-oxetanes reported ranged from clear, colourless liquids to low melting solids, depending generally on the total number of carbons in the molecule. Those containing less than about eighteen carbons were clear, colourless liquids boiling from 100° - 300°C. They exhibited high hydrolytic stability, both under aqueous acid and aqueous base conditions. They were soluble in alkanols, ethers and various perfluorocarbon solvents but insoluble in water and solutions containing high percentage of water. They were non-flammable and exhibited outstanding resistance against thermal and oxidative degradation. These properties made the new compounds useful as 'stable liquid' materials, for example, as transformer fluids, fluids for high temperature power transmissions, or hydraulic systems, or liquid coupled mechanical drives. Vigorous chlorination resulted in substitution of the 2-hydrogen by chlorine, and the 2-chlorine could be readily converted to other interesting chemical intermediates by conventional methods. These polyfluoro-2-hydro-oxetanes were generally prepared by direct irradiation of the two reactants in cylindrical quartz reactors approximately four diameters long, maintained at atmospheric pressure and under reflux from a solid carbon dioxide/acetone cooled condenser. No solvents for the two reactants were used. Ultraviolet light from a low-pressure, 10 watt, quartz, mercury resonance lamp fitted in a spiral around the reactor was employed as the source of energy. Irradiation times ranged from three days (chlorotrifluoroethylene/ ω-hydroperfluorovaleraldehyde) to twelve days (hexafluoropropene-1/ perfluoro-n-butyraldehyde); yields ranged from 27% to 66%. There was no mention of by-products or side reactions in the original publication.[45] Typical examples of the oxetanes successfully synthesized by this method included 3,4,4-trifluoro-3-trifluoromethyl-2-perfluoro-n-propyloxetane, 3,4,4-trifluoro-2,3-bis(trifluoromethyl)-oxetane and 2-(4H-octafluoro-n-butyl)-3,4,4-trifluoro-3-trifluoromethyloxetane, whose structures are given below. Vapour phase chromatography and n.m.r. studies revealed the presence of two isomers



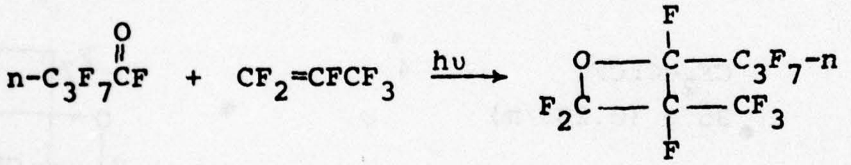




for the oxetanes obtained, the structures given above are for the major component. Several similar polyfluorinated oxetanes were reported in subsequent years.[46-48] Cook and Landrum reported that under actinic irradiation (450 watt Hanovia high-pressure mercury lamp) hexafluoroacetone gave good yields of oxetanes with ethylene, vinyl fluoride and vinylidene fluoride. With vinyl and vinylidene fluoride it was possible to isolate and identify both possible adducts and also determine the isomer distribution, structural assignments were based on proton n.m.r. spectroscopy. Free radical addition of aliphatic aldehydes to fluorinated olefins has been shown to yield ketones derived from addition of an acyl radical to the terminal carbon of the double bond.[49,50] Bissell and Fields have shown that under certain circumstances ketones and oxetanes can be produced simultaneously.[51] They reported that ultraviolet irradiation in the gas phase of mixtures of acetaldehyde and a fluorinated ethylene resulted in the formation of complex mixtures from which the ketone derived from addition of an acetyl radical to the CF_2 group of the olefin and the oxetane derived from cycloaddition of the aldehyde to the olefin could be obtained. Four olefins, tetrafluoroethylene, chlorotrifluoroethylene, bromotrifluoroethylene and 1,1-dichloro-2,2-difluoroethylene were studied. The major product in each case was the ketone. The reactor consisted of a 5 litre flask into which a water-cooled quartz well was inserted, a 100 watt high-pressure mercury vapour lamp was suspended in the well at the centre of the flask. Gaseous reactants were introduced through a vacuum manifold attached to a side arm of the reactor, one of the reactants was introduced from a supply cylinder until the desired pressure was obtained, the second component of the reaction mixture was then introduced from a second supply cylinder until the desired total pressure was reached. The mixture was irradiated until the pressure had fallen to half its initial value. This did not represent complete consumption of either component, but the yields of both ketone and oxetane actually decreased if the irradiation time was extended much further. Sizeable quantities of high boiling telomeric materials accumulated in the bottom of the reactor.

Perfluorinated oxetanes were synthesized photochemically for the first time by Harris and Coffman in 1961.[52] Before the publication of their work the only known example of this class was hexafluoro-oxetane itself, prepared by the electrolytic fluorination of the parent compound, oxetane.[53] Syntheses were carried out either at atmospheric pressure or in 'Vycor' Shaker Bottles depending on the b.p.'s of the reactants. In the case of atmospheric pressure reactions, the reactor consisted of a vertical quartz tube (2" x 10") fitted with a magnetic stirrer, a gas inlet adaptor and a large acetone/solid carbon dioxide cooled condenser vented through a trap, also cooled by acetone/solid carbon dioxide, the exit of which was fitted with a T-tube through which a slow stream of nitrogen passed. The ultraviolet radiation source consisted of a helix shaped (4" x 2½") low pressure mercury lamp constructed of 37 mm. quartz tubing and powered by a 5000 volt, 60 milliamp. transformer. The lamp was fitted around the quartz reaction tube so that its radiation impinged primarily upon the liquid portion of the reaction mixture. Alternatively, a 300 ml. 'Vycor' Shaker Bottle was partially filled with the fluorocarbonyl compound and attached to a Parr hydrogenation assembly. It was then evacuated and pressured to a pre-calculated value with the appropriate gaseous fluoro-olefin. While being shaken, the bottle and its contents were irradiated with two General Electric H-85 C-3 lamps placed as close to the bottle as possible. In both cases, products were separated chromatographically and examined by spectroscopic techniques.

Some perfluoro-oxetanes prepared by the methods described above are given in Table 1. It can be seen from this table that percentage yields of oxetanes prepared from acid or diacid fluorides are very high, in some cases as high as 91%, no by-products were reported. In contrast to this behaviour, irradiation of sym-dichlorotetrafluoroacetone and hexafluoropropene for two days in a 'Vycor' Shaker Bottle led to the formation of the corresponding oxetane (12%), two other involatile compounds, CF_2Cl_2 (1%), CO, CO_2, SiF_4.[52] A number of hydrogen and chlorine containing oxetanes were also reported in the same paper.[52] In a following publication, Harris investigated the photoreactions of acylfluorides in the presence of fluoro-olefins;[24] he stated categorically that 'irradiation of mixtures of polyfluoroacylfluorides and fluoro-olefins leads primarily to the formation of oxetanes; for example, perfluorobutyrylfluoride and hexafluoropropylene give the cis and trans isomers of 2-perfluoro-n-propyl-3-trifluoromethyltetrafluoro-oxetane. Virtually no other products are formed.' When the photoreaction of hexafluoropropylene with perfluoroacylchlorides was examined however, a variety of products was formed. Thus heptafluorobutyrylchloride and hexafluoropropylene yielded at least ten products (Figure 3).[52] In contrast to the reactions of fluoroacyl fluorides with terminal



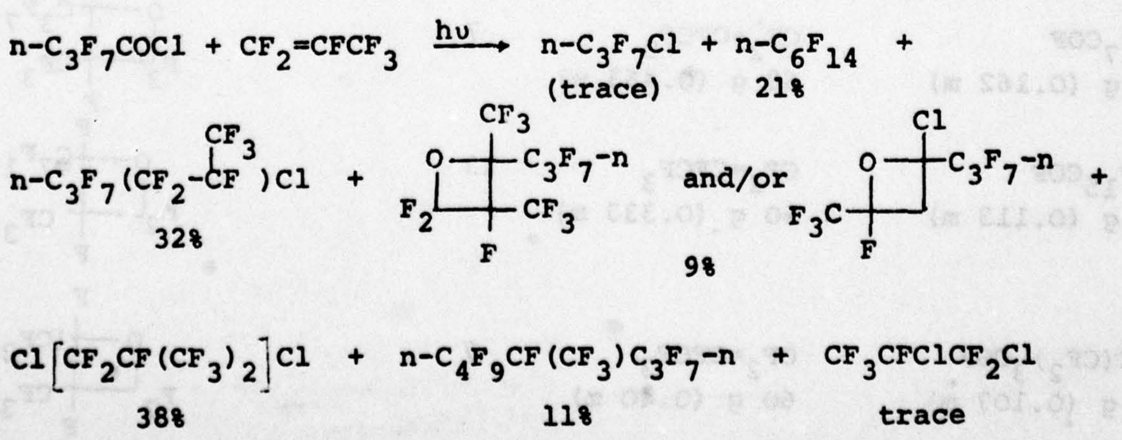
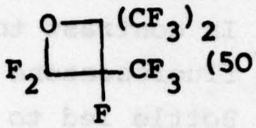
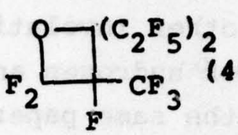
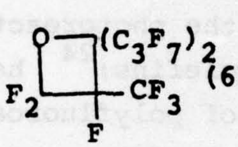
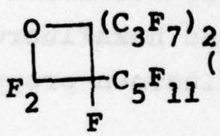
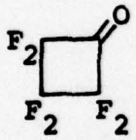
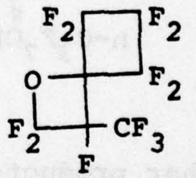
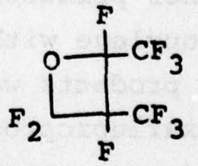
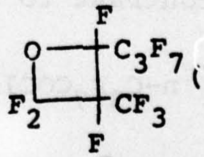
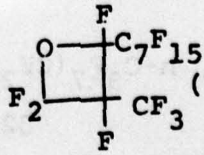
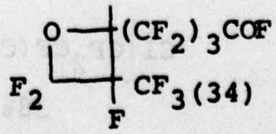
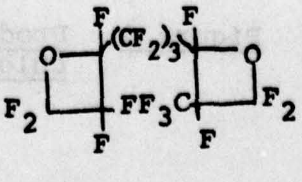


Figure 3. Products of photoreaction of heptafluorobutyrylchloride with hexafluoropropene.

Table 1

Ultraviolet cycloadditions of perfluorocarbonyl compounds to perfluoro-olefins

Carbonyl compound	Olefin	Period of irradiation (days)	Oxetane (% yield)
CF_3COCF_3 39 g (0.235 m)	$CF_2{=}CFCF_3$ 43 g (0.286 m)	7	 (50)
$C_2F_5COC_2F_6$ 43 g (0.162 m)	$CF_2{=}CFCF_3$ 35 g (0.233 m)	5	 (46)
$C_3F_7COC_3F_7$ 45 g (0.131 m)	$CF_2{=}CFCF_3$ 40 g (0.267 m)	8	 (62)
$C_3F_7COC_3F_7$ 45 g (0.123 m)	$CF_2{=}CFC_5F_{11}$ 45 g (0.129 m)	12	 (32)
 17 g (0.133 m)	$CF_2{=}CFCF_3$ 35 g (0.233 m)	4	 (33)
CF_3COF 56 g (0.483 m)	$CF_2{=}CFCF_3$ 95 g (0.633 m)	8	 (38)
C_3F_7COF 35 g (0.162 m)	$CF_2{=}CFCF_3$ 68 g (0.453 m)	7	 (73)
$C_7F_{15}COF$ 40 g (0.113 m)	$CF_2{=}CFCF_3$ 50 g (0.333 m)	13	 (91)
$FOC(CF_2)_3COF$ 26 g (0.107 m)	$CF_2{=}CFCF_3$ 60 g (0.40 m)	7	 (34) and  (31)

fluoro-olefins (in which 1:1 adducts were virtually the exclusive products) only small yields of 1:1 adducts were found. There were also relatively small amounts of the products obtained from the photolysis of acyl chloride itself. The bulk of the products was thought to arise from sequences beginning with additions of the acyl chloride photolysis fragments (i.e. the chlorine atom and the perfluoropropyl radical) to the olefin.[52] A similar behaviour was observed in the photoreaction between perfluorobutyrylbromide and perfluoropropylene.

1.1e. Objectives of work carried out

The application of the Paterno-Büchi reaction to polymer syntheses in the aromatic diketone/diolefin case was only partly successful for reasons discussed earlier (1.1c). On the other hand, literature information on the behaviour of the perfluoroacylfluoride/perfluoro-olefin system on exposure to actinic irradiation made this system an attractive one for use in the synthesis of linear polymers. The use of liquid perfluoro reactants would eliminate the need for solvents and consequently one possible source of side reactions. Irradiations of precisely equimolar mixtures of perfluorodiacidfluorides/perfluorodiolefins would be expected to yield linear high molecular weight perfluoropolyoxetanes since no side reactions seem to compete with oxetane formation.[52] Both monomers would be readily manipulated by conventional vacuum line techniques, and oxygen could be excluded from the mixture by successive freeze - pump - thaw cycles. Products would be expected to be transparent in the energy range required for photopolymerization. The main advantage of the perfluorodiacidfluoride/perfluoro-olefin system however, lies in the absence of competing hydrogen abstraction reactions by the photoexcited carbonyl. The only other reaction which could interfere, the telomerization of the acid fluoride,[52,54] would not lead to termination of the polymer chain although it would result in destruction of the required 1:1 functional group stoichiometry and consequently limit the molecular weight attainable.

As briefly indicated previously (1.1b, c, and d) the photochemistry of carbonyl compounds is complex, it is also an area of considerable activity and it is therefore necessary for workers using carbonyl photochemistry as a synthetic method to be ready to modify procedures in the light of new information. It is for example, established that the detailed course of a photochemical reaction is dependent on the nature of incident light (wavelength and monochromaticity) and the physical conditions of the reagents (gas, solid, solution, nature of solvent, and presence of sensitizers or quenchers). Thus an approach to the investigation of step-growth photopolymerizations leading to perfluoro or highly fluorinated polyoxetanes would involve a compromise between choosing systems which could yield interesting polymers if appropriate reaction conditions could be found and choosing systems known to proceed in high yield and conversion which would consequently be more likely to yield polymers within a reasonable time.

The first objective of the exercise was therefore the photochemical examination of simple systems; firstly, by irradiating a well characterized and vigorously purified diacid fluoride in the presence of an olefin; and secondly, by irradiating a monoacid fluoride in the presence of a diolefin. These preliminary experiments should give experience of the reaction and provide model compounds and spectroscopic data thereon which would prove useful in characterizing the polymers it was hoped to synthesise.

The preparation of reagents and the reactions undertaken are described in the next section, and discussed in the last section of this part of the report.

1.2. Experimental Work Carried out and Results Obtained

1.2a. Monomer syntheses and purification

The monomers required for these investigations were fluorinated olefins and dienes, acyl fluorides and diacyl fluorides, and fluorinated aldehydes and dialdehydes. The particular compounds synthesised were chosen on the basis of the availability and cost of starting materials. Established routes were selected where possible since the objective was to obtain reasonable quantities of pure monomers rather than to investigate novel synthetic organic chemistry of fluorinated compounds. The various monomers obtained and the routes by which they were obtained are listed below.

(i) Perfluorohept-1-ene was synthesized by pyrolysing the corresponding perfluorocarboxylic acid salt:[55]

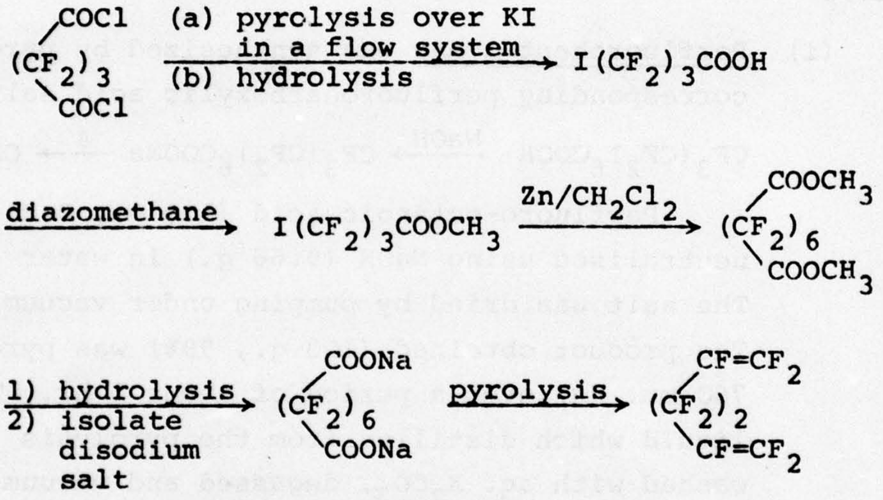
$$CF_3(CF_2)_6COOH \xrightarrow{NaOH} CF_3(CF_2)_6COONa \xrightarrow{\Delta} CF_3(CF_2)_4CF{=}CF_2$$

Perfluoro-octanoic acid (100 g., 0.24 moles) was neutralised using NaOH (9.66 g.) in water (100 mls.). The salt was dried by pumping under vacuum for 8 hrs. The product obtained (103 g., 99%) was pyrolysed (400°C/760 mm. Hg) over a period of about 1 hr. The colourless liquid which distilled from the pyrolysis flask was washed with aq. K_2CO_3, degassed and vacuum transferred from P_2O_5; g.l.c. (didecylphthalate/celite, 25°) indicated only one component. Perfluorohept-1-ene thus obtained was identified by i.r. spectroscopy ($\bar{\upsilon}_{max}$: 1780, 1370, 1320, 1200, 1070, 940 cm.$^{-1}$), the yield after purification was 71 g. (86%).

(ii) Perfluorocyclohexene was provided. It was obtained from the dehydrofluorination of undecafluorocyclohexane. The product was a single component by g.l.c. and had the correct i.r. spectrum.

(iii) Perfluorocyclohexa-1,4-diene was provided. It was obtained from the dehydrofluorination of a mixture of 1H,3H- and 1H,4H-decafluorocyclohexanes, which was obtained from the fractional distillation of the product of fluorination of benzene over cobaltic fluoride. The dehydrofluorination product consisted of a mixture of the required perfluorocyclohexa-1,4-diene, together with perfluorocyclohexa-1,3-diene, and 3H- and 4H-nonafluorocyclohexenes; this mixture was separated by preparative g.l.c. (16' x 3" dia. column, dinonylphthalate/celite (2/1), 100°, nitrogen carrier) the equipment being capable of separating <u>ca</u>. 70 to 100 g. injections of this mixture in <u>ca</u>. 4 hrs. The product was a single component by g.l.c. with the correct i.r. spectrum.

(iv) <u>Perfluorohexa-1,5-diene</u>. The preparation of perfluorohexa-1,5-diene was attempted via the route shown schematically below.



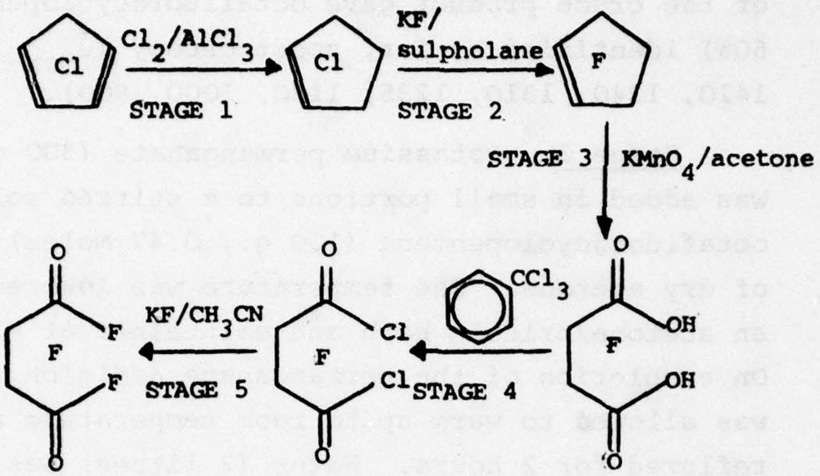
$$(CF_2)_3(COCl)_2 \xrightarrow[\text{(b) hydrolysis}]{\text{(a) pyrolysis over KI in a flow system}} I(CF_2)_3COOH$$

$$\xrightarrow{\text{diazomethane}} I(CF_2)_3COOCH_3 \xrightarrow{Zn/CH_2Cl_2} (CF_2)_6(COOCH_3)_2$$

$$\xrightarrow[\text{2) isolate disodium salt}]{\text{1) hydrolysis}} (CF_2)_6(COONa)_2 \xrightarrow{\text{pyrolysis}} (CF_2)_2(CF{=}CF_2)_2$$

A small quantity of 4-iodohexafluorobutyric acid was available from earlier studies, it was methylated and then coupled to give the diester in a straightforward manner and in near quantitative yield. Pyrolysis of the disodium salt of perfluorooctanedioic acid gave only a low yield of volatile product (5 - 10%) and coupled gas chromatography/mass spectroscopic examination of the product established that although the major component had the molecular formula C_6F_{10} the product was a complex mixture of several components some of which also had the molecular formula C_6F_{10}. These results showed that this was not a viable route to pure perfluorohexa-1,5-diene, this synthesis was abandoned.

(v) Perfluoroglutaryl fluoride was prepared by the route outlined below:



Typical results for the various stages in this synthesis are as follows:

Stage 1. Perchlorocyclopentadiene (780 g., 2.85 moles) and aluminium trichloride (121 g., 0.92 moles) were mixed in a 1 l. R.B. flask using a mechanical stirrer. Chlorine was passed into the mixture; heat was applied initially to start the reaction and thereafter chlorine was passed at such a rate that the temperature of the mixture was maintained at $\sim 45^{\circ}$C by the exothermicity of the reaction. The flow of chlorine was stopped when the reaction temperature fell below 30°C. The black solid obtained was treated with large excess of water until a yellow oil appeared. Recrystallization of this oil from ethanol gave octachlorocyclopentene (649 g., 66%), identified by i.r. spectroscopy ($\bar{\upsilon}_{max}$ 1620, 1200, 770 cm.$^{-1}$).

Stage 2. Octachlorocyclopentene (350 g., 1.02 moles) and dry potassium fluoride (942 g.) were mixed with sulpholane (2.5 litres) in a 5 l. R.B. flask using a mechanical stirrer. The temperature was raised and maintained at 180° - 185° for about 1½ days, the product formed was carried via a nitrogen stream and collected in glass traps cooled in liquid air. Fractional distillation of the crude product gave octafluorocyclopentene (129 g., 60%) identified by i.r. spectroscopy ($\bar{\upsilon}_{max}$ 1780, 1720, 1410, 1340, 1310, 1235, 1180, 1000, 900).

Stage 3. Potassium permanganate (300 g., 1.90 moles) was added in small portions to a stirred solution of octafluorocyclopentene (100 g., 0.47 moles) in 2 litres of dry acetone. The temperature was lowered by means of an acetone/dricold bath and maintained at -20^{o}C or lower. On completion of the permanganate addition, the solution was allowed to warm up to room temperature and then refluxed for 2 hours. Water (2 litres) was then added and the mixture was allowed to stand overnight. It was then filtered, acetone was removed under reduced pressure, the aqueous suspension was acidified with dil. H_2SO_4 and decolourised with SO_2. This solution was extracted with ether (17 hrs.), the ether solution was dried ($MgSO_4$) and filtered. After evaporation of ether, the product was obtained by vacuum distillation (0.01 mm. Hg/140°C), perfluoroglutaric acid (100 g., 88%) was identified by i.r. spectroscopy ($\bar{\upsilon}_{max}$ 3500, 1780, 1180 cm.$^{-1}$).

Stage 4. Perfluoro glutaric acid (140 g., 0.73 moles) was mixed with freshly distilled benzotrichloride (350 g., 1.79 moles) in a 1 l. R.B. flask fitted with a water condenser topped by an acetone-dricold cold condenser and connected to a H_2SO_4 bubbler. The temperature was raised to 212° using an oil bath while stirring was provided by means of a magnetic stirrer. After about 5 hrs. of refluxing the apparatus was modified for fractional distillation and the mixture was distilled (3 foot column/glass helices). The 78° - 160° fraction was retained and found to contain mainly one component by g.l.c. (didecylphthalate/celite, 100°). Perfluoroglutaryl chloride thus obtained (144 g., 90%) was identified by i.r. spectroscopy ($\bar{\upsilon}_{max}$ 1810, 1200, 1110, 990, 890, 805 cm.$^{-1}$).

Stage 5. Perfluoroglutarylchloride (258 g., 1.14 moles) was slowly added to a solution of dry potassium fluoride (1 Kg.) in dry acetonitrile (fractionated from P_2O_5, 2.5 litres) in a 5 l. R.B. flask. The mixture was efficiently stirred using a mechanical stirrer. On addition of the acid chloride, the pot temperature rose; the reaction was assumed to have finished when, after adding all the acid chloride the pot temperature went down to room temperature. The apparatus was then modified for fractionation (3 foot column/glass helices); the 45° - 48° fraction (156 g., 69%) was found to contain mainly acid fluoride and some acetonitrile by g.l.c.

(vi) 5H-Octafluoropentanoyl fluoride was prepared by the route shown below.

$$HCF_2CF_2CF_2CF_2CH_2OH \xrightarrow[\text{Stage 1}]{KMnO_4/CH_3COOH} HCF_2CF_2CF_2CF_2CO_2H$$

$$\xrightarrow[\text{Stage 2}]{PCl_5/HCON(CH_3)_2} HCF_2CF_2CF_2CF_2COCl$$

$$\xrightarrow[\text{Stage 3}]{KF/CH_3CN} HCF_2CF_2CF_2CF_2COF$$

Stage 1. Potassium permanganate (140 g.) was added in approximately 5 g. portions to a stirred solution of 1H,1H,5H-octafluoropentanol (150 g.) in acetic acid (500 cm.^{3}) in a three-necked flask equipped with a reflux condenser, mechanical stirrer and a thermometer. The temperature of the reaction mixture was maintained at 70-80° and regulated by the rate of addition. After completion of the addition the mixture was decolourised by bubbling SO_2 through it at 70-80°C, the mixture was then dried by azeotropic distillation with toluene (750 cm.^{3}). The toluene was removed, and the residual semi-solid white mass was treated with sufficient sulphuric acid (6N) to give a clear solution, about one litre of acid was required.

The solution was ether extracted, dried ($MgSO_4$) and distilled to give crude 5H-octafluoropentanoic acid (137 g., b.pt. 159-164°). It should be noted that the temperature regulation during the oxidation is critically important and care must be taken to avoid an accumulation of unreacted potassium permanganate; on one occasion failure to observe these precautions resulted in an explosively violent reaction.

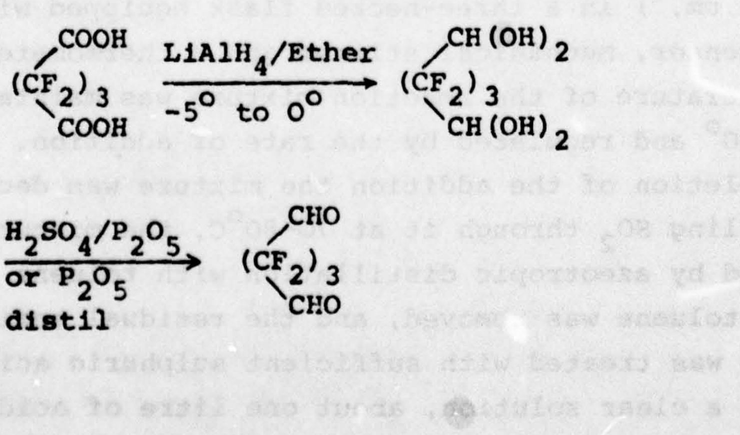
<u>Stage 2</u>. The crude acid was refluxed over phosphorus pentachloride (175 g.) and dimethylformamide (0.2 $cm.^3$) for four hours. Distillation yielded 5H-octafluoropentanoyl chloride (105 g., b.pt. 86-88°C).

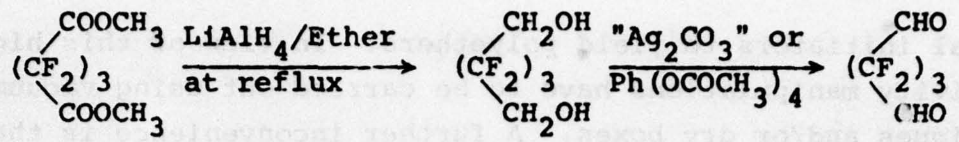
<u>Stage 3</u>. This stage followed the same procedure given for Stage 5 in the synthesis of perfluoroglutaryl fluoride. 5H-Octafluoropentanoyl fluoride was obtained in high yield (> 90%). In early experiments dry diglyme was used as the solvent for this reaction, in several attempts no acyl fluoride was isolated and only <u>ca</u>. 50% of the acyl chloride starting material was recovered.

(vi) <u>Perfluoroadipic acid</u> was prepared by the permanganate oxidation of perfluorocyclohexene following the procedure described in the synthesis perfluoroglutaryl fluoride (Stage 3). The product was dried by azeotropic distillation with benzene in a Dean-Stark apparatus, and recrystallized from dry benzene.

(vii) <u>Perfluorinated aldehydes.</u> Several routes to hexafluoropentane-1,5-diol were attempted and they are listed below.

a)



b) 

$$\begin{matrix}\diagup COOCH_3\\(CF_2)_3\\\diagdown COOCH_3\end{matrix}\xrightarrow[\text{at reflux}]{LiAlH_4/\text{Ether}}\begin{matrix}\diagup CH_2OH\\(CF_2)_3\\\diagdown CH_2OH\end{matrix}\xrightarrow[Ph(OCOCH_3)_4]{\text{"}Ag_2CO_3\text{" or}}\begin{matrix}\diagup CHO\\(CF_2)_3\\\diagdown CHO\end{matrix}$$

Although the literature reports imply that route (a) is a reliable synthesis,[56] when we applied it to dibasic acids it failed at the first stage, satisfactory yields of aldehydrol were not obtained. The process was continued through the dehydration step in the hope of obtaining some dialdehyde for preliminary investigations but after some effort it became clear that this route did not represent a viable source of the required materials. Consequently an examination of the alternative route (b) to fluorinated aldehydes via oxidation of the diol was started. This investigation was unsuccessful but after it had been in progress for some time we found that other workers[57] had duplicated our experience with the first stage of the aldehyde synthesis proposed initially. These workers had also established a more satisfactory procedure for synthesis of polyfluorinated aldehydes from appropriate alkyl esters using the relatively new reagent sodium bis-2-methoxyethoxy aluminium hydride in benzene solution (Vitride). Further, they reported that attempts to prepare perfluoroglutaryl aldehyde led to formation of a cyclic hemiacetal whereas perfluoroadipoyl aldehyde could be obtained in satisfactory yield. We have adopted their procedures and have found them a vast improvement on the previous method and generally satisfactory. However, there are still some practical problems in this synthesis since although the aldehydrol is produced in good yield using the Vitride reagent it is accompanied by a little of the alcohol and possibly other by-products in trace amounts.

The first stage of the synthesis can be satisfactorily accomplished using Vitride [$NaAlH_2(OCH_2CH_2OCH_3)_2$] in ether between -70^{o} and -50^{o}. Literature reports recommend a mixture of sulphuric acid and P_2O_5 for the dehydration stage but in our hands a more satisfactory result was obtained by heating an intimate mixture of aldehydrol and P_2O_5 under reduced pressure, the initial dehydration being followed by rigorous drying and purification by trap to trap vacuum transfer from fresh P_2O_5. Perfluoroaldehydes are extremely sensitive to moisture (reverting to the aldehydrol) and nucleophilic reagents; also they are readily polymerized by acids, bases or radical initiators to yield polyethers. In view of this high reactivity manipulations have to be carried out using vacuum line techniques and/or dry boxes. A further inconvenience is that unless considerable care is taken perfluoroaldehydes are converted to polyethers or other reaction products on storage; however, we have found that rigorously dried perfluoroaldehydes can be stored unchanged in a deep freeze at -20° for several weeks, the drying stage requires at least six successive trap to trap transfers from fresh P_2O_5. Perfluorooctanal and perfluorobutanal were prepared by the Vitride/P_2O_5 route.

1.2b. Irradiations

Two series of experiments were carried out the first with perfluoroglutaryl fluoride and either perfluorohept-1-ene or perfluorocyclohexene and the second with perfluorooctanal either neat or with various perfluoroalkenes and ordinary hydrocarbon alkenes.

1.2b(i) Reactions with perfluoroglutaryl fluoride

General procedure

Starting materials were accurately weighed to give a 2:1 olefin/acid fluoride molar ratio and were introduced into a flask containing P_2O_5. They were degassed by means of 4 or 5 freeze-pump-thaw cycles on a conventional vacuum line and then vacuum transferred into cylindrical quartz vessels and sealed under reduced pressure (10^{-3} torr). After irradiations, tubes were frozen in liquid air, hot spotted, opened and connected through two traps to the vacuum line. The two traps were connected to the vessel in series, the one nearest to it being at -78°C (acetone/dricold bath) and the other one being at -178°C (liquid air). Products were thus separated by volatility.

The results obtained are summarized in Table 2.

1.2b(ii) Reactions with fluorinated aldehydes

The reactivity of fluorinated aldehydes imposes considerable experimental difficulties and makes the use of vacuum line techniques obligatory. Infrared spectroscopy was excluded as an analytical technique since the aldehydes showed a marked tendency to polymerize on the KBr windows of the cell. Irradiations were carried out using a Rayonet Photochemical Reactor equipped with RUL 3000Å phosphor-coated mercury lamps.

Octafluorohexane-1,6-dial. A sample of this dialdehyde, prepared by lithium aluminium hydride reduction of perfluoroadipic acid and subsequent dehydration over P_2O_5, was obtained as a colourless liquid. It was purified by repeated vacuum transfer from fresh P_2O_5, and then condensed in a quartz n.m.r. tube which had been previously flame dried under vacuum. The contents of the tube were degassed by freeze-thaw cycles, the tube evacuated to 10^{-5} torr, and sealed. A ^{19}F n.m.r. was recorded and the irradiation commenced. Initially the n.m.r. spectrum showed two peaks of equal intensity but on irradiation a third peak appeared progressively as one of the original two disappeared. Eventually the growing peak achieved the height of the stable peak whilst the disappearing peak disappeared altogether. Throughout the irradiation the nature of the material in the tube changed, initially water-white and mobile it became viscous, then semi-solid and ultimately a white solid. It was found that the white solid turned into a viscous clear liquid in the n.m.r. machine, presumably it melted at the temperature of the probe (c. 35°C), and from this stage on, the cooling fan of the reactor was switched off to ensure that the contents of the tube remained in the liquid phase. The irradiation was stopped when there were only two peaks of equal intensity in the n.m.r. spectrum. The tube was scored around the neck and sealed onto the vacuum line before being opened. There were no volatile products, the tube was removed from the line and the contents recovered. The product was a white waxy solid at room temperature and was identified as perfluoroadipic acid.

Perfluorooctanal. This aldehyde was prepared by Vitride reduction of perfluorooctanoic acid and subsequent dehydration over P_2O_5. It was purified by repeated vacuum transfer from P_2O_5 and was a colourless mobile liquid. Samples of this aldehyde and mixtures of it with perfluorocyclohexene, perfluorocyclohexa-1,4-diene and heptene were degassed by freeze/thaw cycles and sealed from the vacuum line in flamed out quartz n.m.r. tubes. Each tube was irradiated for 24 hrs. The reactions were monitored

Table 2

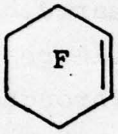
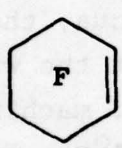
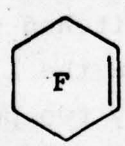
EXPT	STARTING MATERIALS[a]				
	OLEFIN	ACID FLUORIDE	Lamp[b]	Time (Hrs)	Temp ($^{\circ}$C)
1	$F_3C(CF_2)_4CF=CF_2$	$OFC(CF_2)_3CFO$	A	89.50	55
2	$F_3C(CF_2)_4CF=CF_2$	$OFC(CF_2)_3CFO$	B	65.80	40
3	$F_3C(CF_2)_4CF=CF_2$	$OFC(CF_2)_3CFO$	C	160.75	30
4	$F_3C(CF_2)_4CF=CF_2$	$OFC(CF_2)_3CFO$	D	91.00	300
5	$F_3C(CF_2)_4CF=CF_2$	$OFC(CF_2)_3CFO$	A	224.00	$+8 \rightarrow -20$
6		$OFC(CF_2)_3CFO$	A	25.00	55
7		$OFC(CF_2)_3CFO$	A	89.50	55
8		$OFC(CF_2)_3CFO$	B	65.80	40
9	$F_3C(CF_2)_4CF=CF_2$		C	160.75	30
10	$F_3C(CF_2)_4CF=CF_2$		A	224.00	$+8 \rightarrow -20$[c]
11		$OFC(CF_2)_3CFO$	A	224.00	$+8 \rightarrow -20$[c]

Table 2 (cont.)

EXPT	PRODUCTS[d]			COMMENTS ON LOW VOLATILITY PRODUCTS
	STARTING MAT. RECOVERED	-196^{o} TRAP	LOW VOLATILITY MATERIALS	
1	87.9	6.9	5.0	Mobile liquid containing at least 6 components by g.l.c.[k]
2	74.7	25.3		
3	70.8	19.0	10.0	Orange wax/mixture of at least 6 components by g.l.c.[l]
4		53.3	46.6	[m]
5	92.5	3.1	4.3	Heavy yellow-brown oil
6	94.2	2.2	3.5	Decomposed thermally at high T giving off v. volatile gases and yellow liquid (b. 140°) - 8 components (g.l.c.)[f]
7	92.1	2.1	5.7	yellow liquid - gave on standing 24.4% of its mass as an oil[g]
8	57.1	20.0	22.8	Gave 19.3% of its mass as a waxy solid[h]
9	74.0[e]		26.0	Most probably telomers of the olefin[m]
10	100.0			No change in the olefin
11	75.0	20.0	5.0	Orange waxy solid soluble in hot H_2O giving strong acid soln.

TABLE 2

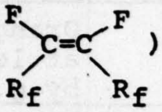
Footnotes: a. olefin/acid fluoride ratio: 2:1

b. Lamp A: HANOVIA 450-W Hg Lamp
Lamp B: RAYONET RPR-208 253.7 nm.
Lamp C: HANOVIA PCR 1L/5W Low P Hg Lamp
Lamp D: HANOVIA 125W medium P Hg Lamp

c. using refrigerated methanol bath

d. as % of total weight of starting materials

e. plus isomers by i.r. evidence (peak at 1720 cm.$^{-1}$



).

f. Gc/MS examination of the 8 component mixture revealed the presence of a substance (m/e ≈ 469) which could be either $OFC(CF_2)_6CFO$ or the 1:1 adduct. I.r. evidence (strong - COF absorption 1880 cm.$^{-1}$) seems to favour $OFC(CF_2)_6CFO$

g. I.r. spectrum of oil showed strong -COF absorption (1880 cm.$^{-1}$) strong R_f-COOH absorption (1780 cm.$^{-1}$) and strong bands around 1000 cm.$^{-1}$, characteristic of oxetanes.

h. waxy solid obtained by treating involatile materials with CCl_4. I.r. spectrum failed to reveal strong -COF band. Material slightly soluble in H_2O giving strongly acid solution (pH = 1 → 2)

k. Gc trace → Col 'A'/30°C i.r. spectrum similar to that of starting materials.

l. Orange wax soluble in hot H_2O (strongly acidic solution), in acetone, insoluble in Et_2O, CCl_4. I.r. spectrum shows the presence of strong -COF absorption (1880 cm.$^{-1}$)

m. Low volatility materials heated at 200°C/0.01 mm. Hg to yield a yellow oil and a remaining red brown viscous liquid. I.r. spectra of both materials appeared very similar. No -COF absorption around 1880 cm.$^{-1}$, strong band at 1720 cm.$^{-1}$. Probably telomers of perfluoroolefin.

n. I.r. examination of low volatility fraction showed a much stronger peak at 1720 cm.$^{-1}$ and a smaller peak at 1800^{-1} (terminal perfluoroolefin)

Fraction heated at 280°C/0.01 mm Hg for 2 hrs. to yield a colourless fairly mobile liquid and a yellowish oil displaying similar i.r. and n.m.r. spectra. Gc traces (Col. 'O_{30}' at 165°C) show 4 and 7 components respectively - probably different telomers of the perfluoroolefin.

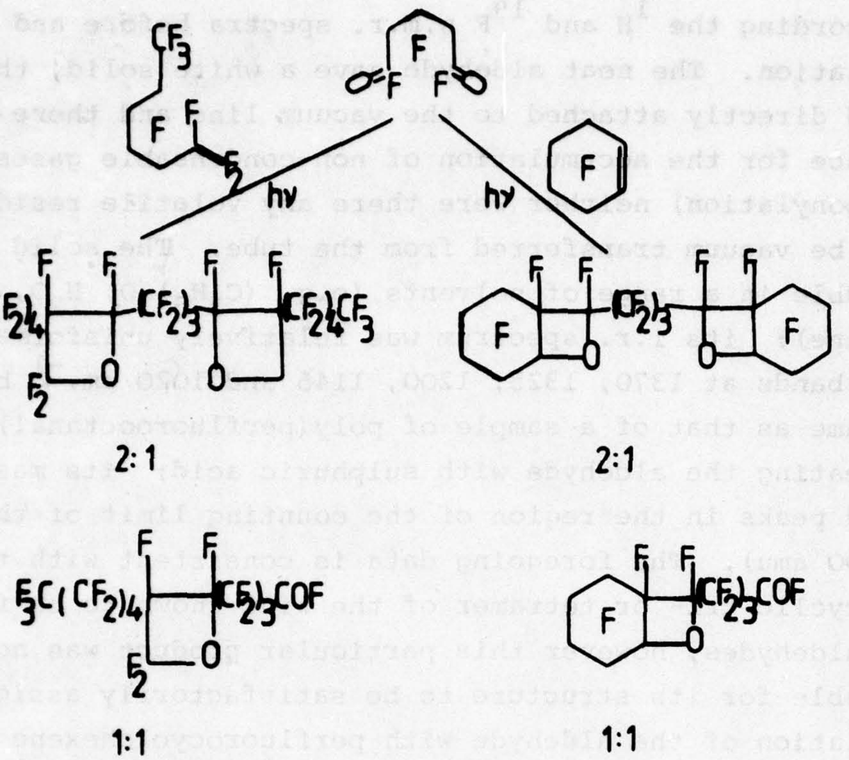
by recording the ^1H and ^{19}F n.m.r. spectra before and after irradiation. The neat aldehyde gave a white solid, the tube was opened directly attached to the vacuum line and there was no evidence for the accumulation of non-condensable gases (i.e. no decarbonylation) neither were there any volatile residues which could be vacuum transferred from the tube. The solid was insoluble in a range of solvents (e.g. $(C_2H_5)_2O$, H_2O, $CHCl_3$ and pyridine); its i.r. spectrum was relatively uninformative showing broad bands at 1370, 1325, 1200, 1145 and 1020 cm.$^{-1}$ but was not the same as that of a sample of poly(perfluorooctanal) obtained by treating the aldehyde with sulphuric acid; its mass spectrum showed peaks in the region of the counting limit of the instrument ($\sim$ 1000 amu). The foregoing data is consistent with the formation of a cyclic tri- or tetramer of the kind known to be formed by many aldehydes, however this particular product was not sufficiently tractable for its structure to be satisfactorily assigned. Irradiation of the aldehyde with perfluorocyclohexene and perfluorocyclohexa-1,4-diene resulted in the formation of the same white solid and the recovery of the unchanged olefinic components. The irradiation product of the aldehyde/heptene mixture was a viscous yellow oil which was not characterized.

1.2c. Discussion and conclusions

(i) Reactions with acyl fluorides

The initial experimental work carried out involved the study of a model reaction between a perfluorodicarbonyl compound (namely hexafluoroglutarylfluoride) and two different perfluoromonoolefins (namely perfluorohept-1-ene and perfluorocyclohexene).

The aim was to determine the conditions under which the model reaction could give a respectable yield of 1:1 or 2:1 adducts, and then to attempt the actual polymer forming reaction (diacid fluoride in the presence of a diolefin) under the same conditions. The statement, "the irradiation of mixtures of polyfluoroacyl fluorides and fluoroolefins leads primarily to the formation of oxetanes ... virtually no other products are formed",[24] together with the high yields of perfluorooxetanes reported for certain acid fluoride/terminal fluoroolefin systems (see Section 1.1d,



p.12) gave cause for optimism that high yields of oxetanes could be obtained without too much trouble, despite the possibilities of olefin isomerisation and acyl fluoride decarbonylation.

The experimental procedure adopted was to degas the reactants over P_2O_5 by freeze-thaw cycles, they were then transferred to quartz ampoules and sealed in vacuo (10^{-3} to 10^{-5} mm. Hg). The ampoules were then irradiated under a variety of conditions. Four different light sources were used. It seems reasonable to assume that the proposed reactions proceed via initial population of the carbonyl n,π^* triplet which in turn requires overlap between the absorption spectrum of the acyl fluoride and the emission spectra of the lamp; now the absorption band of perfluoroacyl fluorides is reported as λ_{max} 215 (ε=66),[24] whereas the short wavelength end of the spectrum of a mercury lamp consists predominantly of lines at 185, 238, 248 and 254 nm, overlap will therefore inevitably be poor which accounts for the long (several days) irradiation periods reported for successful polyfluorooxetane syntheses despite the use of high powered lamps. We used an Hanovia 5 watt low pressure lamp, two Hanovia medium pressure lamps (125 and 450 watts) and a set of

8 lamps in a Rayonet Photochemical Reactor (800 watts giving 120 watts radiative energy at 253.7 nm). Some of these lamps have considerable heat output, however many of the reported successful syntheses of polyfluorooxetanes were carried out at low temperatures (frequently the olefin component was hexafluoropropene under reflux at atmospheric pressure, b.p. -28^{o}) and so in our work some irradiations were carried out in cooled thermostat baths. A series of irradiations were carried out for periods of 1 to 9 days, with one of the four lamps listed above, and at temperatures in the range -20^{o} to 300^{o}C (but generally *ca*. 30^{o} to 40^{o}C). After irradiation the ampoules were opened and separated into fractions by volatility using conventional vacuum line techniques, the various fractions were examined by gas chromatography, mass and infrared spectroscopy. In reactions at high temperatures there was extensive decomposition, all other experiments resulted predominantly in the recovery of starting materials. In no case was there any evidence for the formation of oxetanes, although there was a small extent of reaction in several cases resulting in the formation of small amounts of very volatile products and of wax like, partially water soluble and acidic materials (probably telomer acid fluorides).

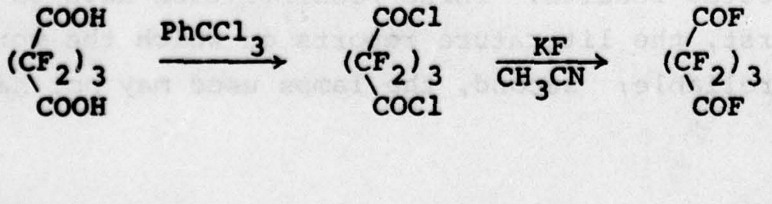
$$FCO(CF_2)_3COF \xrightarrow{h\upsilon} FCO(CF_2)_{3n}COF + (COF)_2,\ COF_2,\ CO.$$

Irradiation of perfluorohept-1-ene by itself, using the 5 watt Hanovia low pressure lamp which definitely has significant output at 185 nm where the olefin might reasonably be expected to absorb, resulted in a 26% conversion to a mixture of telomers (g.c./mass spec. and i.r. evidence) and considerable monomer isomerization (i.r. evidence, $R_fCF{=}CF_2$ at 1800 cm.$^{-1}$ decreases and a new band at 1720 cm.$^{-1}$ $R'_fCF{=}CFCF_3$ appears). Irradiation of perfluoroglutaryl fluoride by itself gave low conversion to a waxy acidic solid.

The results summarized above were very disappointing and their accumulation consumed many project man-hours. It is worth considering why this apparently straightforward chemistry failed to give the expected results. Three possibilities have to be considered; first, the literature reports on which the work was based may be unreliable; second, the lamps used may not have sufficient output at the required wavelengths; and third, the starting materials are either not what they are supposed to be or may contain impurities which were not present in materials used in earlier work. The first question can be dismissed since the literature reports originate from a reputable establishment, are well documented, and have been repeated and extended by several other groups. The second point is less easy to deal with, however, the fact that we can observe telomerization reactions of both acid fluoride and olefin components can be taken as good evidence that light is absorbed by monomers to some extent. Nevertheless, it would be much more satisfactory if a high intensity light source incorporating a broad band monochromator were available for preparative work which requires wavelengths shorter than the 254 nm band of the mercury lamp. Equipment of this type was not available to us during the course of this work. On balance it seems that since others have successfully used mercury lamp sources we ought to have been able to get by with them as well, however a more readily regulated system would offer advantages. So, having ruled out the light source question, we are left with doubts about our reactants. The olefin preparation is a standard procedure:-

$$CF_3(CF_2)_6COONa \xrightarrow{\Delta} CF_3(CF_2)_4CF{=}CF_2 + NaF + CO_2$$

- g.l.c., i.r. and n.m.r. analysis enables us to be sure that the purified material is perfluorohept-1-ene; similarly, the perfluorocyclohexene used was reliably pure. We have been making perfluoroglutaryl fluoride routinely for several years now and it has always proved satisfactory in the uses to which it has been put, naturally this was the last component we suspected but eventually we came to believe that this material may contain critically important impurities. Earlier work with acid fluorides does not specify the origin of the material but it seems likely that either electrochemical fluorination or fluorination of perfluoro acids with sulphur tetrafluoride were the methods used; on the other hand we synthesised our material by exchange fluorination from the acyl chloride -



$$\begin{matrix}COOH\\ /\\ (CF_2)_3\\ \backslash\\ COOH\end{matrix} \xrightarrow{PhCCl_3} \begin{matrix}COCl\\ /\\ (CF_2)_3\\ \backslash\\ COCl\end{matrix} \xrightarrow[CH_3CN]{KF} \begin{matrix}COF\\ /\\ (CF_2)_3\\ \backslash\\ COF\end{matrix}$$

- in our case therefore, we may have solvent impurities or residual traces of acid chloride functionality. Presently we believe that it is traces of residual acyl chloride which must be causing the problem since such groups will absorb at 258 nm ($\varepsilon \sim 40$) and therefore overlap strongly with the intense 254 nm band of the mercury lamp; acyl chlorides, or their photolysis products could be acting as quenchers for the excited state required for oxetane formation, or interfering with oxetane formation at some other stage. If this is a correct rationalization then the perfluoroacylchloride must be effective at very low concentrations since it was not detected by g.l.c. although traces of residual acetonitrile were. Another attempt to identify chloride was made by shaking a sample of perfluoroglutaryl fluoride with aqueous silver nitrate, again no silver chloride was found.

The final item checked in an attempt to find a rationalization of the results obtained was the transmission behaviour of the batch of quartz used to prepare the reaction tubes, it turned out to be normal quartz glass with no unexpectedly strong absorptions in the region 200 - 250 nm.

The main conclusion to be drawn from the above discussion is perhaps the trivial one that this area of synthetic organic chemistry is not an easy one in which to operate, certainly it was abundantly clear that it was not sensible to pursue the initially proposed polymer syntheses in the face of these complete failures. High purity reagents are required for the serious investigation of any reaction and this requirement is of particular importance both in photochemistry and in polymer chemistry. Any worker proposing to continue these investigations would be well advised, in the light of our experience, to pay particular attention to both the rigorous purification of starting materials and the provision of a radiation source having a high intensity in the 215 nm region; however, we feel that even if these conditions are satisfied this area is unlikely to repay the considerable efforts which will be required if any progress is to be made.

(ii) Reactions with fluorinated aldehydes

The catalogue of disappointments started somewhat earlier when fluorinated aldehydes were investigated as potential monomers, since in this case it proved difficult to repeat literature syntheses of the monomers (see Section 2.1a(vii)). It was some consolation to the student doing the work (R.B. Tulloch) when, during the course of this investigation, another group published a paper recording similar experience.[57] The alternative synthesis described by these workers allowed the required fluorinated aldehyde to be prepared.

Attention was focussed mainly on an examination of the photochemical reaction between perfluorooctanal and various alkenes. In this case the problem of overlap between the output of the lamp and the absorption band of the carbonyl compound (encountered with acyl fluorides) does not occur and all irradiations carried out gave products. Also an anticipated problem (namely decarbonylation) did not occur. Nevertheless the investigation failed to give any oxetanes which is particularly strange in view of the literature reports reviewed in the Introduction (p.12). Irradiation of neat perfluorooctanal gave a white solid which was fairly intractable and was provisionally assigned as a cyclic trimer or tetramer. When the aldehyde was irradiated in the presence of olefins this same product was isolated and the olefins were recovered unchanged.

It is hard to provide any reasonable rationalization of these results since they are clearly at variance with well established work. Some doubt must fall on the purity of the fluorinated aldehydes used in this work, and clearly this work requires careful checking. The student involved left the project and the topic was not reopened in the remaining time.

Conclusions

The work with fluorinated compounds was unexpectedly but uniformly disappointing in its outcome. In some instances the wisdom of hindsight allows rationalizations to be constructed but in general it has to be admitted that the work reported here has not advanced our understanding of the chemistry of these systems.

In the face of these repeated failures other projects were started, these also involve step-growth photopolymerization of carbonyl compounds, they were more successful and are described in Part 2 of this report.

Part 2

2.1. Introduction

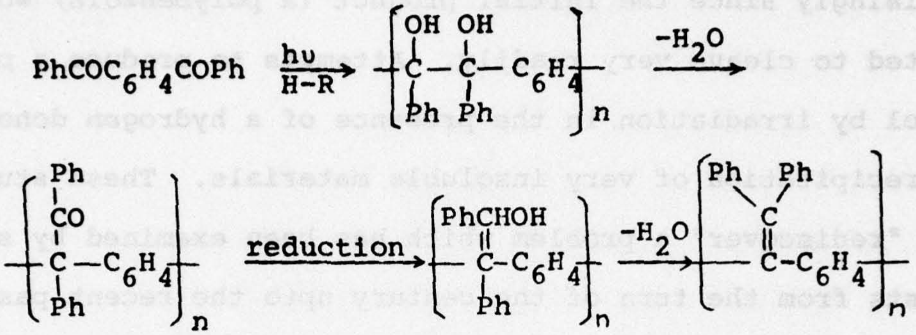
This part of the report describes several topics involving the use of aromatic carbonyl compounds as potential monomers in step-growth photopolymerization. The initial project (Part 1) ran into considerable difficulties and, since the accumulation of negative results is an unrewarding activity even to the most experienced researcher, the projects reported here were started in an attempt to provide positive results to give some encouragement and confidence to the beginning research students working on the grant. This was not, however, the only criterion applied in selecting these topics, the other criteria being that the work should be in the general area of step-growth photopolymerization and that the intended products of the syntheses attempted should be of a kind likely to be of interest to the Grantor.

The work done can conveniently be sub-divided as follows:-

(i) Attempts to extend the well established photochemical synthesis of polybenzopinacols[58] to polymers with more than two adjacent C_6H_5-C-OH units in the repeating block. This work did not yield new polymers but studies of model reactions provide some interesting observations on the limitations of reactions which were previously thought to be quite general.

(ii) Attempts to extend the photoreductive coupling of diphenylmethane and benzophenone (which gives 1,1,2,2-tetraphenylethanol) to the synthesis of polymers. This extends the general area of photoreductive polymerization and it was thought that dehydration of the initial product might yield a totally conjugated polymer.

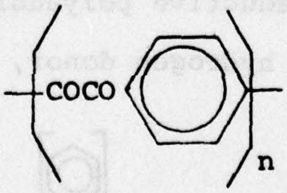
(iii) An alternative route to a totally conjugated polymer can be envisaged starting with the photoreductive polymerization of dibenzoylbenzenes. The product polybenzopinacol might then be dehydrated, reduction of the resultant polybenzopinacolone followed by a further dehydration yielding the required conjugated structure.



+ isomers ? + isomers ? + isomers ?

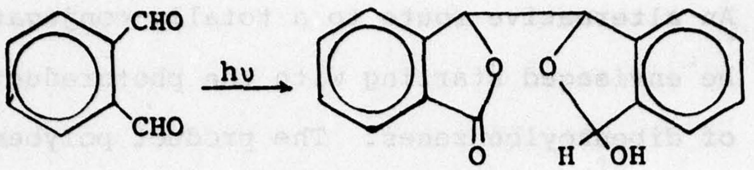
Most of the work carried out on this topic was concerned with attempting to optimise the d.p. attained in the first step.

(iv) The final topic in this part of the report is concerned with an examination of some aspects of the photopolymerization of aromatic aldehydes. At the outset the question in mind was whether step-growth photopolymerization could be used in a synthesis of polymers of the kind



which might prove useful in the synthesis of polyheteroaromatic structures.

Irradiation of phthalaldehyde has been thoroughly studied and gives the result shown below.[59] However, there have been no reports of irradiations of



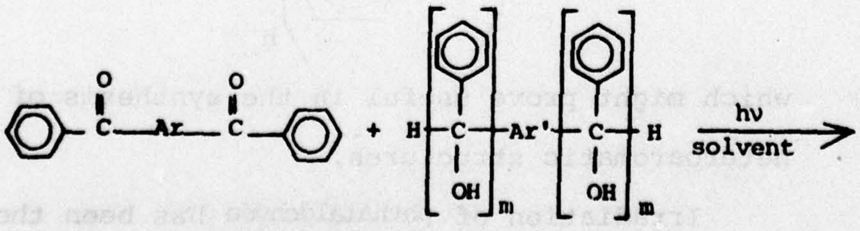
either tere- or iso-phthalaldehyde. Direct irradiation of either dialdehyde in solution or solid state has no effect, not too surprisingly since the initial product (a polybenzoin) would be expected to cleave very readily. Attempts to produce a polypinacol by irradiation in the presence of a hydrogen donor lead to the precipitation of very insoluble materials. These studies lead us to "rediscover" a problem which has been examined by several chemists from the turn of the century upto the recent past,[60] namely the nature of the photopolymer of benzaldehyde.

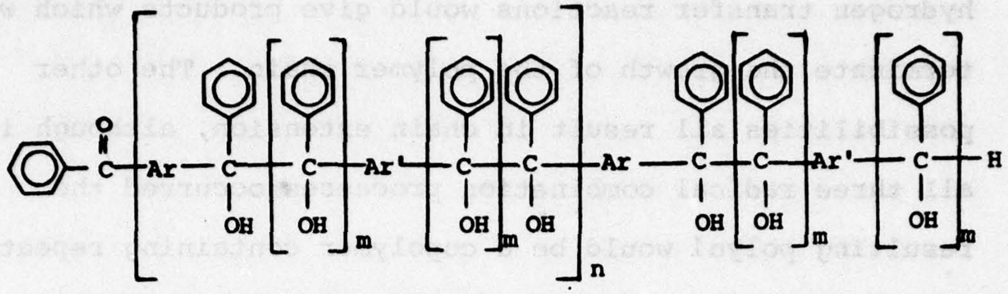
These four topics are described in the following sections of the report.

2.2. Attempts to Synthesise Poly(pentaphenylglycerols), and Related Work

2.2a. Introduction

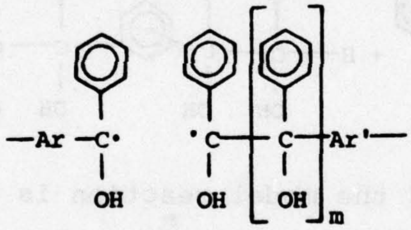
The original idea was the synthesis of perphenylated polymers with more than two adjacent C_6H_5COH groups in the repeat unit. One conceivable way of effecting such a synthesis could in principle be the photoreductive polyaddition of an aromatic bisketone to a suitable hydrogen donor, as shown below.





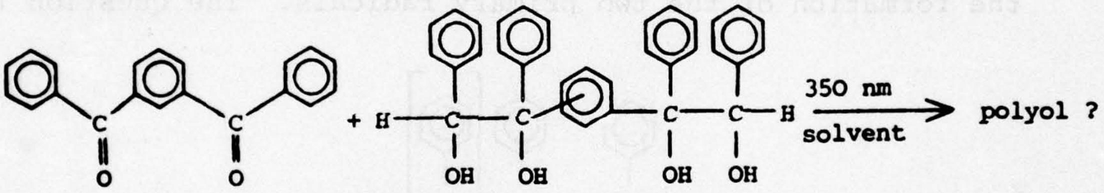
where $m > 2$

On the basis of literature information regarding the behaviour of photoexcited carbonyl groups of the benzophenone type in the presence of hydrogen donors it might be expected that irradiation of such a mixture at the appropriate wavelength would result in the formation of the two primary radicals. The question to be



where $m > 1$

answered was whether the cage reaction between the two radicals would take place, and if so to what extent; further it was essential to know what other processes, if any, would occur. Possible reaction paths for the two primary radicals considered beforehand included in-cage and out-of-cage combination and hydrogen transfer. It is clear that the in-cage reaction is the only process which would bring about formation of a homopolymer. Diffusion out of the cage and radical combination would result in the formation of a structure with either pinacol units in it or with 2m+2 C_6H_5COH units. A hydrogen atom transfer would result in complete reduction of the bisbenzophenone to the benzhydrolended product and oxidation of the alcoholic reagent. Only hydrogen transfer reactions would give products which would terminate the growth of the polymer chain. The other possibilities all result in chain extension, although if all three radical combination processes occurred the resulting polyol would be a copolymer containing repeating units with varying numbers of adjacent C_6H_5COH groups, 2, m + 2, 2m + 2. It was decided to proceed with this idea in the hope that at least some information on the photochemical behaviour of these systems would be obtained; the reaction below was chosen as an initial objective for this investigation.



The study of the model reaction is an essential preliminary step in the investigation of any potential step-growth polymerization. It was in this context that the photoreaction between benzophenone and triphenylglycol was undertaken, the product(s) of this reaction being appropriate model(s) for the repeat unit(s) of the anticipated polyol.

2.2b. The photochemical synthesis of triphenylglycol, the resolution of an old dispute

Triphenylglycol was required for the investigation of the model reaction, accordingly various syntheses were considered. One of the standard texts of organic photochemistry[61] reported that irradiation of benzophenone and benzyl alcohol gave triphenylglycol, no mention of by-products or reaction conditions appeared in the text. A reference was made to an old paper by Ciamician and Silber.[62] When the reaction reported was attempted on a small scale (nitrogen streamed benzene solution, 350 nm ultraviolet light) a white solid was obtained at nearly quantitative yield, which, after recrystallization and drying was found to be benzopinacol. Repetition of the reaction at various concentrations and for different irradiation times yielded constantly the same product, benzopinacol, unequivocally identified by melting point determination, elemental analyses and spectroscopic examinations. Even variation of the benzophenone-benzylalcohol molar ratio seemed to produce no alterations in the nature or yield of the final product. Examination of the solvent after irradiation by t.l.c. on silica revealed the presence of traces of benzopinacol and several other products. Careful reading of the original work revealed that Ciamician and Silber themselves appeared not to be definite about the formation of triphenylglycol from the benzophenone-benzylalcohol mixture on exposure to sunlight. In the same paper, however, references were made to earlier work by them, and also by a rival group, headed by Paterno; these references appeared to be interesting from several points of view. These very early studies of the 'actions of sunlight' on organic substances have significantly contributed to the development of modern organic photochemistry and represent considerable achievements with limited resources. However, in a series of papers published by both Ciamician and Paterno over a period of about twenty years it becomes clear that the two father figures of organic photochemistry held each other in pretty low esteem and never really agreed on whether triphenylglycol was produced on irradiating benzophenone in benzylalcohol or not.

In the original paper proposing the formation of triphenylglycol,[63] Ciamician and Silber described three separate insolations of benzophenone dissolved in neat benzylalcohol (1:2 $^{w}/w$) for periods from 4 to 5 months. The main product isolated by them was benzopinacol. Other products reported were hydrobenzoin, triphenylglycol and a resin, which the authors attributed to the action of light on benzaldehyde, itself a possible reaction product arising from the oxidation of benzylalcohol, however, benzaldehyde was not isolated by them.

The reaction was re-investigated by us. A 1:2 $^{w}/w$ solution of benzophenone in benzylalcohol (25g:50g) was transferred into a Pyrex tube, nitrogen streamed for 20 mins, the tube was quickly stoppered and the solution was irradiated for 18 hrs. at 350 nm. At the end of the irradiation period the solution was yellow and the inside surface of the tube was covered with a layer of white crystals. Examination of the tube contents by t.l.c. on silica (benzene, chloroform) and i.r. spectroscopy revealed the presence of unreacted starting materials, benzopinacol and small amounts of benzaldehyde. No triphenylglycol was isolated or detected by t.l.c. on silica; concentrations greater than 1% would have readily been detected. The reaction was repeated increasing the irradiation time to 89 hrs. Again as in the previous case the solution was yellow and the inside surface of the tube was covered with white crystals. Benzopinacol and benzaldehyde were easily identified by t.l.c. on silica (benzene, chloroform) and i.r. spectroscopy, along with unreacted starting materials and hydrobenzoin. The interesting feature of this experiment was the detection by t.l.c. on silica of triphenylglycol. Attempts to isolate the product by fractional precipitation (ethanol solvent) were, however, unsuccessful, probably due to the small amounts of material present.

A third investigation was undertaken under the same conditions. This time, however, colourless crystals which formed on the inside wall of the reaction tube were periodically broken by means of a long spatula in order to allow the ultraviolet light to penetrate the solution. After 180 hrs of irradiation a crop of crystals and a viscous bright yellow solution had formed inside the tube. The crystals were separated by filtration and the yellow oil recovered was nitrogen streamed and re-irradiated for a further 120 hrs. The crystals separated were found to consist of a mixture of unreacted benzophenone, benzopinacol, hydrobenzoin and triphenylglycol by t.l.c. on silica (benzene, chloroform). The yellow oil also deposited a fresh crop of crystals during the 120 hrs. irradiation period. Examination of these crystals (ca. 1.5g) by i.r. spectroscopy showed the material to be triphenylglycol by comparison with an authentic specimen. The yellow oil was found to consist of benzaldehyde, hydrobenzoin and traces of benzopinacol, benzylalcohol and unreacted benzophenone. Attempts to obtain a pure sample of triphenylglycol by repeated recrystallizations from various solvents were largely unsuccessful, since a very faint spot corresponding to benzopinacol was always present on the t.l.c. plates (benzene).

These experiments certainly confirmed the correctness of Ciamician's observations. It would also appear that the formation of triphenylglycol from benzophenone/benzylalcohol is time dependent. The formation of benzaldehyde was also confirmed. Finally, irradiation of a 1:1 molar mixture of benzophenone and benzylalcohol in benzene solution (0.0035 total concentration) for

160 hrs (350 nm) afforded triphenylglycol in ca. 8% yield.

2.2c. Ground state syntheses of triphenylglycol

The first attempt to synthesize the above mentioned compound (method A) was based on an established route,[64] namely the action of benzoin on an excess of phenylmagnesiumbromide. The exercise afforded 60% of nearly pure triphenylglycol. Repeated recrystallizations gave 45% of a white crystalline solid which on examination by t.l.c. on silica was found to be a single compound.

Triphenylglycol was also prepared (method B) by reduction of the corresponding carbonyl compound, α-phenylbenzoin (2,2-diphenyl-2-hydroxyacetophenone), itself prepared by the action of one mole of benzil on one mole of phenylmagnesiumbromide.

Pure triphenylglycol (85%) was obtained from this preparation, M.pts and spectroscopic data for the products obtained by the two methods were identical. Elemental analyses were satisfactory.

2.2d. The photoreaction between benzophenone and triphenylglycol

Following preparation, characterization and rigorous purification of triphenylglycol, the irradiation of a 1:1 molar ratio of this compound and benzophenone in benzene was investigated.

In the first experiment triphenylglycol (2.90g, 0.01 mole) prepared by method A and benzophenone (1.82g, 0.01 mole) were dissolved in benzene (350 mls) in a long Pyrex tube. The clear, colourless solution was nitrogen streamed, the tube was quickly stoppered and irradiated for 18.4 hrs at 350 nm. This experiment yielded unchanged starting materials, as indicated by t.l.c. on silica (benzene, chloroform, ethanol) and i.r. spectral examination.

Repetition of exactly the same reaction using triphenylglycol prepared by method B yielded identical results.

In a subsequent experiment, benzophenone (0.273g, 0.0015 mole) and triphenylglycol (0.435g, 0.0015 mole) prepared by method B were dissolved in benzene (50 mls) in a Pyrex tube. The solution was degassed by several freeze-pump-thaw cycles and tube was sealed under reduced pressure (10^{-3} mm Hg). Irradiation for 94 hrs at 350 nm afforded quantitative recovery of starting materials. During this experiment a parallel photoreaction between benzophenone and benzhydrol (1:1 molar ratio) was carried out in order to test the efficiency of the ultraviolet lamps: benzopinacol was quantitatively obtained after 3 hrs of irradiation.

Repetition of this reaction using triphenylglycol prepared by method A gave the same result.

On the basis of the literature information available on the photoreactions of benzophenone with alcoholic hydrogen donors, one would expect some if not all the processes shown in Figure 4 to occur upon irradiation of the benzophenone/triphenylglycol system. The quantitative recovery of starting materials is a surprising result. It seemed remarkable and led to a considerable effort in purifying the triphenylglycol and seeking evidence for the presence of an impurity which could act as an efficient quencher of triplet benzophenone.

Benzene solvent and benzophenone were also exhaustively searched for impurities. Repetitions of the irradiations using more rigorously purified materials made no difference to the result.

One hypothesis considered was that the hydrogen atom transfer illustrated in Fig. 4 did in fact occur in low yield and that the α-phenylbenzoin formed acted as a quencher in very low concentrations.

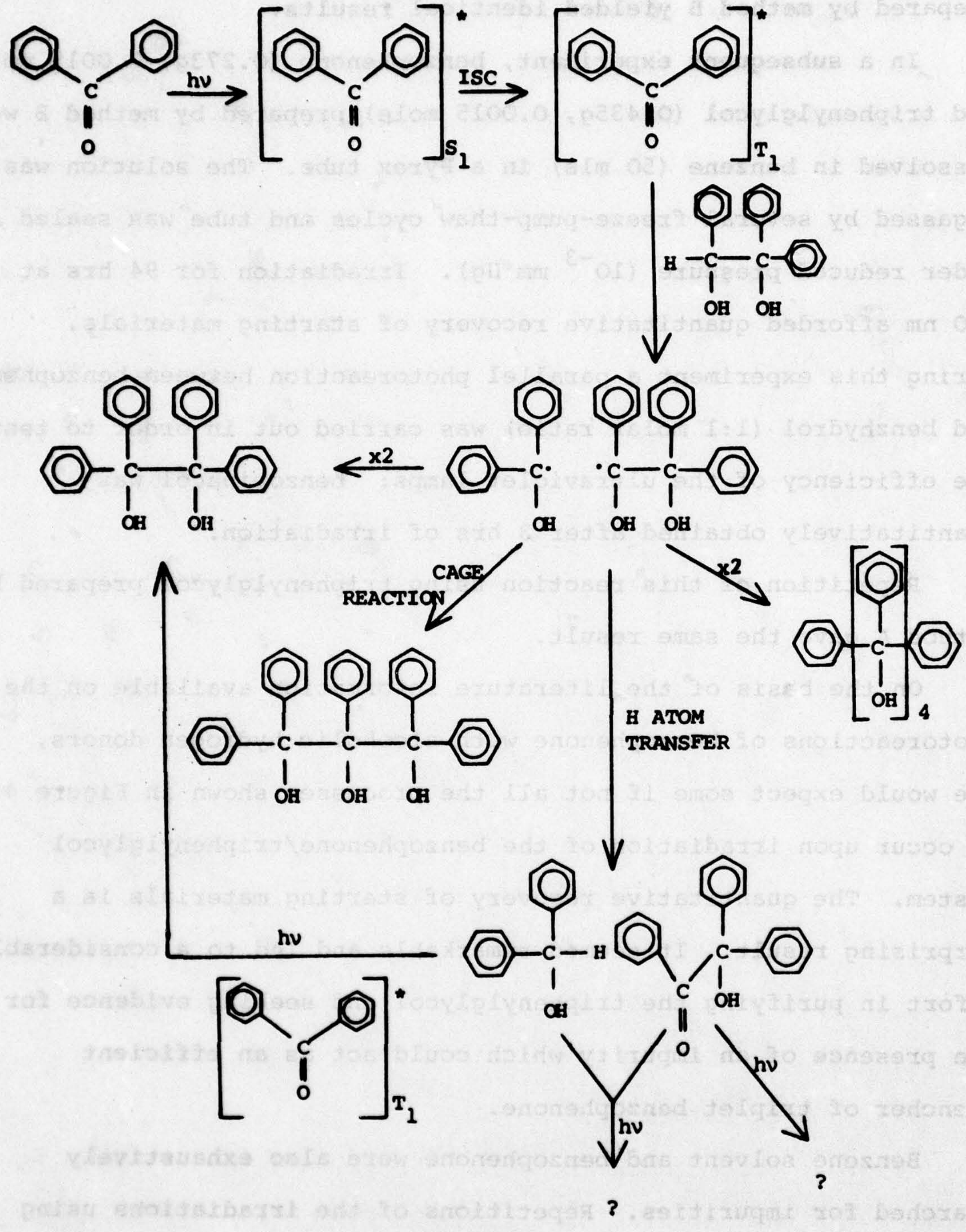
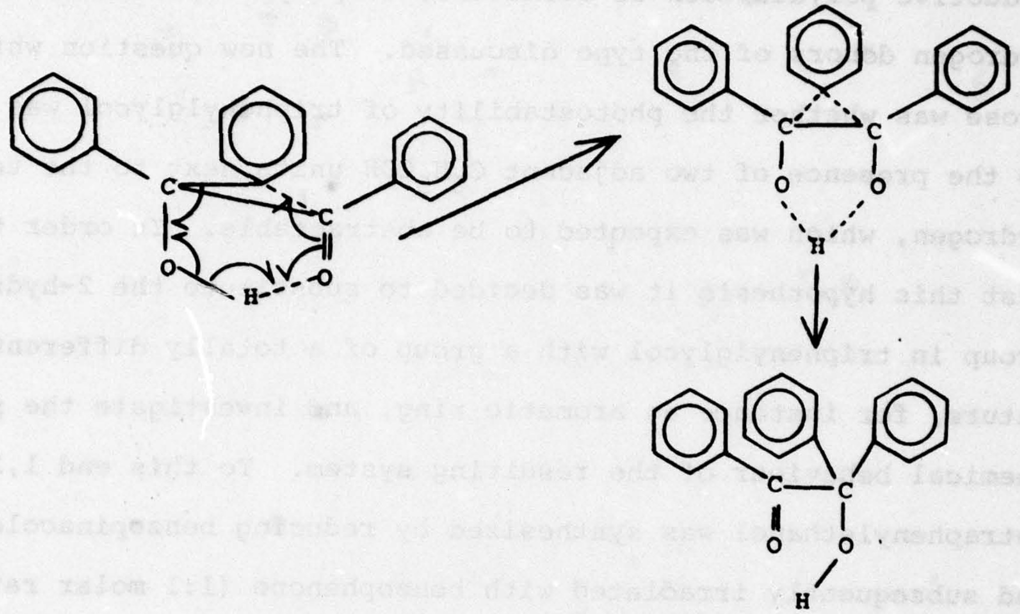


Fig. 4

The hypothesis seemed worth investigating since one could postulate a degenerate isomerization pathway involving a photoenolization and phenyl migration which might have accounted for the postulated quenching. The photochemistry of α-phenylbenzoin



is not discussed in the literature, despite the very extensive investigations reported on benzoins in general.[65] When irradiated under the conditions described previously, α-phenylbenzoin proved to be particularly photolabile, both on its own and in the presence of equimolar amounts of benzhydrol.

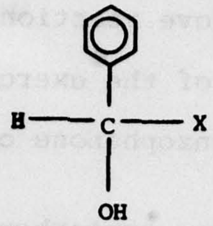
Finally, the 'quencher theory' was excluded by the irradiation of a nitrogen streamed benzene solution containing a 1:1:1 molar mixture of benzophenone, benzhydrol and triphenylglycol (0.0035M total concentration) at 350 nm for 12 hrs, a 1:1 molar mixture of triphenylglycol and benzopinacol was obtained, benzophenone and benzhydrol having completely disappeared. This reaction confirmed the observations that the tertiary hydrogen in triphenylglycol is inert towards abstraction by triplet benzophenone.

2.2e. The photoreactivity of 1,2,2,2-tetraphenylethanol

The observations described above concerning the photochemical behaviour of triphenylglycol certainly put an end to the hopes of obtaining poly(pentaphenylglycerol)s by the photoreductive polyaddition of bisketones to polyphenylated alcoholic hydrogen donors of the type discussed. The new question which arose was whether the photostability of triphenylglycol was due to the presence of two adjacent C_6H_5COH units next to the tertiary hydrogen, which was expected to be abstractable. In order to test this hypothesis it was decided to substitute the 2-hydroxy group in triphenylglycol with a group of a totally different nature, for instance an aromatic ring, and investigate the photochemical behaviour of the resulting system. To this end 1,2,2,2-tetraphenylethanol was synthesized by reducing benzopinacolone and subsequently irradiated with benzophenone (1:1 molar ratio) in benzene solution (0.0056M total concentration) for 12 hrs. at 350 nm. Infrared spectroscopic examination and t.l.c. on silica (benzene, chloroform, ethanol) established that no detectable reaction had taken place; starting materials were quantitatively recovered.

As in the case of triphenylglycol, irradiation of a benzene solution containing a 1:1:1 molar mixture of benzophenone, benzhydrol and 1,2,2,2-tetraphenylethanol (0.0035M total concentration) at 350 nm for 24 hrs resulted in the formation of a 1:1 molar mixture of benzopinacol and 1,2,2,2-tetraphenylethanol. No other products were detected by t.l.c. on silica, benzophenone and benzhydrol having disappeared completely.

Thus, it was established that the tertiary hydrogen in the structure shown below is abstractable when X = H or C_6H_5 but nonabstractable when X = $(C_6H_5)_2COH$ and $(C_6H_5)_3C$.



In an attempt to examine the possibility of other versions of the system shown being inert to hydrogen abstraction by benzophenone triplet, hydrobenzoin (X = ($C_6H_5CH(OH)$ and 1-phenylethanol (X = CH_3)) were irradiated in the presence of either benzophenone or its difunctional analogue, m-dibenzoylbenzene.

Irradiation of a 1:1 molar solution of benzophenone and 1-phenylethanol in benzene (350 nm) resulted in 100% disappearance of both starting materials after 140 hrs of irradiation. Benzopinacol and acetaldehyde were among the reaction products immediately recognized. At least three more products were identified by t.l.c. on silica (benzene).

Irradiation of a 1:1 molar mixture of m-dibenzoylbenzene and hydrobenzoin in benzene presented special problems due to the low solubility of the diol. However the portion of it that did dissolve in benzene at 0.0035M total concentration reacted readily with the photoexcited benzophenone-type carbonyl of m-dibenzoylbenzene yielding hydroxyl containing materials (350 nm, 160 hrs). Again a bright yellow colour developed shortly after the lamps were turned on. The irradiation was repeated using methylene chloride solvent in order to ensure complete solubility of both starting materials. After only 38 hrs of irradiation solution was again bright yellow and slightly turbid. Examination of the tube contents revealed that some starting materials had been left unchanged but most of them had reacted to give several products as shown by t.l.c. on silica (benzene).

The products from the above reactions were not rigorously examined, the main objective of the exercise being to establish whether photoreaction with benzophenone occurred or not.

2.2f. Attempts to prepare pentaphenylglycerol via ground state chemistry

The investigations reported above revealed that the model reaction for the polymer synthesis formulated in section 2.2a does not occur due to a rather surprising inertness of triphenylglycol towards benzophenone triplets. Attempts to further investigate this behaviour led to the discovery of another molecule exhibiting the same remarkable inertness.

At the same time, the preparation of the expected product, pentaphenylglycerol was undertaken via ground state synthesis in order to examine its stability, determine its properties and provide a reference for comparison. The compound is reported in the literature[66] and the recipe for its preparation given in the original paper was followed in every detail. The original worker reported that pentaphenylglycerol was obtained as a white crystalline solid (m.pt 163°) from the reaction of phenyl lithium on diethylmesoxalate, and that its elemental analysis was satisfactory. In our hands this reaction gave only triphenylcarbinol.

In the original paper, the following colour test for 'pentaphenylglycerol' was suggested: 'The product from pentaphenylglycerol + acetyl chloride + dimethylaniline in cold for 5 mins was treated with a solution of hydroxylamine and the mixture made alkaline with alcoholic KOH, heated and cooled. A reddish-wine colour was produced on acidification and addition of

$FeCl_3$ solution'. The test was carried out twice on a sample of the reaction product and on a sample of pure triphenylcarbinol. In both cases the same reddish-wine colour was produced. The author has been unable to ascertain the significance attached by the original worker to the colour test, although clearly it is not characteristic of pentaphenylglycerol. Careful repetition of the original recipe gave identical results.

2.2g. Discussion and conclusions

The basic question asked in this Section was: 'Can poly(pentaphenylglycerols) and higher analogues be prepared by the photoreductive addition of aromatic bisketones to suitable alcoholic hydrogen donors?' The answer to this question, based on the results described in Section 2.2d, would appear to be no; thus step-growth photoreductive polymerization would appear to be limited to the synthesis of polypinacols. Syntheses leading to structures with more than three Ph-C-OH units in sequence have not been examined, partly in view of the absence of reports on such compounds in the literature and partly due to the doubts on the possibility of their existence arising from the failure to isolate pentaphenylglycerol from the reaction described in 2.2f.

Although the question regarding the synthesis of poly(pentaphenylglycerols) and higher analogues was answered, some new questions have been uncovered:

(i) The old dispute between Ciamician and Paterno regarding the formation of triphenylglycol was resolved in favour of Ciamician (Section 2.2b). However, when the reaction was repeated by us a bright yellow colour was observed after a few hours of ultraviolet irradiation, indicating the formation of an intermediate. Such a species might act as an internal light filter and this would account for the slow reaction rate observed and the failure of the reaction to go into completion even after 300 hrs. of irradiation. Alternatively, one could attribute the bright yellow colour to the photolysis of benzaldehyde, itself a product of the benzylalcohol/benzophenone photoreaction; photolysis of neat colourless benzaldehyde was found to yield yellow coloured materials (see Section 2.5).

(ii) The inertness of triphenylglycol and 1,2,2,2-tetraphenylethanol towards benzophenone triplet is another question not easy to deal with. It is known that steric hindrance can be important in photoreductions.[67,68] Comparative molecular model studies of the compounds examined here have shown that *for both structures* the tertiary hydrogen, which was expected to be abstractable, appears to be only marginally more hindered than the tertiary hydrogen in benzhydrol or hydrobenzoin. In our view, it seems unlikely that the <u>complete</u> lack of reactivity exhibited by these compounds can be accounted for by steric hindrance; on the other hand, the C-C σ bond separating the $(OH)HC(C_6H_5)$ group from the $(C_6H_5)_2COH$ group (in triphenylglycol) and the $(C_6H_5)_3C$ group (in 1,2,2,2-tetraphenylethanol) should rule out any electronic interactions between the groups, at least of the type known and understood by us. Finally, the 'quencher theory' having been ruled out (see 2.2d), we are left with no explanation to suggest for these observations.

Other authors have commented on the unexpected selectivity of the benzophenone triplet in hydrogen abstraction reactions. Thus, although it is well established that hydrogen abstraction occurs readily from toluene and diphenylmethane it has been reported that the tertiary hydrogen of triphenylmethane is not abstractable.[69] In the case of these three hydrocarbons it is not difficult to construct a rationalization of these observations in terms of steric hindrance. On the other hand if steric effects are controlling the abstractability of the tertiary hydrogens in benzhydrol, hydrobenzoin, triphenylglycol and tetraphenylethanol the effects depend on rather subtle differences which are not readily detected by examination of space filling molecular models.

(iii) The failure to isolate pentaphenylglycerol or detect high molecular weight products from the reaction between diethyl mesoxalate and excess of phenyllithium is another problem which arose during the course of these investigations. Evidence presented in Section 2.2f tends to suggest that the original claim to have synthesized pentaphenylglycerol[66] was erroneous. The original author's only evidence, apart from the 'colour test' which has been shown to be meaningless, is the good agreement found and calculated analytical figures. However, the occlusion of methanol solvent in the molecule due to inadequate drying might have lowered elemental analysis figures, leading to the wrong conclusions.

The formation of triphenylcarbinol from the reaction of a large excess of phenyllithium with diethyl ketomalonate is not inherently unreasonable and it is interesting to note that the product yield obtained in this work and by the original author corresponds to the formation of a third of a mole of carbinol for each diethyl ketomalonate consumed. A detailed study of this reaction was not undertaken; however if it is assumed that the initial attack of phenyllithium takes place at the central ketogroup and is followed by elimination of carbon monoxide and ethoxide anion, the beginnings of a possible rationalization can be constructed. Although it may be that pentaphenylglycerol is inherently unstable and fragmented as fast as it is formed; this would be surprising since examination of space filling models would not lead one to suspect that the compound is significantly more sterically hindered than, say, benzopinacol. However, the observation that benzopinacol gives radicals by C-C bond homolysis under mild conditions[70] may be quoted in support of the postulated instability of pentaphenylglycerol.

2.2h. Experimental

Readily available materials

Benzylalcohol (technical grade) was purchased from Hopkin & Williams Ltd., and stored over 4A molecular sieves; prior to use it was twice fractionally distilled (15 cm x 4 cm dia., glass helices); the fraction distilling between 205° and 206° was collected (lit.[71] 205.03°/760 mm Hg). The product gave a single spot on t.l.c. on silica (chloroform, ethanol, benzene).

Benzhydrol was obtained from departmental stock, recrystallized twice from ethanol/water (70:30) and sublimed twice (95^{o}/0.005 mm Hg); the product had a melting point of 69^{o} (lit.[71] 69^{o}) and gave a single spot on t.l.c. on silica (ethanol, benzene, chloroform, toluene, acetonitrile).

Benzophenone (technical grade) was purchased from Hopkin and Williams Ltd. and recrystallized twice from ethanol/water (70:30) and once from cyclohexane, melting at 48.5^{o} (lit.[71] 49^{o}). It gave a single spot on t.l.c. on silica (benzene, ethanol, chloroform, acetonitrile, toluene, ethylacetate, carbon tetrachloride, acetone/water 50:50).

1-Phenyl ethanol (technical grade) was purchased from BDH Laboratory Reagents and stored over 4A molecular sieves; prior to use it was distilled twice under reduced pressure (15 cm x 4 cm dia., glass helices, 98^{o} - 100^{o}/20 mm Hg, lit.[71] 98^{o} - 99^{o}/20 mm Hg). The product gave a single peak on analytical g.l.c. (Col. 'A'/140^{o}).

Diethyl ketomalonate ($C_2H_5OCOCOOC_2H_5$) was purchased from Aldrich Chemicals, and used as obtained without purification. Its m.s. and i.r. spectrum were consistent with the assigned structure.

Benzoin, benzil and benzopinacolone were all obtained from departmental stock, recrystallized twice from appropriate solvents, dried under vacuum and identified by infrared spectroscopy (KBr discs) and melting point determinations. Purities were checked by t.l.c. on silica (benzene).

Sodium borohydride was purchased from BDH Laboratory Reagents and used as obtained.

Solvents

Benzene (analytical grade) was purchased from Hopkin & Williams Ltd., twice fractionally distilled (15 cm x 4 cm dia., Dixon gauzes) and stored over sodium wire for two weeks. Prior to use it was redistilled under nitrogen into a dry flask. Analytical g.l.c. indicated a single component (Col. 'A'/60°).

Methylene chloride (technical grade) was obtained from departmental stock, fractionated twice (40° - 42°) and stored over anhydrous magnesium sulphate for two days. It was redistilled under nitrogen (41°) before use.

Ethanol and 1,4-dioxane were obtained from departmental stock and used without purification.

Synthesis of hydrobenzoin from benzoin

Sodium borohydride (2.7 g, 0.072 mole) in water (50 mls) was added to a solution of benzoin (15.0 g, 0.072 mole) in 1,4-dioxane (200 mls) contained in a conical flask and the mixture was boiled (20 mins.). Following destruction of unreacted $NaBH_4$ with dilute CH_3COOH and evaporation of the solution, a white solid was obtained which was washed with water and recrystallized twice (ethanol/water 60:40) to give hydrobenzoin (12.1 g, 80%), m.pt. 147° - 148° (lit.[71] 149° - 150°), identified by mass spectrometry (correct molecular ion at m/e 214 and expected fragment ions) and infrared spectroscopy. The substance was recrystallized three more times from the same solvent and finally from a large volume of ethanol/water (80:20); m.pt. 147.5° (big plates, single spot on t.l.c. on silica).

Synthesis of m-dibenzoylbenzene

m-Dibenzoylbenzene was initially prepared according to the published route.[72]

However, the unsatisfactory yield obtained by this procedure necessitated a more detailed investigation of the reaction. Analysis of the reaction by-products by t.l.c. (benzene, chloroform) revealed the presence of low mobility substances (possible polymeric materials), some unidentified products, and isophthalic acid. The latter, which could be recovered in up to 20% yield, must have resulted from the hydrolysis of unreacted isophthaloyl chloride.

In an attempt to improve the yield of the reaction, the following modified procedure was used: doubly distilled isophthaloyl chloride (200 g) were dissolved in sodium dried benzene (2000 mls) with vigorous stirring. Finely ground anhydrous aluminium chloride (400 g) was added in small portions over a period of ca. 6 hrs.; when the addition was complete, the mixture was stired at room temperature for 6 hrs. and then refluxed for another 6 hrs. Following hydrolysis of the mixture, organic materials were extracted with benzene (2 x 1000 mls) and the extracts boiled three times with activated animal charcoal. The colourless solution obtained was evaporated and the recovered white solid was recrystallized three times from cyclohexane to give pure m-dibenzoylbenzene (196 g, 70%) as shown by t.l.c. on silica using a variety of eluents. This product had the correct m.s. and i.r. spectrum, m.pt. $103^{\circ} - 104^{\circ}$, and elemental analysis (found C, 83.68; H, 5.29; calculated for $C_{20}H_{14}O_{2}$; C, 83.90; H, 4.93).

A small sample of the purified m-dibenzoylbenzene was dissolved in a large volume of boiling cyclohexane, and the solution was left to cool slowly over a period of several days. Large prisms of material, some of them nearly 2.5 cm long were obtained, having a very sharp melting point of 103.8°.

Preparation of 1,2,2,2-tetraphenylethanol

To a solution of benzopinacolone (3.48 g., 0.01 mole) in ethanol (100 mls) a solution of sodium bromohydride (0.38 g, 0.01 mole) in water was slowly added. After frothing had subsided, the mixture was refluxed for 2 hrs. Addition of 2 litres of water caused the precipitation of a white powdery material which was recovered by filtration, washed with copious amounts of water, recrystallized from 50:50 methanol/water and dried under vacuum to give 1,2,2,2-tetraphenylethanol (2.8 g, 80%), m.pt. 150° (lit.[71] 151°); found C, 88.89; H, 6.20; calculated for $C_{26}H_{22}O$: C, 89.14; H, 6.29. The material gave a single spot on t.l.c. on silica (benzene, chloroform, ethanol, methanol). The mass spectrum showed no molecular ion, the highest peak being at m/e 332 (molecular ion-18); the other main peaks were at 224, 243, 182, 167, 165, 152, 105, 77. The infrared spectrum of the recrystallized product (nujol mull) showed a triplet of peaks in the OH stretching region, 3600 (strong-sharp), 3540 (weak-sharp), ca. 3450 (broad-very weak) cm^{-1}. The product was re-purified by sublimation at 140°/0.005 mm Hg; the infrared spectrum of this product (m.pt. 151-5°) showed a quartet of peaks in the OH stretching region at 3590 (strong-sharp), 3560 (weak-sharp), 3540 (medium-sharp), 3450 (medium-broad) cm^{-1}, in addition to peaks at $\bar{\upsilon}_{max}$: 3080, 3050, 3020, 2960, 2920, 1590, 1490, 1445, 1045, 1030, 705 cm^{-1}, (spectrum recorded as KBr disc). In an attempt to ensure the complete dryness of the product, a benzene solution of a sample of the sublimed 1,2,2,2-tetraphenylethanol was refluxed in a Dean-Stark apparatus; there was no change in the infrared spectrum or the m.pt. of the recovered sample.

Preparation of α-phenylbenzoin

A saturated solution of benzil (16 g) in ether was slowly added (30 mins) to a stirred ether solution (200 mls) of phenylmagnesiumbromide (from 15 g bromobenzene) at 0°. The resulting solution was refluxed for 30 mins, then hydrolysed by pouring into 1 litre 10% HCl/ice water mixture. A brown viscous mass was obtained which was treated several times with ethanol to give a whitish powder (65%); this was recrystallized several times from ethanol/water (70:30) giving α-phenylbenzoin (50%), a white crystalline solid m.pt. 87° (lit.[71] 88°); found: C, 83.89; H, 5.95; calculated for $C_{20}H_{16}O_2$: C, 83.31; H, 5.59. This material gave a single spot on t.l.c. on silica (benzene, chloroform, ethanol, acetone/water, acetonitrile). The product was further purified by sublimation (90°/0.005 mm Hg); the sublimed material melted at 88.8°. The mass spectrum showed no molecular ion the highest peak being m/e 184 with prominent peaks at m/e 183, 151, 106, 105, 77; clearly there is extensive fragmentation in the source. The u.v. spectrum in cyclohexane revealed three peaks at 350 (38), 347 (84), and 317 (258) nm (ε) in addition to strong aromatic bands. The i.r. spectrum (KBr disc) showed $\bar{\upsilon}_{max}$: 3500, 3050, 3040, 1675, 1600, 1580, 1500, 1450, 1350, 1250, 1185, 1030, 850, 700 (doublet) cm^{-1}. The n.m.r. spectrum showed a multiplet in the aromatic proton region at δ 7.7(15) and a singlet at δ 4.91(1) which disappeared on addition of D_2O assigned to the hydroxyl group.

Preparation of Triphenylglycol

Method A:[64] Finely ground benzoin (21.2 g, 0.1 mole) was slowly added to a vigorously stirred ether solution of phenylmagnesiumbromide (from 55 g, bromobenzene). Addition, over a period of 1 hr, was carried out at 20°, the resulting mixture was stirred for 5 hrs. at room temperature and then gently refluxed for 6 hrs.; it was then hydrolysed by pouring into 5% HCl/ice water mixture. A powdery product was obtained in 60% yield which, after repeated recrystallizations from ethanol yielded pure triphenylglycol (45%), m.pt. 165° (lit.[63,73] 168°, 164°).

Method B: A solution of sodium borohydride (0.01 mole) in water was slowly added to a stirred solution of α-phenylbenzoin (0.01 mole) in ethanol (150 mls). After initial vigorous frothing had subsided, the mixture was refluxed for 3 hrs. A white material precipitated on addition of 1 litre of water; it was recovered by filtration, washed with water, recrystallized from ethanol/water (70:30) and dried under vacuum to give triphenylglycol (85%), m.pt. 166°.

Materials obtained by both methods gave, after repeated recrystallizations from ethanol/water (70:30), single spots on t.l.c. on silica (benzene, toluene, chloroform, acetonitrile, methanol, acetone/water, ethanol, carbon tetrachloride, ethylacetate, chloroform/carbon tetrachloride). Elemental analyses were as follows: method A: C. 82.91; H, 5.94; method B: C, 82.73; H, 6.25; calculated for $C_{20}H_{18}O_2$: C, 82.38; H, 6.44. Both samples displayed the same spectral characteristics. The infrared spectrum (KBr disc) showed $\bar{\nu}_{max}$: 3570, 3470, 3090, 3070, 3040, 2940, 1500, 1450, 1190, 1065, 1045, 1030, 900, 760, 750, 700, 620 (doublet). The ^{1}H n.m.r. spectrum ($CDCl_3/CD_3COCD_3$, TMS ext. ref.) showed a multiplet at δ 7.7(15), doublets at δ 5.59 (J = 4 Hz, 1) and δ 4.04 (J = 4 Hz, 1), and a singlet at δ 3.88(1); the signals at δ 4.04 and 3.88 disappeared on addition of D_2O allowing their assignment as hydroxyl protons attached to the secondary and tertiary carbons respectively.

Sublimation of triphenylglycol ($130^\circ/0.005$ mm Hg) afforded a material (m.pt. 166.8°) whose i.r. spectrum in the solid state (KBr disc) displayed 3 peaks in the OH stretching region ($\bar{\nu}_{max}$: 3560, 3520, 3460 cm^{-1}) and 2 peaks in the C-H aliphatic stretching region ($\bar{\nu}_{max}$: 2930, 2890 cm^{-1}). There were also some minor differences in the fingerprint region of the spectrum. Elemental analysis figures, and ^1H n.m.r. spectrum of the sublimed were not different from those of the recrystallized material. The substance gave a single spot on t.l.c. on silica (benzene, chloroform, ethanol, acetonitrile). The solution phase infrared spectrum of the sublimed material in the OH stretching region was the same as the one for the recrystallized material.

2.3. Application of the Photoreaction Between Diphenylmethane and Benzophenone to Polymer Synthesis

2.3a. The diphenylmethane/benzophenone photoreaction

(i) Literature reports

The diphenylmethane-benzophenone photoreaction was first investigated by Paterno and Chieffi almost 60 years ago.[10] Their experiment consisted of insolating 20 g (0.109 mole) of benzophenone and 25 g (0.148 mole) of diphenylmethane in a sealed tube. Such a mixture constitutes a liquid mass at ambient temperature, so the authors found it more convenient not to use a solvent. Hard crystals were observed forming on the inside wall of the tube after only two days of insolation; they were separated after ten days and the remaining solution was insolated again until reaction was complete. The solid material obtained was dissolved in boiling benzene and an 'almost pure' novel compound crystallized on cooling. In order to make sure that the solid material obtained from the insolation was in fact pure, the authors treated it successively with the following hot solvents: ethanol, 'acetic ether', 'acetic acid', 'acetic ether' again and finally benzene, still leaving an insoluble portion ['acetic ether' is the literal translation, we think this was probably ethylacetate]. All the samples thus obtained melted at 212° - 214°. The novel compound was found to be only slightly soluble in the above solvents (in cold) and also in diethylether, chloroform, carbon disulphide, p-xylene, fused phenol, fused thymol etc. It was found to be soluble in hot solvents giving large, well defined needles on cooling. The results of elemental analysis and ebullioscopic molecular weight determination in ethanol and benzene were in good agreement with the values calculated for $C_{26}H_{22}O$, the 1:1 addition product.

Treatment of the product with P_2O_5 in xylene afforded tetraphenylethylene, identified by means of elemental analysis and m.pt. determination. Treatment with phosphorous and iodine afforded tetraphenylethane similarly identified.

On the basis of the above evidence the authors assigned to the product the structure of 1,1,2,2-tetraphenylethanol.[10]

The compound was further studied by Bergmann and Engel[74] who isolated two forms of it, one melting at 235° (α) and another melting at 216° (β), the latter prepared by the insolation of the benzophenone-diphenylmethane mixture. They attributed this phenomenon to isomerism of 1,1,2,2-tetraphenylethanol, resulting from inability of the $(C_6H_5)_2COH$ and $(C_6H_5)_2CH$ groups present in the molecule to rotate freely about the ethane C-C bond.

Wegler[75] re-investigated the insolation experiment and obtained a product which, after three recrystallizations from acetone melted at 215° - 217°. Attempts to replace the OH group by chlorine never gave halogenated derivatives, and only after repeated recrystallizations was a homogeneous product obtained, identified as tetraphenylethylene. By repeating the recrystallization of the photochemically prepared 1,1,2,2-tetraphenylethanol fifteen times, its m.pt. was raised to 229°. The same result was obtained when treatment with the solvent was carried out in cold, so the author concluded that his results could not be interpreted as the β-form being rearranged to the α-form. When the β-form was heated for several hours in pyridine at 135°, its melting point was lowered somewhat and recrystallization of the product yielded the α-form from which it was concluded that the β-form was impure α and that heating with pyridine changed the impurities to materials readily removed by subsequent recrystallization. The author considered the reported cases of benzophenone photoreduction in the presence of aliphatic and aromatic hydrocarbons, where benzopinacol and the dimerized hydrocarbons are formed and concluded that impurities in the β-form were probably benzopinacol and tetraphenylethane. He then prepared an artificial mixture of α and 20% benzopinacol and tetraphenylethane and claimed that it behaved exactly like the so-called β-form. He attributed the easy purification of the β-form by boiling it in pyridine to the decomposition of benzopinacol present into benzophenone and benzhydrol which could then be easily removed by recrystallization. When the α-form was treated with sodium in benzene, $CH_2(C_6H_5)_2$, $(C_6H_5)_2CO$, $(C_6H_5)_2CHOH$, C_6H_5COOH and predominantly $(C_6H_5)_2C{=}C(C_6H_5)_2$ were obtained, whereas treatment of the β-form with boiling benzene in the presence of sodium gave an intense blue-green colour attributed by the author to the presence of benzopinacol.[75]

In the same year that Wegler published his results, 1,1,2,2-tetraphenylethanol was independently prepared by Richard via ground state synthesis and its melting point was determined to be 236.5°.[76]

Three years earlier the same compound was prepared by the action of phenylmagnesiumbromide on α,α-diphenylacetophenone and the reported melting point was 232° - 233°.[77] In 1937, a similar reaction, namely the action of phenylmagnesiumbromide on $C_6H_5CHClCOCl$ afforded 1,1,2,2-tetraphenylethanol melting at 232.5° - 233°.[78]

1,1,2,2-Tetraphenylethanol was also obtained in low yield by boiling benzopinacol in cyclohexanone; this sample had a m.pt. of 232° - 233°.[79] The following year the same author reported the repetition of the benzophenone-diphenylmethane insolation experiment initially performed by Paterno and Chieffi;[10] he obtained a product which, after recrystallizations, melted at 217° - 218° on a copper block whereas m.pt. determination using a Kofler apparatus caused sublimation to minute needles which became opaque at 230° - 232° and melted sharply at 243° - 244°.[80] Further studies of the photochemical reaction by Banchetti yielded a product which melted at 206° - 210°;[80] treatment of the product with a large volume of acetone yielded a compound melting at 217° - 218°. Considerable reduction in the volume of acetone yielded small amounts of benzopinacol, identified on the basis of its 'behaviour under the microscope'.[80] Further recrystallization of 1,1,2,2-tetraphenylethanol from acetic acid caused a rise in the melting point to 223° - 224° whereas recrystallization from acetic anhydride yielded a material melting at 227° - 228°. Finally, boiling the material in cyclohexanol for one hour and recrystallization of the nearly pure material thus obtained from chloroform-acetone and then chloroform-ethanol yielded a product melting at 244°.[80] Having satisfied himself on the question of the purity of 1,1,2,2-tetraphenylethanol thus obtained, and having established the formation of benzopinacol from the photochemical experiment, Banchetti did not investigate the possible formation of any other by-products. He concluded that the best way to obtain 1,1,2,2-tetraphenylethanol in high yield was the insolation of the benzophenone-diphenylmethane mixture; purification of material from the last traces of benzopinacol (itself a low yield by-product of the photoreaction) necessitated however heating the ethanol with a high boiling solvent - preferably cyclohexanol - followed by recrystallization. This method afforded a non-specified high yield of pure material melting at 244°.[80]

Another preparation of the ethanol appeared in the literature in 1956:[81] treatment of 0.01 mole of the ketoester $C_6H_5C(O)$-$CH(C_6H_5)$-O-$C(O)CH_3$ in diethylether with 0.01 mole phenylmagnesiumbromide, refluxing for 30 mins, cooling, adding another 0.05 mole phenylmagnesiumbromide during 40 mins and refluxing for 15 mins gave after evaporation of diethylether solvent and purification from chloroform 38% pure 1,1,2,2-tetraphenylethanol. The melting point of the compound was however reported to be 231° - 232.5°.[81] A few years later a group of American workers obtained 1,1,2,2-tetraphenylethanol by the addition reaction of sodium diphenylmethide with benzophenone in liquid ammonia solvent followed by recrystallization from methylene chloride; 86% of pure compound were obtained, melting at 243° - 244°.[82]

From the above summary it is clear that the literature in this area presents a rather confused picture, it was therefore necessary to re-examine the photoreaction of benzophenone with diphenylmethane before proceeding to the intended polymerization of bifunctional monomers. Results of this re-examination are presented below and the literature claims reviewed thereafter.

(ii) Experimental results

(a) Irradiations without solvent

A 1:1 molar mixture of benzophenone and diphenylmethane (starting with 15 g benzophenone) forming a homogeneous liquid mass was transferred into a cylindrical Pyrex tube and nitrogen streamed for $^3/4$ hr. The tube was quickly stoppered and irradiated at 350 nm (ca. 40^o). After 30 hrs. of irradiation the inside walls of the tube were covered with a thick layer of colourless crystals and remaining solution was bright yellow. The tube was opened, crystals were broken by means of a long spatula and left as a solid precipitate at the bottom of the tube. The solution was nitrogen streamed again for $^3/4$ hr. and re-irradiated for another 60 hrs. Again colourless crystals had formed in the inside wall of the tube. Following opening of the tube, destruction of the crystalline layer, nitrogen streaming and stoppering, solution was re-irradiated for a further 14 hr. period; a new layer of crystals had formed and yellow colour appeared somewhat more intense. At that stage the tube was opened, the crystals were filtered off and the bright yellow solution obtained was nitrogen streamed and re-irradiated for 29 hrs. yielding another layer of hard colourless crystals. At that point the reaction was stopped, the crystals were filtered off, combined with the crop obtained from the previous filtration and dissolved in boiling benzene. Slow cooling of the benzene solution yielded 17.3 g (ca. 60%) of a white crystalline material in well defined needles. Examination of the needles by t.l.c. on silica (benzene) revealed the presence of one component only, whereas examination of the yellow solution revealed the presence of the same material and also benzophenone and diphenylmethane. Examination of the recrystallization solvent by the same method revealed the presence of the crystalline material, benzophenone and diphenylmethane. No benzopinacol was detected. Melting point of the crystals obtained was found to be 228^{o} - 229^{o}.

The same reaction was attempted using a 20% excess of diphenylmethane. This time however colourless crystals formed in the inside wall of the tube were not broken but were left to accumulate. After 130 hrs. of irradiation a bright yellow colour was observed inside the tube. Working-up the reaction products as before afforded ca. 40% of the white crystalline solid which, after recrystallizations from benzene and chloroform was found to melt at 229^{o} - 230^{o}. Examination of the white solid, yellow solution and recrystallization solvents by t.l.c. on silica (benzene, chloroform) failed again to reveal the presence of benzopinacol or other by-products. Boiling the white crystalline material in pyridine for 1.5 hrs., precipitation with water and recrystallization of the product thus obtained from benzene large crystals (70%), m.pt. 231^{o}.

(b) Photoreactions in benzene solvent

An 1:1 molar mixture of benzophenone and diphenylmethane (starting with 10 g benzophenone) was dissolved in benzene (0.01M with respect to both reagents) in a cylindrical Pyrex tube. The clear, colourless solution was nitrogen streamed for 1 hr, tube was quickly stoppered and irradiated at 350 nm for 110 hrs. A white precipitate had formed at the end of the irradiation period, the solution being again bright yellow. The crystalline material was recovered by filtration, m.pt. 230^{o} - 231^{o}. I.r. spectroscopy (KBr disc) showed $\bar{\upsilon}_{max}$: 3540, 3080, 3060, 3020, 2920, 1600, 1580, 1480, 1445, 1340, 1160, 1075 (doublet), 1050, 1030, 740, 700, 650 (doublet), 620 (triplet), 580, 560 cm^{-1} and was clearly distinct from the i.r. spectrum of benzopinacol (KBr disc) υ_{max}: 3568-3540 (characteristic doublet in the O-H stretching region), 3080, 3060, 3020, 1600, 1580, 1495, 1445, 1340, 1320, 1160, 1030, 760, 740, 700, 650 (doublet), 610 cm^{-1}. Analysis of the crystalline material by t.l.c. on silica (benzene, chloroform) revealed the presence of one reaction product only, together with two very faint spots corresponding with starting materials. Recrystallization of the product from chloroform did not cause a significant alteration in the melting point (231^{o} - 232^{o}), or the solid state i.r. spectrum (KBr disc). The highest peak in the mass spectrum occurred at m/e = 332 (parent ion (350)-18, most probably loss of water), with major peaks at 343, 342, 339, 183, 182, 177, 152, 105, 77. The material was recrystallized once more from benzene and dried under vacuum for 24 hrs. (m.pt. 232^{o}). Treatment of the material according to Banchetti's procedure[80] resulted in partial (20%) loss of material but no significant increase in the melting point was observed (m.pt. 232^{o} - 233^{o}). Elemental analysis gave: C, 88.86; H, 6.60; calculated for $C_{26}H_{22}O$, C, 88.70; H, 6.75. The ^{1}H F.T. n.m.r. spectrum of the material in $CDCl_3/CD_3COCD_3$ (ext. TMS ref.) showed a singlet at δ 7.13 (aromatic H) and four singlets at δ 5.23(A), δ 4.73(B), δ 3.02(C) and δ 2.81(D); peaks (C) and (D) disappeared on addition of D_2O; the integrated intensities were in the ratio (A) + (B) : (C) + (D) = 1:1. On the basis of the above evidence peaks (A) and (B) were assigned to the tertiary hydrogen in 1,1,2,2-tetraphenylethanol and peaks (C) and (D) to the hydroxyl hydrogen.

In a later experiment, diphenylmethane (2.10 g, 0.0125 mole) and benzophenone (2.275 g, 0.0125 mole) were dissolved in benzene

(50 mls, 0.5M with respect to both reagents). The clear solution was nitrogen streamed for 1 hr, the Pyrex tube was quickly stoppered and the solution irradiated at 350 nm for 309.2 hrs. The solution became bright yellow and a white precipitate was formed at the bottom of the tube. The precipitate was separated by filtration, washed with a little cold benzene and dried under vacuum. Both the white precipitate and the yellow solution were examined by t.l.c. on silica (benzene, chloroform, ethanol). In both solvent and precipitate 1,1,2,2-tetraphenylethanol was identified. Starting materials were not present, indicating that reaction had gone to completion. Analysis of the solvent, however, revealed the presence of spots corresponding to 1,1,2,2-tetraphenylethane and biphenyl ($C_6H_5-C_6H_5$). A very faint spot corresponding to benzopinacol was also observed. Analysis of the quantitatively recovered precipitate, m.pt. $216^o - 218^o$ showed the presence of some benzopinacol (faint spot). Recrystallization of the product from chloroform yielded pure 1,1,2,2-tetraphenylethanol, m.pt. $230^o - 231^o$. Isolation of pure benzopinacol from the recrystallization liquors was not possible, probably due to small amounts of material present. Over 95% of pure tetraphenylethanol was obtained from the recrystallization.

(iii) Discussion of present results and literature claims

The results of the present experiments lead to the following conclusions:

(a) The diphenylmethane-benzophenone photoreaction at 350 nm is a slow one, both in benzene solvent and without the use of solvent.

(b) Irradiation of a neat benzophenone-diphenylmethane mixture is difficult to study because of the hard crystals which keep forming on the inside walls of the cylindrical Pyrex irradiation tube. These crystals considerably diminish the amount of light reaching the interior of the tube, it follows that irradiation times reported should be treated with caution.

(c) Irradiation of neat reagents for up to ca. 150 hrs. (just over 6 days) under the above mentioned conditions resulted in only partial reaction, with 1,1,2,2-tetraphenylethanol as the only detectable product.

(d) During all irradiations a bright yellow colour has been observed. Yellow colours are frequently observed during photoreductions of aromatic carbonyl compounds, and they have been attributed to the formation of structures such as those shown in Figure 5. Formation of a similar structure from the combination of two benzophenone ketyl radicals can be excluded since in the photoreduction of benzophenone in benzhydrol where two such primary radicals are initially formed, no yellow colour is observed. Again, as in the case of the benzophenone-benzylalcohol photoreaction examined in 2.2b such coloured species could act as internal light filters and could account for the low reaction rate.

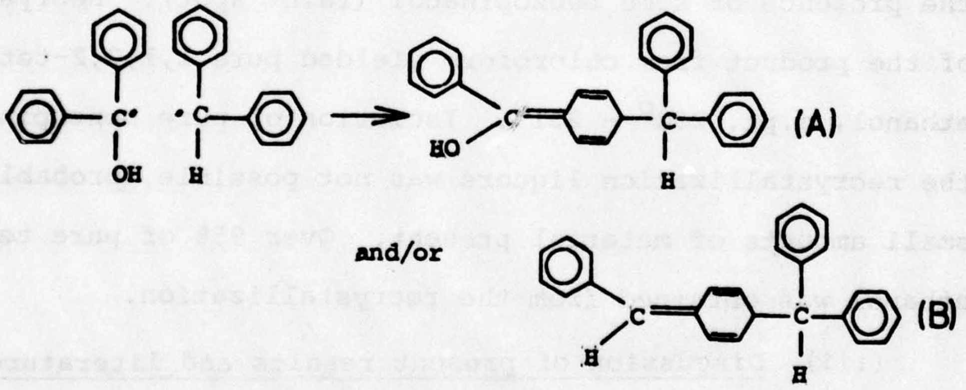


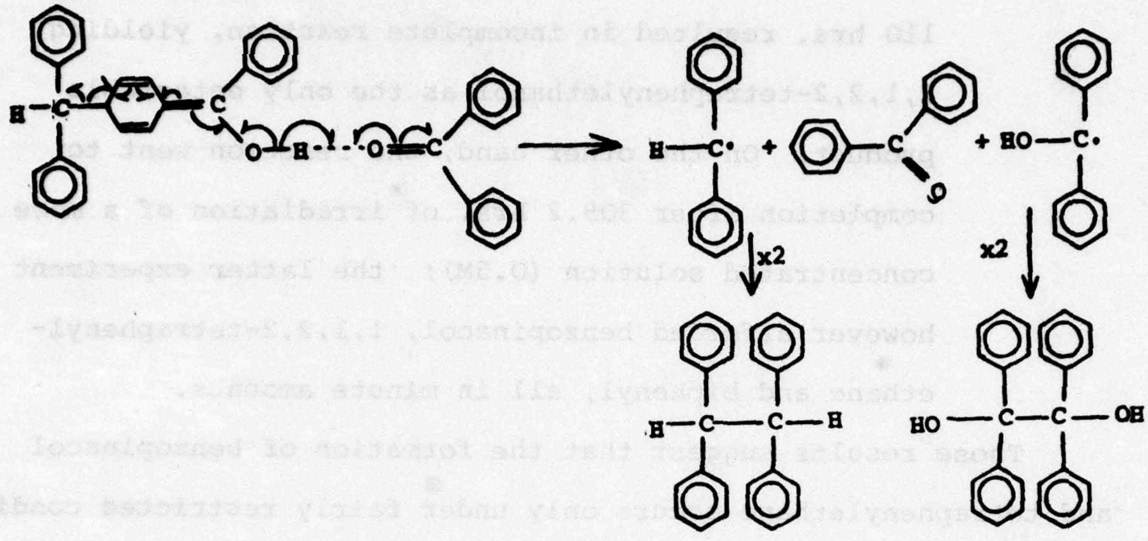
Figure 5

(e) Irradiation of a dilute benzene solution (0.01M total concentration) of benzophenone-diphenylmethane for 110 hrs. resulted in incomplete reaction, yielding 1,1,2,2-tetraphenylethanol as the only detectable product. On the other hand, the reaction went to completion after 309.2 hrs. of irradiation of a more concentrated solution (0.5M); the latter experiment however afforded benzopinacol, 1,1,2,2-tetraphenylethane and biphenyl, all in minute amounts.

These results suggest that the formation of benzopinacol and tetraphenylethane occurs only under fairly restricted conditions; thus neither are found in any of the irradiations of mixtures of benzophenone and diphenylmethane either neat or in dilute solution (0.01M) whereas at higher concentration (0.5M) these out-of-cage products were formed in detectable quantities. Clearly the factors which control whether the in-cage product (1,1,2,2-tetraphenylethanol) or the out-of-cage products are formed must be fairly subtle. A detailed investigation of the effects of concentration and duration of irradiation have not been undertaken since it is established that under a wide range of conditions the required product, tetraphenylethanol is formed in > 95% yield; this would allow polymers of d.p. > 20 to be obtained from irradiation of suitable bifunctional analogues. Nevertheless it is possible to speculate about the explanation of these observations.

In the first instance it may be that the relative proportions of in-cage and out-of-cage reaction are controlled by the details of the medium's composition. Alternatively it may be that the out-of-cage products arise from a reaction of an intermediate (such as A, Figure 5) with ground state benzophenone, that is by a process somewhat analogous to that suggested previously by

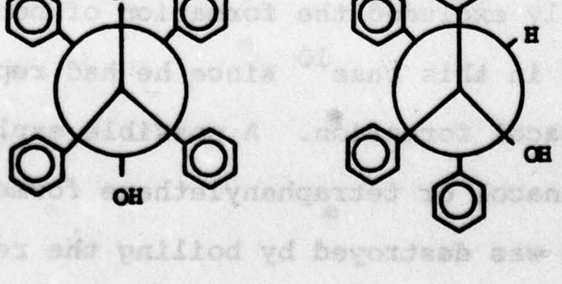
Filipescu,[83] and shown below.



Such a reaction could only occur when the concentration of (A) becomes high enough and therefore the probability of it coming in contact with a benzophenone molecule becomes significant. Increasing the concentration of the solution would also make the reaction more probable by increasing the chance of intermediate (A) coming in contact with a ground state benzophenone molecule. Irradiation of the neat benzophenone/diphenylmethane system may not lead to the formation of intermediate A in sufficiently high concentration because of the filter effect of the precipitating tetraphenylethanol. Thus the coloured structure (A) postulated in Figure 5 could be important in the rationalization of the observed slow reaction rate, the appearance of the yellow colour and the minute amounts of benzopinacol and 1,1,2,2-tetraphenylethane obtained under some conditions. It could not however explain the formation of biphenyl, which is most probably due to the prolonged irradiation of benzophenone in benzene solution.[84-89] Such a reaction is known to yield benzopinacol and biphenyl as the main products,[84,89] and by itself would account for the formation of both products mentioned above, would not however explain the formation of 1,1,2,2-tetraphenylethane.

The almost exclusive formation of 1,1,2,2-tetraphenylethanol in these reactions is a marked exception to the normal behaviour of triplet benzophenone in the presence of hydrogen donors, where benzopinacol formation is the main process. Even with aromatic hydrocarbon hydrogen donors which are structurally fairly closely related to diphenylmethane the in-cage dimerization of the primary radicals formed from initial hydrogen abstraction appears to be a relatively low yield process; toluene and cumene yield only ca. 50% of the corresponding cage products when irradiated in the presence of benzophenone.

On the other hand, the cage reaction product of the benzophenonediphenylmethane reaction is a peculiar compound in itself, being insoluble or only slightly soluble in a very wide range of laboratory solvents in the cold, this being a property not shared by closely related structures such as benzopinacol, 1,2,2,2-tetraphenylethanol, triphenylglycol etc. The ^{1}H F.T. n.m.r. spectrum of the material displays two distinct tertiary hydrogens and two hydroxyl hydrogen resonances. This could be attributed to the existence of two stable conformational isomers of the material, as shown below, although it is worth noting that the related structures listed above do not show this effect. Due to the low



solubility of the material in most cold solvents it was not possible to investigate its solution phase i.r. spectrum or examine its photoreactivity with benzophenone in benzene solution at concentrations comparable to those of previous experiments.

Deciding whether the experimental results obtained in our hands are in agreement with earlier reports is a rather difficult task. Earlier papers recorded limited experimental details; the irradiation source was the sun rather than a lamp of defined output, the temperature was not recorded and may well have been significant (ground temperatures in the North African desert may reach 70°C) and almost all these early papers are devoid of quantitative information. Spectral and chromatographic evidence not being available to these early workers, the melting point of the product acquired a central role in the determination of purity. Ways of drying of 1,1,2,2-tetraphenylethanol however were rarely specified and occlusion of traces of solvent can be critical in melting point determinations. Once these points are taken into account, an idea of the difficulties arising in assessing previous results becomes clear.

Wegler's claim[75] that as much as 20% benzopinacol and hydrocarbon can be present as the by-products of the insolation experiment seems to be grossly exaggerated. Wegler must have expected to observe the formation of benzopinacol in view of the reported behaviour of benzophenone on insolation in the presence of various hydrogen donors; it is however surprising that Paterno categorically excluded the formation of benzopinacol or any other by-products in this case[10] since he had reported so many examples of benzopinacol formation. A possible explanation could be that any benzopinacol or tetraphenylethane formed in Paterno's experiments was destroyed by boiling the reaction product in benzene before examination. In our hands, boiling a toluene solution containing a 1:1 molar mixture of benzopinacol and 1,1,2,2-tetraphenylethane for 3 hrs. resulted in the total disappearance of starting materials and formation of 1,1,2,2-tetraphenylethanol with traces of benzophenone and benzhydrol as by-products.

Banchetti claimed to have isolated benzopinacol out of his own insolation experiment, by considerably reducing the volume of the mother liquors of recrystallization of the crude 1,1,2,2-tetraphenylethanol. He did not however specify the percentage of benzopinacol isolated. On the other hand, the evidence for the pinacol formation (behaviour under the microscope) is open to question.[80]

Banchetti's purification technique should also be considered with great caution since 1,1,2,2-tetraphenylethanol itself is not very stable at high temperatures, decomposing by cleavage of the ethane C-C bond.[90] The reported by-products, benzopinacol and 1,1,2,2-tetraphenylethane are very soluble in solvents like acetone and chloroform even at room temperature; it should therefore be adequate to wash and then recrystallize the product from one of these solvents. In our hands, purification of a 1,1,2,2-tetraphenylethanol sample (already recrystallized from chloroform and benzene) using Banchetti's method (boiling with cyclohexanol) did not significantly affect the m.pt. or the i.r. spectrum of the material recovered. It was however interesting to notice traces of $(C_6H_5)_2CO$ and $(C_6H_5)_2CH_2$ present in cyclohexanol (t.l.c. on silica, benzene) probably resulted from partial thermal decomposition of the tetraphenylethanol at relatively high temperatures. In one of our initial irradiations of neat benzophenone and diphenylmethane, the crude product obtained was recrystallized from benzene and chloroform only; t.l.c. on silica, ^{13}C F.T. n.m.r. and ^{1}H F.T. n.m.r. evidence however showed the product to be pure. No benzopinacol or 1,1,2,2-tetraphenylethane were detected which directly contradicts Banchetti's assertions. The long arguments concerning melting points demonstrate the shortcomings of this particular criterion of purity; it is worth noting that 1,1,2,2-tetraphenylethanol prepared via ground state chemistry has also given varying melting points, 235°,[74] 232°-233°,[79] 243°-244°,[82] 236.5°,[76] 232°-233°,[77] 231°-232.5°,[81] 232.5°-233°.[78] It seems quite likely that the compound exists in two isomeric forms, possibly cisoid and transoid conformational isomers, having different m.pts.; ^{1}H F.T. n.m.r. evidence supports this proposition. The varying m.pts. recorded could thus result from varying proportions of the two isomeric forms.

On the basis of the results obtained from the model reaction, one would expect the irradiation of an aromatic bisketone in the presence of an equimolar amount of a bisbenzylbenzene to yield a linear polymer containing at least 95% tetraphenylethanol units in the backbone. By analogy with the model reaction the polymer formation would be expected to be slow and the product would be expected to contain a small percentage of benzopinacol and tetraphenylethane units. The formation of these two types of unit would be chain propagating rather than chain terminating and indeed no reactions which would be chain terminating were observed in this study of the model reaction, apart from the formation of traces of biphenyl which presumably arose from reaction of benzophenone with the solvent. Finally, crosslinking and/or branching might occur via the tertiary hydrogen in the tetraphenylethanol and tetraphenylethane types of unit of the proposed polymer.

For the actual polymer forming reaction, m-dibenzylbenzene and m- and p-dibenzylbenzenes were selected as appropriate monomers. Benzene was chosen as the solvent.

2.3b. Monomer Syntheses

(1) Discussion

The preparation, purification and characterization of m-dibenzoylbenzene has already been described in section 2.2h.

The preparation of arylalkylated aromatic hydrocarbons has been the subject of many reports. Zincke obtained 1,4-, 1,2-dibenzylbenzene and diphenylmethane by the action of metallic zinc on a mixture of benzylchloride and benzene.[91] Similar results were obtained by Thiele and Balhom, who reacted benzene with formaldehyde in the presence of sulphuric acid.[92] Huston and Friedmann showed that the aluminium chloride catalysed reaction of benzylchloride with benzene gave a complex mixture from which they isolated diphenylmethane, anthracene, anthraquinone, a little 1,2-dibenzylbenzene and 1,4-dibenzylbenzene, m.pt. 85°-86° (alcohol).[93]

Japanese workers reported the synthesis of p-phenylenedibenzyl in a very impure state (melting point range: 20°) by stirring a mixture of benzene and benzylchloride in tetrachloroethane with zinc powder under nitrogen; the impure material was found to be photoconductive.[94] Profft, Drechsler and Oberender,[95] obtained low yields of 1,4-dibenzylbenzene (m.pt. 86.5°) from the reaction of tetrachlorodurene with benzene under Friedel-Crafts conditions.

Pure 1,4-dibenzylbenzene, m.pt. 84°-85° (acetone) was prepared by the one-step hydrolysis and decarboxylation of $C_6H_5-CH_2-p-(C_6H_4-CH(CCl_3)C_6H_5)$;[96] the same compound was also obtained from the action of N_2H_4/KOH at over 190° on 1,4-(p-bromobenzoyl)benzene.[96]

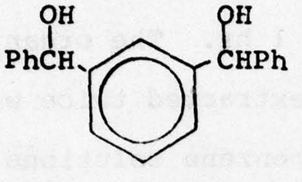
Possible routes for alkane preparation from the corresponding carbonyl compound include the Clemensen reduction and the Wolff-Kishner reduction.

The Clemensen reduction involves treating the carbonyl compound with amalgamated zinc and concentrated HCl, yielding hydrocarbon as the main product, but also variable quantities of the secondary alcohols (in the case of ketones) and unsaturated substances. Purely aromatic ketones however do not give satisfactory results; pinacols and resinous products often predominate.[97] The Wolff-Kishner reduction affords hydrocarbons upon heating the corresponding hydrazone or semicarbazone of the carbonyl compound with potassium hydroxide or with sodium ethoxide in a sealed tube.[97,98] The Huang-Minlon modification of the reaction (formation and decomposition of the hydrazone in one reaction vessel) is experimentally more convenient and reported to proceed in better yield.

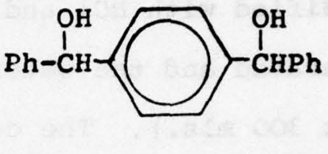
Finally arylalkanes may also be synthesized by reduction of the corresponding arylalkylhalides or arylalkyltosylesters.[98] This synthetic route would involve reduction of the corresponding carbonyl compound to the alcohol, conversion of the alcohol to the arylalkylhalide or to the tosyl ester, and finally reduction with an efficient reducing agent, such as $LiAlH_4$.

In our hands, attempts to prepare m-dibenzylbenzene by reducing the corresponding dicarbonyl compound, m-dibenzoylbenzene via either the Wolff-Kishner reduction (Huang-Minlon modification), or the Clemensen reduction gave unsatisfactory results. A mixture of products was obtained in the latter case which was found difficult to separate, whereas the former route resulted in the formation of dark intractable tars. Repetition of the Japanese workers' experiment[94] yielded a small quantity of a mixture comprising at least 10 components (t.l.c. on silica, benzene).

The failure to obtain the arylalkylated hydrocarbons by the above described routes led to the investigation of alternative syntheses of 1,4- and 1,3-dibenzylbenzene. Most of these routes involved initial syntheses of bis-benzhydrols -



and



- and conversion of their hydroxyl groups to a leaving group such as halide or tosyl which could be displaced by hydride ion. The most satisfactory route proved to be via the lithium aluminium hydride reduction of the bis-benzhydrylchlorides.

(2) Experimental

(a) p-Bis-benzhydrol

Magnesium turnings (48.60 g) in a 3 necked round bottom flask fitted with a mechanical stirrer, pressure equalizing dropping funnel, double surface reflux condenser, nitrogen gas inlet and thermometer well were covered with 1.8 litres freshly distilled THF. The dropping funnel was filled with dry bromobenzene (314.00 g) and a few drops were added with efficient stirring. The reaction started smoothly after about 5 mins, without the use of catalyst. Addition of bromobenzene was regulated by monitoring the pot temperature which was maintained between 70°-80°. The solution got progressively darker and was dark brown after about 2½ hrs. when most of the magnesium had been consumed. After addition of bromobenzene had finished, pot contents were stirred for a further 1 hr. period, at the end of which temperature dropped to 30°.

Slow addition of terephthalaldehyde (67.0 g) on 0.7 litre THF was then started with efficient stirring, taking care to maintain the pot temperature below 40°. After all the terephthalaldehyde solution had been added, the pot contents were dark red. The mixture was boiled under reflux for 2 hrs., cooled to room temperature, and carefully poured into ice/water (2.5 litres) acidified with HCl and stirred for 1 hr. The organic layer was separated and the water layer was extracted twice with benzene (2 x 300 mls.). The combined THF/benzene solutions were dried over anhydrous magnesium sulphate and finally volatile solvents were removed under vacuum to give 116 g. of crude product (80%). Recrystallizations from ethanol/water (75:25) afforded 70% of pure p-bis-benzhydrol (t.l.c. on silica, benzene, chloroform), m.pt. 169°-170° (lit.[99] 171°).

The reaction did not proceed in ether solvent due to the low solubility of terephthalaldehyde in that medium.

(b) p-Bis-benzhydrylchloride

p-Bis-benzhydrol (40 g) and freshly distilled thionylchloride (180 mls) were heated under reflux for 2 hrs. The excess thionylchloride was distilled off under reduced pressure and 100 mls of acetic acid plus 2 drops of concentrated hydrochloric acid were added. The white solid which precipitated was filtered off and treated again with 60 mls of glacial acetic acid plus two drops of concentrated hydrochloric acid. The solution was boiled with decolourizing charcoal, filtered hot and the colourless filtrate allowed to cool. The colourless dichloride which crystallized out was filtered and dried by pumping under vacuum for 48 hrs. at 60°. White needles were obtained from chloroform/hexane, m.pt. 190° (lit.[100] 197°-198°).

(c) m-Bis-benzhydrol

To m-dibenzoylbenzene (100 g) in 2000 mls ethanol in a 5 litre round bottom flask fitted with reflux condenser was slowly added a solution of $NaBH_4$ (45 g) in water (300 mls). The resultant solution was refluxed for 5 hrs. and cooled to room temperature. Following the destruction of unreacted borohydride with 5% acetic acid solution, the volume of solvent was reduced to 200 mls. Addition of a large volume of water caused the precipitation of a white material which was collected on a filter, washed successively with water, 5% HCl solution and 5% aqueous sodium carbonate solution, and then boiled with activated animal charcoal in ethanol solution. m-Bis-benzhydrol (80%) was obtained after recrystallizations from ethanol/water (70:30), m.pt. 151°-153°.

(d) m-Bis-benzhydrylchloride

This synthesis was carried out in exactly the same way as that of the para-isomer (see above). A dark oil was obtained in 90% yield which was examined by Lassaigne's method and was found to contain chlorine. This product was not purified but was used as obtained for reduction to m-bis-benzylbenzene. The infrared spectrum of the oil was recorded (contact film, $\bar{\nu}_{max}$: 3080, 3060, 3020, 2940, 1600, 1590, 1490, 1450, 1210, 1150, 1075, 1030, 1000, 830, 790, 760, 730, 700, 625, 580 cm.$^{-1}$

(e) p-Bis-benzylbenzene

$LiAlH_4$ (10 g, 0.26 mole) in a 2 litre 3 necked round bottom flask fitted with a mechanical stirrer, pressure equalizing dropping funnel, nitrogen gas inlet and double surface reflux condenser leading to a concentrated sulphuric acid bubbler was covered with 1 litre sodium dried ether; the mixture was stirred vigrously for 30 mins. and then cooled to 0° by means of an ice/water/salt bath.

p-Bisbenzhydrylchloride (32.7 g, 0.1 mole) was shaken with ether (0.5 litres) and the resulted slurry was slowly added to the mixture in the flask with vigorous stirring. The colour of the mixture changed eventually from grey to light green. After addition was complete, the mixture was gently refluxed for 12 hrs. The excess lithium aluminium hydride was destroyed by successive slow additions of water (10 g), 10% NaOH (15 g) and water (30 g)[101] resulting in the formation of a granular precipitate which was filtered off, washed with two 200 mls portions of benzene and destroyed by slowly adding it into a large volume of 6N HCl until a clear solution was formed. The combined ethereal and benzene solutions were dried over anhydrous magnesium sulphate and finally the solvents were removed under reduced pressure. A whitish solid was obtained which was recrystallized several times from hot ethanol, boiled with activated animal charcoal and then recrystallized several times from methanol and ethanol to give a yellowish crystalline material impure 1,4-bisbenzylbenzene (30%), melting at 83°-85° (lit.[71] 86°).

(f) <u>m-Bis-benzylbenzene</u>

This synthesis was carried out in the same way as that of the para-isomer apart from the addition of the m-bisbenzhydrylchloride which was easier since the compound is soluble in ether. Reaction afforded a brown oil which was distilled, dissolved in benzene and boiled with activated animal charcoal, filtered; the solvent was removed and the residue distilled to yield a yellow oil; absence of chlorine from the oil was established by Lassaigne's test. Finally a yellowish oil was obtained by distillation at 220° - 239°/14 mm Hg (lit.[71] 229°-231°/14 mm Hg, 226-227°/19 mm Hg).

(g) Purification and proof of structure of dibenzylbenzenes

1,4-Dibenzylbenzene was purified by two more recrystallizations from absolute ethanol, boiling with activated animal charcoal in benzene, sublimation at 106°/0.01 mm Hg, another recrystallization from ethanol and washing with the same solvent (10°). It was then pumped under reduced pressure (0.01 mm Hg) at 40° for 48 hrs. This procedure gave 20% of pure product, m.pt. 85.8° (lit.[71] 86°) as big plates (Found: C, 92.56; H, 7.12; calculated for $C_{20}H_{18}$: C, 92.98; H, 7.02%). The substance gave a single spot on t.l.c. on silica (benzene, chloroform); $\bar{\nu}_{max}$ (KBr disc): 3070, 3060, 3020, 2900 (doublet), 2430, 1950, 1915, 1600, 1595, 1510, 1490, 1450, 1430, 1415, 1335, 1320, 1210, 1175, 1160, 1105, 1070, 1030, 930, 855, 760, 725, 700, 600, 485, 460 cm^{-1}. The mass spectrum extended to m/e = 258 corresponding to the parent ion; main peaks at 192, 167, 150, 121, 120, 90, 77. Lassaigne's test on the sample showed the absence of chlorine as did the mass spectrum. The ^1H n.m.r. spectrum in $CDCl_3$ (int. TMS ref.) showed two peaks in the aromatic hydrogen region (δ 7.10, δ 6.96) and a singlet at δ 3.80.

1,3-Dibenzylbenzene was purified by further distillations between 220°-235°/15 mm Hg and finally by a distillation at 140°/13 mm Hg under nitrogen. A colourless oil was obtained. (Found: C, 92.73; H, 7.23%; calculated for $C_{20}H_{18}$: C, 92.88; H, 7.02%) t.l.c. on silica (benzene, chloroform) gave a single spot; $\bar{\nu}_{max}$ (contact film): 3100, 3080, 3040, 3020, 2900, 2840, 1940, 1870, 1800, 1600, 1490 (doublet), 1445 (doublet), 1090, 1075, 1030, 1000, 770, 750, 730, 700, 600, 550, 460, 430 $cm.^{-1}$ Lassaigne's test on the product showed the absence of chlorine. The mass spectrum extended to m/e = 258, corresponding to the parent ion; main peaks at 181, 180, 168, 166, 153, 91, 77.

2.3c. Polymerizations

(i) A preliminary investigation

1,4-Dibenzylbenzene (1.2918 g, 0.005 mole) and 1,3-dibenzoylbenzene (1.4316 g, 0.005 mole) were dissolved in benzene (50 mls, 0.2M with respect to both reagents) in a cylindrical Pyrex vessel. The clear, colourless solution was nitrogen streamed for 30 mins., the tube was quickly stoppered and irradiated at 350 nm. for 24 hrs. A bright yellow colour developed at an early stage during the irradiation and a trace of a white precipitate appeared at the bottom of the tube. Benzene solvent was removed by freeze-drying and a yellow material was quantitatively recovered showing both hydroxyl and benzophenone-type carbonyl bands in the i.r. region. The presence of the strong carbonyl band was attributed to either unreacted monomer or to low molecular weight material formed; thus the earlier expectation that the polymerization reaction might be a slow one was confirmed. On the other hand, the presence of the hydroxyl band indicated that, as expected, hydrogen abstraction was taking place and that the benzophenone-type ketyl radical of m-dibenzoylbenzene was in fact yielding products either by diffusion out of the cage and dimerization or by in-cage combination with the radical resulting from p-bisbenzylbenzene. The i.r. spectrum of the yellowish powder displayed the following absorptions (KBr disc, $\bar{\upsilon}_{max}$:) 3540, 1520 - ca. 3400 (broad), 3080, 3050, 3020 (strong), 2900, 1655, 1600, 1580, 1510, 1480, 1445, 1420, 1320, 1275, 1160, 1090, 1030, 1000, 845, 830, 780, 740 (doublet), 700, 640, 620, 555 cm.$^{-1}$ Comparison with the i.r. spectrum of polybenzopinacol M (prepared by irradiation of m-dibenzoylbenzene in isopropanol/benzene)^2 (KBr disc, $\bar{\upsilon}_{max}$: 3560, 3500 - ca. 3400 (broad), 3060, 3020 (weak), 2960 (possibly occluded solvent or incorporated isopropanol moieties), 1600, 1560, 1495, 1450, 1420, 1330, 1265, 1155, 1100, 1030, 920, 790, 765, 750, 700, 645, 615 cm.$^{-1}$) revealed that the two spectra differ in many regions; differences in the relative intensities of the O-H and aromatic C-H absorptions were evident, the yellow material having a much stronger C-H aromatic group of peaks. Differences in the fingerprint region of the spectrum were also observed. Washing the material obtained with cold hexane in order to eliminate any unreacted bisbenzylbenzene, followed by drying under vacuum, did not alter the colour, weight or the solid state i.r. spectrum.

(ii) Examination of the effect of concentration

The experiments recorded in Table 3 were carried out in the same way as in the previous experiment (cylindrical Pyrex tubes, nitrogen streaming followed by stoppering, irradiation at 350 nm). In all cases, the solutions went bright yellow and a trace of a white precipitate was observed at the bottom of the tube; it was separated from the yellow solution by filtration, washed with a few drops of cold benzene, dried under vacuum and weighed; in all cases it amounted to ca. 5% of the total weight of the two reactants used, and was insoluble in a wide range of laboratory solvents.

Benzene solvent was removed from yellow solutions by freeze-drying and yellow solids were obtained which were dried by pumping under reduced pressure and examined by i.r. spectroscopy (KBr discs). The spectra obtained from experiments A, B and C were very similar and comparable to the i.r. spectrum of the yellow product obtained from the 24 hrs. irradiation, but the benzophenone-type carbonyl band was much weaker, indicating that longer irradiation times resulted in increased consumption of at least one of the monomers (m-dibenzoylbenzene). The relative intensities of the carbonyl band in the spectra of the three products was roughly the same, indicating that in the concentration range 0.1M - 1M reaction rate (as monitored by carbonyl consumption) was not dramatically changing.

Table 3

Irradiations of equimolar solutions of m-dibenzoylbenzene/m- and p-dibenzylbenzene of varying concentrations

Expt.	Bisketone	Alkane	Solvent	Total concn.	Irradiation time
A	m-dibenzoyl-benzene 0.7158g 0.0025 mole	p-bisbenzyl-benzene 0.6459g 0.0025 mole	benzene 50 mls	0.1M	240 hrs
B	m-dibenzoyl-benzene 0.7158g 0.0025 mole	p-bisbenzyl-benzene 0.6459g 0.0025 mole	benzene 25 mls	0.2M	240 hrs
C	m-dibenzoyl-benzene 0.7158g 0.0025 mole	p-bisbenzyl-benzene 0.6459g 0.0025 mole	benzene 12.5 mls	0.4M	240 hrs
D	m-dibenzoyl-benzene 2.860g 0.01 mole	m-bisbenzyl-benzene 2.580g 0.01 mole	benzene 20 mls	1M	240 hrs

The benzene-soluble material from experiment D was dried by pumping under reduced pressure following removal of solvent; a portion of it was precipitated from benzene/60°-80° petroleum ether and a white powder was thus obtained analyzing as follows: C, 85.98; H, 5.92. In the i.r. spectrum of this product the carbonyl peak appeared considerably stronger than in the i.r. spectra of the yellow products obtained from experiments A, B and C, indicating that consumption of carbonyl in the reaction between the two meta isomers was qualitatively slower than in the reaction between m-dibenzoylbenzene and p-dibenzylbenzene.

Another portion (2.0 g) of the crude yellow product isolated from experiment D was dissolved in benzene (10 mls), nitrogen streamed, and irradiated at 350 nm for 435 hrs. Again, a white solid precipitated during irradiation (ca. 6%), which displayed an i.r. spectrum similar to those of the white precipitates obtained previously. The yellow benzene solution was separated, and the solvent was removed by freeze-drying yielding a yellow solid which was precipitated from benzene/60^o-80^o petroleum ether. The white powder obtained from precipitation was examined by i.r. spectroscopy; a very small absorption at ca. 1660 $cm.^{-1}$ was observed indicating that most of the m-dibenzoylbenzene had been consumed. The solution phase i.r. spectrum of this product (CCl_4 solvent, saturated solution, 0.1 mm cell) showed a singlet at 3560 $cm.^{-1}$ (O-H), a doublet at 3060-3020 $cm.^{-1}$ (aromatic C-H), and a broad singlet at 2920 $cm.^{-1}$ (aliphatic C-H); the relative intensities of the O-H and aromatic C-H peaks were roughly the same (aromatic C-H slightly stronger). The solution phase i.r. spectrum of polybenzopinacol M^2 examined under the same conditions showed a singlet at 3560 $cm.^{-1}$ and a shoulder at 3600 $cm.^{-1}$ (O-H), a very broad absorption between 3500-3400 $cm.^{-1}$ (hydrogen bonded O-H), two singlets at 3060-3030 $cm.^{-1}$ (aromatic C-H), and a strong singlet at 2960 $cm.^{-1}$ (aliphatic C-H, possibly due to occluded solvent). The O-H peak was considerably stronger than the two aromatic C-H peaks.

The above preliminary investigations led to the conclusion that the product obtained from the m-dibenzoylbenzene/m-dibenzylbenzene reaction was not a polybenzopinacol (by comparative solid state and solution phase i.r. evidence). This was an encouraging result and gave the incentive for a more thorough examination of the polyaddition reaction.

(iii) Large scale experiments

(a) m-Dibenzoylbenzene/p-dibenzylbenzene (25.834 g, 0.1 mole) were dissolved in sodium-dried benzene (500 mls, 0.4M with respect to both reagents). The solution was nitrogen streamed for 30 mins, the cylindrical Pyrex tube was quickly stoppered and irradiated at 350 nm for 263 hrs. During irradiation a white material precipitated, whereas remaining solution became bright yellow. The white material (A) was recovered by filtration, washed with a little cold benzene, dried by pumping under reduced pressure, weighed (2.482 g) and examined by i.r. spectroscopy (KBr disc); spectrum obtained was essentially the same as the ones recorded for previously obtained white precipitates. The yellow solution separated yielded, following removal of solvent by freeze-drying and pumping under reduced pressure, a yellow material (B) (51.980 g) which was spectroscopically examined (i.r., KBr disc); it was then redissolved in benzene (500 mls) and re-irradiated for a further 144 hrs. period, yielding another white precipitate (C) (0.832 g) and a yellow solid (D) (51.140 g).

Solid (D) was then divided into 2 x 25 g portions. Two benzene solutions were made:

25 g of solid (D) in 100 mls benzene
25 g of solid (D) in 250 mls benzene

The two solutions were re-irradiated for 118 hrs, yielding only slight white precipitates (ca. 1% of the weight of solid (D) used) and yellow solids (E) (from 25 g (D)/100 mls C_6H_6) and (F) (from 25 g (D)/250 mls C_6H_6).

(b) m-Dibenzoylbenzene/m-dibenzylbenzene

m-Dibenzoylbenzene (28.631 g, 0.1 mole) and m-dibenzylbenzene (25.834 g, 0.1 mole) were dissolved in sodium dried benzene (500 mls, 0.4M with respect to both reagents). The solution was nitrogen streamed for 30 mins., the cylindrical Pyrex tube was quickly stoppered and irradiated at 350 nm for 263 hrs. During irradiation a white material precipitated, whereas remaining solution became bright yellow. The white material (G) was recovered by filtration, washed with a little cold benzene, dried by pumping under reduced pressure, weighed (2.482 g) and examined by i.r. spectroscopy (KBr disc); spectrum obtained was the same as the ones recorded for previously obtained white precipitates. The yellow solution separated yielded, following removal of solvent by freeze-drying and pumping under reduced pressure, a yellow material (H) (51.980 g) which was spectroscopically examined (i.r., KBr disc); it was then redissolved in benzene (500 mls) and re-irradiated for a further 144 hrs. period, yielding another white precipitate (I) (1.044 g) and a yellow solid (J) (50.920 g).

Solid (J) was then divided into 2 x 25 g portions. Two benzene solutions were made:

25 g of solid (J) in 100 mls benzene
25 g of solid (J) in 250 mls benzene

The two solutions were re-irradiated for 118 hrs, yielding only slight white precipitates, and yellow solids (K)(from 25 g (J)/100 mls C_6H_6) and (L) (from 25 g (J)/250 mls C_6H_6). Following spectral examinations, solids (K) and (L) were combined, dissolved in 250 mls of benzene and re-irradiated (350 nm) for 171 hrs., yielding again very slight white precipitates (< 1% of the combined (K) + (L) weight) and a yellow benzene-soluble solid (M) (48.932 g).

(iv) Characterization of products

All products obtained from experiments described in (iii) were dried by pumping under reduced pressure before examination.

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I.r. spectra (KBr discs) were the same as the ones obtained for corresponding products described in (i) and (ii), spectra of (B) + (D), (E), (F), (H), (J), (K), (L), (M), all displayed absorptions at 1660 cm.$^{-1}$, indicating the presence of benzophenone-type carbonyl groups attributable to either unreacted monomer or low molecular weight polymer chains capped with aromatic carbonyl ends.

Products (E) and (F) were combined, dissolved in benzene and the bright yellow solutions thus obtained were added dropwise to a 10-fold excess of 60°-80° petroleum ether with efficient stirring. A white solid (N) was obtained in 89% yield, which was collected and dried under vacuum. (N) was redissolved in benzene forming a bright yellow solution. Second precipitation from 60°-80° petroleum ether afforded a white solid (O) (80%) which was dried by pumping under vacuum for 6 days at 40°; elemental analysis gave: C, 86.54; H, 7.18; (O) still displayed a weak absorption at 1660 cm.$^{-1}$ in the i.r. spectrum. It did not form films on casting on a clean Hg surface (CH_2Cl_2 solvent). Small, brittle fibres were drawn out of the melt; it became tacky between 188°-207° and melted between 207°-220°.

Similarly, product (M) was precipitated from benzene/60°-80° petroleum ether yielding a powder (P) (80%) which was dried in the same way as (O). No films were obtained, but small, brittle fibres were drawn out of the melt. (P) became tacky between 165°-177° and melted between 177°-192°.

The number average molecular weights of the samples were determined by the isopiestic method in chloroform and are recorded below:

Sample	Total Irr^n time (hrs)	$\bar{M}_n$	Sample	Total Irr^n time (hrs)	$\bar{M}_n$
(B)	263	2780	(H)	263	2030
(D)	407	3560	(J)	407	2130
(E)	525	3590	(K)	525	3320
(F)	525	3530	(L)	525	3410
(O)	525	3690	(M)	525	3510
			(P)	696	3670

Polymer characterization was attempted by F.T. ^{1}H n.m.r. spectroscopy (see Figure 4).

Spectra of samples (O) and (P) were run in CDCl$_3$ solvent (ext. TMS reference) and compared to the spectra of p-bisbenzylbenzene, polypinacol M,[64] 1,1,2,2-tetraphenylethanol, benzopinacol and 1,1,2,2-tetraphenylethane.

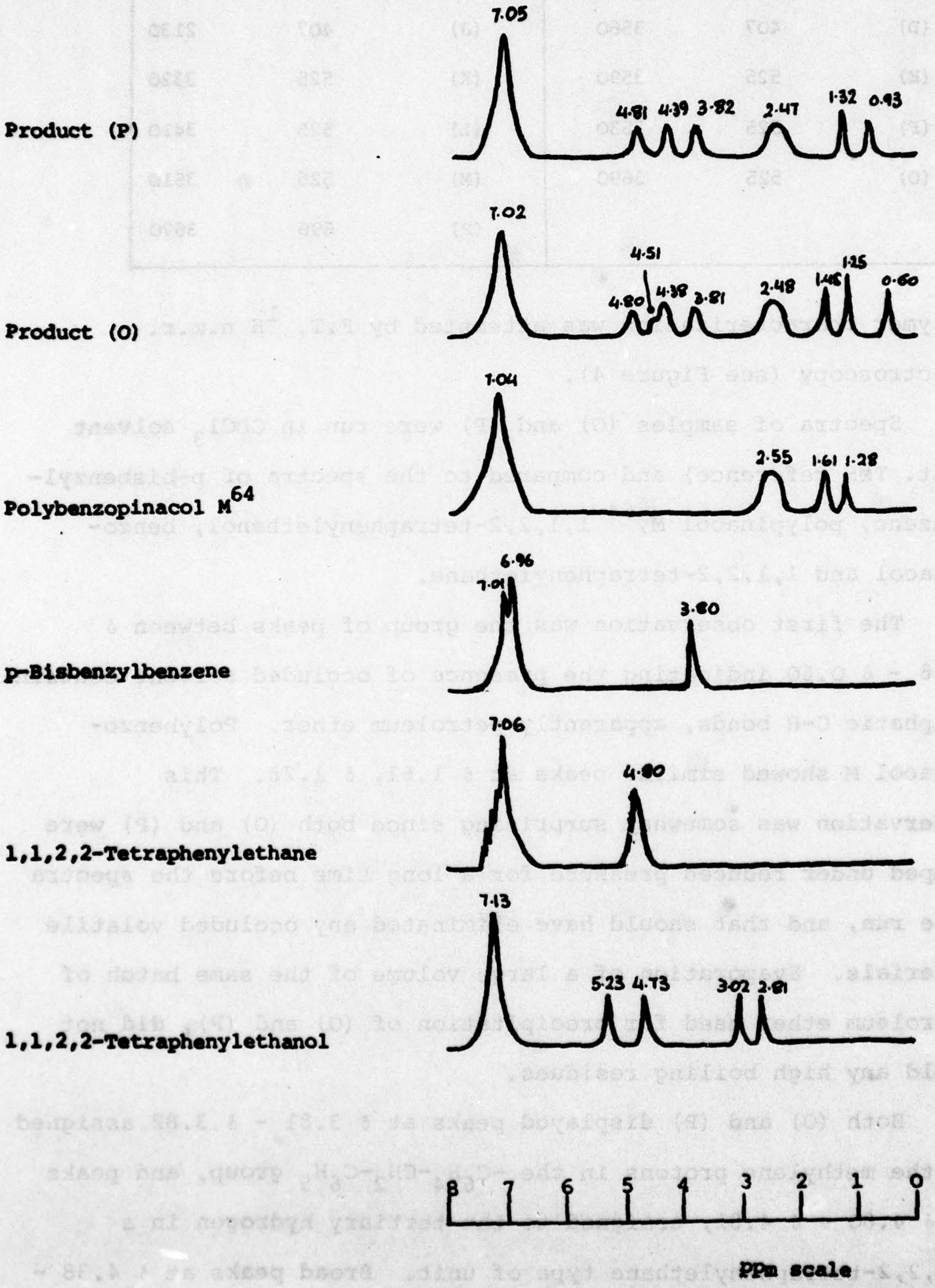
The first observation was the group of peaks between δ 1.48 - δ 0.60 indicating the presence of occluded solvent containing aliphatic C-H bonds, apparently petroleum ether. Polybenzopinacol M showed similar peaks at δ 1.61, δ 1.28. This observation was somewhat surprising since both (O) and (P) were pumped under reduced pressure for a long time before the spectra were run, and that should have eliminated any occluded volatile materials. Evaporation of a large volume of the same batch of petroleum ether used for precipitation of (O) and (P), did not yield any high boiling residues.

Both (O) and (P) displayed peaks at δ 3.81 - δ 3.82 assigned to the methylene protons in the $-C_6H_4-CH_2-C_6H_5$ group, and peaks at δ 4.80 - δ 4.81, assigned to the tertiary hydrogen in a 1,1,2,2-tetraphenylethane type of unit. Broad peaks at δ 4.38 - δ 4.39 however could not be unequivocally assigned to any

Figure 4

Comparative F.T. ^{1}H n.m.r. spectra of some phenylated substances

(CDCl$_3$ solutions, ext. TMS ref.).



structure since the tertiary proton resonance in 1,1,2,2-tetraphenylethanol occurs at δ 5.23 and δ 4.73.

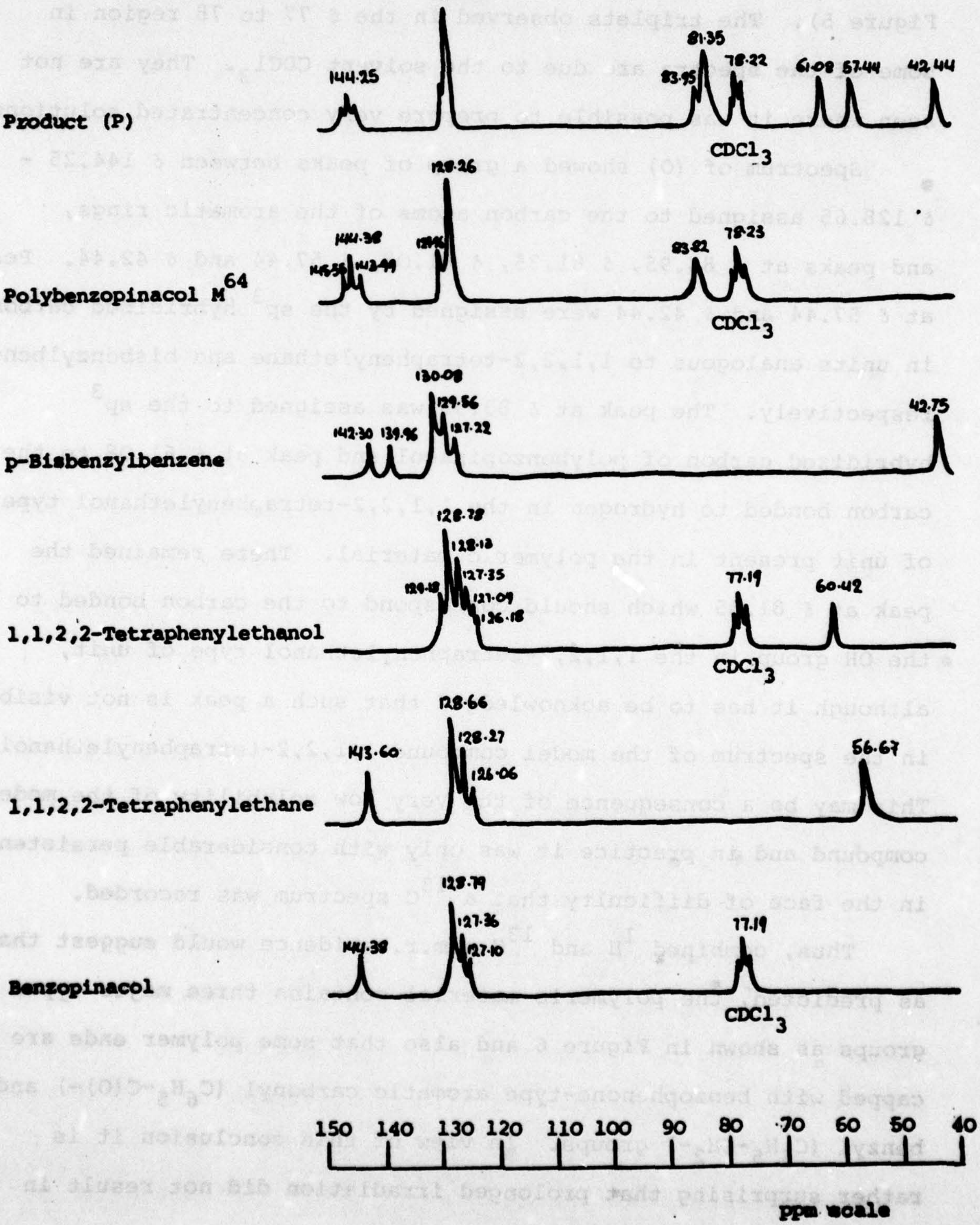
Comparative F.T. ^{13}C n.m.r. spectroscopy proved a more useful technique for the characterization of the materials (see Figure 5). The triplets observed in the δ 77 to 78 region in some of the spectra are due to the solvent $CDCl_3$. They are not seen where it was possible to prepare very concentrated solutions.

Spectrum of (O) showed a group of peaks between δ 144.25 - δ 128.65 assigned to the carbon atoms of the aromatic rings, and peaks at δ 83.95, δ 81.35, δ 61.08, δ 57.44 and δ 42.44. Peaks at δ 57.44 and δ 42.44 were assigned by the sp^3 hybridized carbons in units analogous to 1,1,2,2-tetraphenylethane and bisbenzylbenzene respectively. The peak at δ 83.95 was assigned to the sp^3 hybridized carbon of polybenzopinacol and peak at δ 61.08 to the carbon bonded to hydrogen in the 1,1,2,2-tetraphenylethanol type of unit present in the polymeric material. There remained the peak at δ 81.35 which should correspond to the carbon bonded to the OH group in the 1,1,2,2-tetraphenylethanol type of unit, although it has to be acknowledged that such a peak is not visible in the spectrum of the model compound 1,1,2,2-tetraphenylethanol. This may be a consequence of the very low solubility of the model compound and in practice it was only with considerable persistence in the face of difficulty that a ^{13}C spectrum was recorded.

Thus, combined ^{1}H and ^{13}C n.m.r. evidence would suggest that, as predicted, the polymeric material contains three major types of groups as shown in Figure 6 and also that some polymer ends are capped with benzophenone-type aromatic carbonyl (C_6H_5-C(O)-) and benzyl (C_6H_5-CH_2-) groups. In view of this conclusion it is rather surprising that prolonged irradiation did not result in the formation of higher molecular weight products.

Figure 5

Comparative F.T. ^{13}C n.m.r. spectra of some phenylated substances ($CDCl_3$ solutions, ext. TMS ref.).



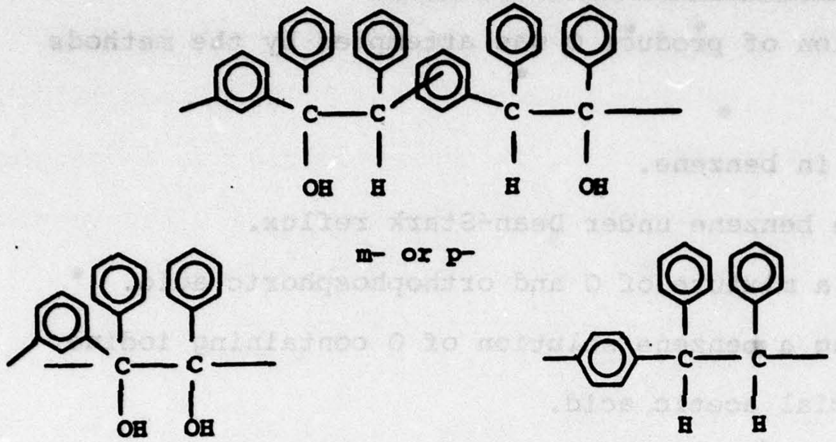


Figure 6

2.3d. Reactions of the polymers

(i) Depolymerization

A sample of the polymeric material (O) was introduced into a 3 necked round bottom flask fitted with water condenser, thermometer pocket and nitrogen gas inlet. The flask was slowly heated by means of a free flame until the polymer had melted and then temperature was raised up to 350° and maintained there for 5 mins. A black tar was formed which was left to cool under nitrogen. Examination of the black tar by i.r. spectroscopy and t.l.c. on silica (benzene) revealed the presence of m-dibenzoylbenzene, p-bisbenzylbenzene, diphenylmethane and benzophenone amongst the pyrolysis products.

A similar treatment of polybenzopinacol M prepared by Andrews[2] gave a black tar with a different i.r. spectrum, and m-dibenzoylbenzene, m-bisbenzhydrol, benzophenone and benzhydrol were identified amongst the pyrolysis products by t.l.c. on silica (benzene).

These results are consistent with the structures assigned to these materials.

(ii) Treatment with dehydrating agents

The dehydration of product O was attempted by the methods listed below.

(a) Dry HCl in benzene.

(b) H_2SO_4 in benzene under Dean-Stark reflux.

(c) Heating a mixture of O and orthophosphoric acid.

(d) Refluxing a benzene solution of O containing iodine and glacial acetic acid.

(e) Refluxing a benzene solution of O containing toluene p-sulphonic acid.

(f) Heating a solution of O in xylene with P_2O_5.

Method (a) had no effect; methods (b), (d) and (e) resulted in the disappearance of the hydroxyl band in the i.r. spectrum and the appearence of a strong band at 1680 $cm.^{-1}$ (assigned to a benzopinacol type of unit); method (c) had only a very limited effect and method (f) resulted in extensive decomposition.

Parallel model compound studies

In view of the results recorded above a careful examination of similar reactions with the model compound, 1,1,2,2-tetraphenylethanol, was made and these results are recorded here.

(a) 1,1,2,2-tetraphenylethanol (2.00 g, 0.0057 mole) in hot glacial acetic acid (150 mls) was boiled under reflux for 1 hr. in the presence of a crystal of iodine. After cooling, solution was treated successively with water (50 mls), 0.1M aqueous potassium carbonate (50 mls), dilute aqueous thiosulphate (30 mls) and water (50 mls). A yellowish precipitate was obtained which was dissolved in benzene (100 mls) and kept over anhydrous magnesium sulphate overnight. Following removal of benzene solvent and drying under reduced pressure, the yellowish material (1.82 g) was examined by i.r. spectroscopy and t.l.c. on silica (benzene) and shown to contain tetraphenylethylene, benzopinacolone and 1,1,2,2-tetraphenylethane.

(b) 1,1,2,2-tetraphenylethanol (10.00 g., 0.028 mole) in hot benzene (200 mls) was boiled under reflux for 3 hrs. in the presence of P_2O_5 (20.00 g). After cooling, benzene solution was filtered and excess P_2O_5 was destroyed by careful addition of water. Evaporation of the benzene solvent yielded a white material (9.0 g) displaying no O-H band but C-H aliphatic and benzopinacolone-type carbonyl bands in the i.r. region (KBr disc). Recrystallizations of the white material from chloroform/methanol and benzene/ethanol yielded ca. 7 g of pure tetraphenylethylene, m.pt. 223° - 224°, identified by solid state i.r. spectroscopy (KBr disc) and mass spectrometry (m/e extended to 332 corresponding to the parent ion. The mother liquors from recrystallizations were found by t.l.c. on silica (benzene) to contain benzopinacolone and 1,1,2,2-tetraphenylethane.

1,1,2,2-tetraphenylethanol was recovered unchanged after being boiled under reflux (1 hr.) in either benzene or toluene (0.028M). Traces of benzophenone and diphenylmethane were observed on t.l.c. on silica (benzene), resulting probably from partial thermal decomposition of the ethanol.

Refluxing an equimolar toluene solution of benzopinacol and 1,1,2,2-tetraphenylethane (0.1M with respect to both reagents) for 3 hrs. resulted in total consumption of both starting materials and formation of 1,1,2,2-tetraphenylethanol, identified by t.l.c. on silica (benzene) and i.r. spectroscopy (KBr disc). Traces of benzophenone, diphenylmethane and benzhydrol were also observed on the t.l.c. plates.

Finally, heating 1,1,2,2-tetraphenylethanol under nitrogen at 350° for 5 mins. (round bottom flask, free flame) resulted in total decomposition of the material and quantitative formation of benzophenone and diphenylmethane, identified by t.l.c. on silica (benzene) and i.r. spectroscopy (contact film).

2.3e. Discussion and Conclusions

The bisbenzophenone/bisbenzylbenzene photopolymerization was found to be similar to the model reaction in some respects, e.g. the slow reaction rate, the early appearence of the yellow colour during irradiations and the formation of products containing three main types of unit as shown in Figure 6. However some new questions have arisen:

(a) The origin and structure of the white insoluble precipitates obtained in all photoreaction.

(b) The failure of the polymer forming reaction to proceed to completion even at prolonged irradiations, contrary to the behaviour of the benzophenone/diphenylmethane system and despite the presence of unreacted $-C_6H_4-CH_2-C_6H_5$ and $-C_6H_4-C(O)-C_6H_5$ residues in the polymeric materials, detected by n.m.r. and i.r. spectroscopy.

(c) The slower rate of molecular weight increase observed for the m-dibenzoylbenzene/m-dibenzylbenzene system, relative to the corresponding m-/p- one, although both systems gave materials of roughly the same molecular weight after 525 hrs. of irradiation.

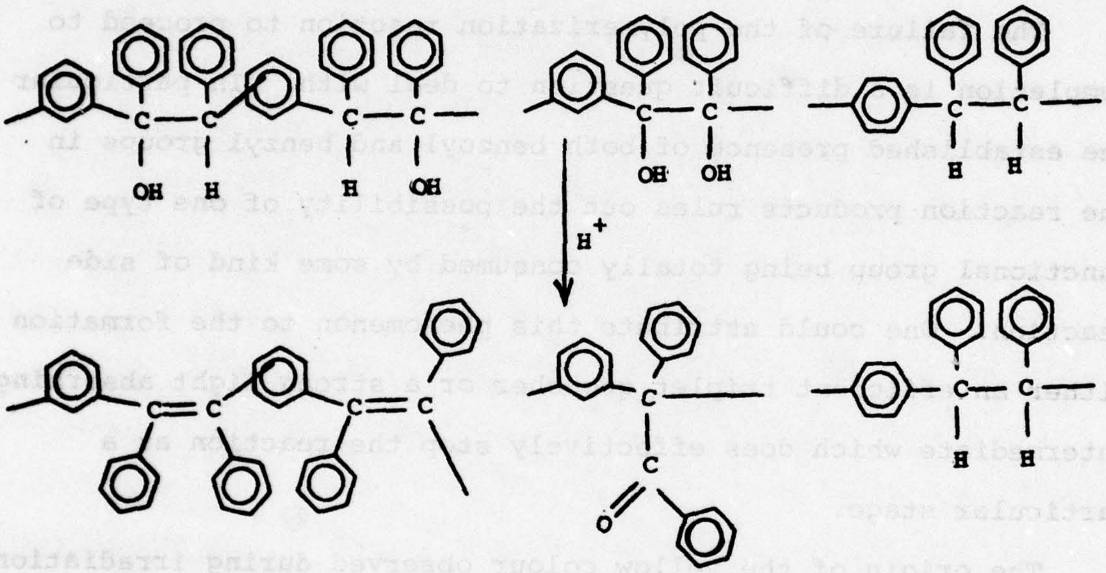
A typical i.r. spectrum of the white precipitate from the above photo-reactions has already been described in 2.3.c.ii. Attempts to measure $\bar{M}_n$ of such materials in solution failed due to extremely low solubility in a wide variety of solvents.

Similarly, low solubility in deuterated solvents prevented examination by n.m.r. spectroscopy. It is possible that these white precipitates might be either branched or crosslinked materials, formed by the interaction of a photoexcited bis-benzophenone carbonyl and tertiary hydrogen in either a 1,1,2,2-tetraphenylethanol type of unit or a 1,1,2,2-tetraphenylethane type unit.

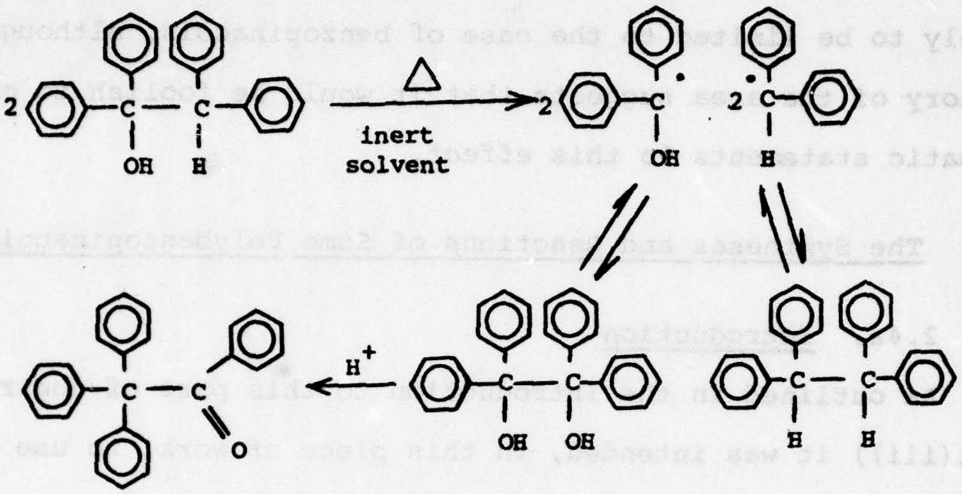
The failure of the polymerization reaction to proceed to completion is a difficult question to deal with. In particular the established presence of both benzoyl and benzyl groups in the reaction products rules out the possibility of one type of functional group being totally consumed by some kind of side reaction. One could attribute this phenomenon to the formation of either an efficient triplet quencher or a strong light absorbing intermediate which does effectively stop the reaction at a particular stage.

The origin of the yellow colour observed during irradiations is difficult to account for. Precipitation of the yellow crude polymeric materials from benzene/60^{o}-80^{o} petroleum ether afforded white powders whose i.r. spectra and $\bar{M}_n$ were not different from those of the crude materials. Treatment of the white powders with benzene at room temperature resulted in the formation of bright yellow solutions. Evaporation of benzene solvent gave yellow materials, whereas addition of excess 60^{o}-80^{o} petroleum ether to the yellow benzene solutions caused the precipitation of white materials; the i.r. spectra of these products were superimposable. It was first thought that some kind of association between benzene solvent and the product occurs which gives rise to the coloured species. However the same cycle of colourless to yellow changes can be effected using chloroform, which probably excludes such an explanation.

Treatment of the polymeric materials with dehydrating agents eliminated the hydroxyl peak in the i.r. region and gave rise to a new peak at 1680 cm.$^{-1}$ attributed to a benzopinacolone-type carbonyl group. This was observed both in reactions carried out at high temperature and room temperature, and is consistent with the expected reaction scheme shown below. The 1,1,2,2-tetraphenylethanol type of unit would be expected to loose HOH giving a conjugated structure; the benzopinacol type of unit would be expected to rearrange to a benzopinacolone one[102] and the 1,1,2,2-tetraphenylethane structure would be expected to be unreactive.



The model compound 1,1,2,2-tetraphenylethanol appears to be partially dissociating at temperatures of ca. 80° or over yielding radicals by rupture of the ethane C-C σ bond. In the absence of dehydrating agents these radicals appear to recombine forming the initial product, or diffuse out of the cage and dimerize yielding benzopinacol and 1,1,2,2-tetraphenylethane, all the steps are reversible and since the ethanol derivative is very insoluble, it is normally the predominant product. Addition of dehydrating agent at high temperatures causes the rearrangement of the benzopinacol component of this system to benzopinacolone (see below). This hypothesis would explain the observed behaviour



of the ethanol and its formation from benzopinacol and tetraphenylethane. At room temperature 1,1,2,2-tetraphenylethanol is known to dehydrate quantitatively to tetraphenylethylene (perchloric acid/methylenechloride solvent), no by-products were reported.[103]

It can be concluded that the photoreductive addition of m-dibenzoylbenzene to p- or m-dibenzylbenzene at 350 nm leads to the formation of low molecular weight materials ($\bar{M}_n$ ca. 3500) containing units analogous to 1,1,2,2-tetraphenylethanol, benzopinacol and 1,1,2,2-tetraphenylethane. In contrast to the model reaction, polymerization does not proceed to completion even at prolonged (over 700 hrs.) irradiations. The products obtained decompose thermally at high temperatures to yield starting materials together with traces of diphenylmethane and benzophenone. Treatment with dehydrating agents results in the elimination of water and the occurrence of rearrangements, both results being entirely consistent with the structures assigned to the polymers.

It would seem on the basis of the results obtained in this work that truly successful photoreductive polymerization is likely to be limited to the case of benzopinacols, although the history of the area suggests that it would be foolish to make dogmatic statements to this effect.

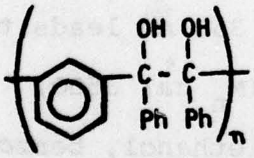
2.4. The Syntheses and Reactions of Some Polybenzopinacols

2.4a. Introduction

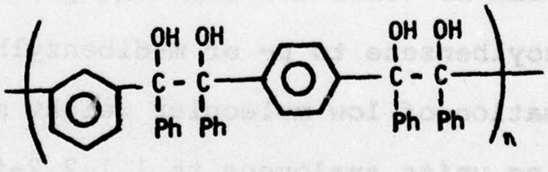
As outlined in the introduction to this part of the report (2.1(iii)) it was intended, in this piece of work, to use step-growth photoreductive polymerization as the first stage in the synthesis of novel aromatic polymers. The overall objectives of the work are summarized below.

Step 1. Preparation of polybenzopinacols.

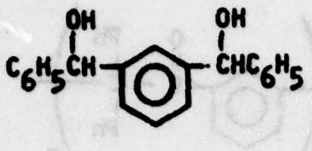
The first step in the projected work involved the synthesis of the following polybenzopinacols (2.4A, 2.4B). This area has been the subject of previous investigations and two approaches to the synthesis are possible depending on whether isopropanol or a dibenzhydrol is used as the hydrogen donor, previous work[8] implies that the latter method offers the best chance of obtaining high molecular weight products and this approach was investigated first. The diketone, m-dibenzoylbenzene, was irradiated with the meta- and p-dibenzhydrols 2.4C and 2.4D. Due to the poor solubility of



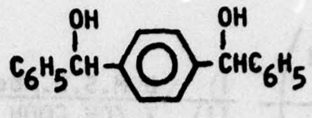
2.4A



2.4B



2.4C



2.4D

the m- and p-bisbenzhydrols, three sets of conditions were used in this previously uninvestigated reaction.

i) m-Dibenzoylbenzene dissolved in benzene at room temperature in the presence of either undissolved m- or p-bisbenzhydrol was irradiated with the intention of allowing the diol to dissolve as the reaction proceeded. This technique was used successfully by the Belgian group with different monomers.

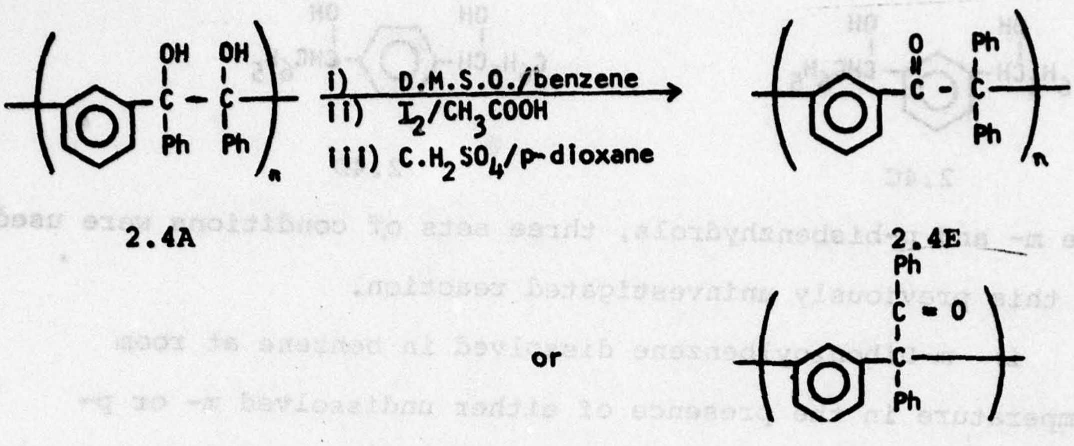
ii) m-Dibenzoylbenzene dissolved in hot benzene with either m- or p-bisbenzhydrol was irradiated.

iii) Irradiation of m-dibenzoylbenzene dissolved in acetonitrile at room temperature with m- or p-bisbenzhydrol; both monomers being readily soluble.

Since none of these procedures yielded high molecular weight polymers the photoreductive polymerization of m-dibenzoylbenzene in isopropanol-benzene solution was investigated in an attempt to optimise $\bar{M}$ for polymer 2.4A.

Step 2. Catalytic Dehydration of Polybenzopinacols.

Having made a polybenzopinacol with a reasonable molecular weight the next intended step was the acid catalyzed dehydration of the polybenzopinacol involving a pinacol-pinacolone rearrangement, three different catalysts were tried, all were known to give high conversions in the model reaction.



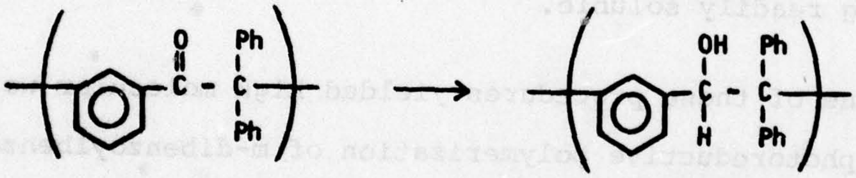
2.4A 2.4E

2.4F

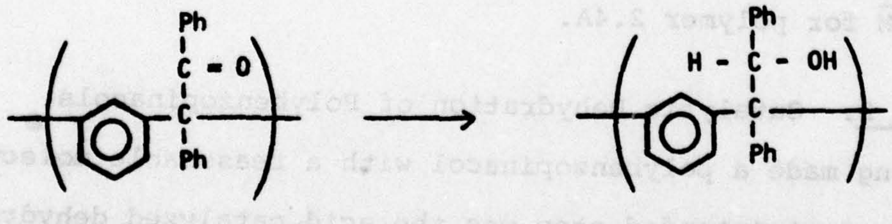
Two possible products may be produced depending on whether chain migration or phenyl migration takes place.

Step 3. Reduction of Polybenzopinacolone (2.4E or 2.4F) using $NaBH_4$.

This reaction could be carried out in either toluene or 1,4-dioxan, with the possible outcomes shown below.



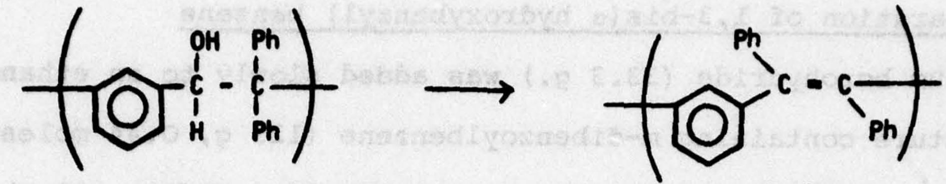
2.4E 2.4G



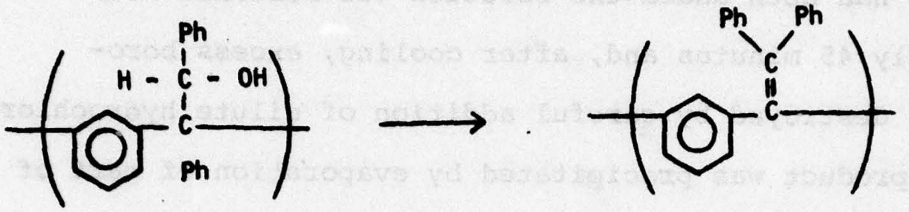
2.4F 2.4H

Step 4. Dehydration of Polymers 2.4G and/or 2.4H.

The final step was to be the acid catalyzed dehydration of the products to give polymers 2.4J and/or 2.4K.



2.4G 2.4J

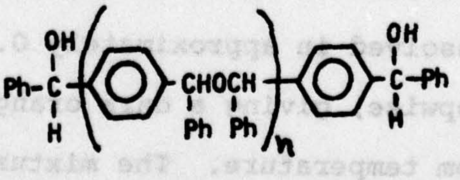


2.4H 2.4K

The likely properties of polymers with the novel structures 2.4J and 2.4K are difficult to predict; but in recent years considerable efforts have gone into attempts to synthesise totally conjugated aromatic and heteroaromatic polymers, and this seemed to be an interesting synthetic project related to the general area of this research.

2.4b. Monomer syntheses

Meta-dibenzoyl benzene was prepared as described in Section 2.2. p-Bisbenzhydrol was prepared by reacting terephthaldehyde with phenylmagnesium bromide. The first attempt at this synthesis gave a yellow wax which was probably a telomer with the structure shown below, the dehydration resulting from an injudicious use of excess acid during the work up procedure.



Subsequent preparations gave the expected product. m-Bisbenzohydrol was obtained by sodium borohydride reduction of m-dibenzoylbenzene.

Preparation of 1,3-bis(α hydroxybenzyl) benzene

Sodium borohydride (33.3 g.) was added slowly to an ethanol-water mixture containing m-dibenzoylbenzene (125 g, 0.44 moles), the whole system was purged with N_2 continually. After all the borohydride had been added the solution was refluxed for approximately 45 minutes and, after cooling, excess borohydride was destroyed by careful addition of dilute hydrochloric acid. The product was precipitated by evaporation of part of the ethanol and then recrystallized from ethanol/water. Yield: 82%; Found: C, 82.6; H, 6.0%. Calculated for $C_{20}H_{18}O_2$: C, 82.7; H, 6.3%; with correct infrared spectrum.

Preparation of 1,4-bis(α hydroxybenzyl) benzene

All apparatus was dried in the oven and assembled hot and flushed with dry nitrogen. The magnesium turnings (97.28 g) were covered by T.H.F. (ca. 1.4 litres) in a 3 litre 3 necked R.B. flask. The dropping funnel was then filled with 314 gms (2 moles) of bromobenzene, which was added slowly. An iodine crystal was necessary to initiate the reaction which then proceeded smoothly. The temperature was maintained in the range 65° - 75°C by the reaction exothermicity and regulation of the rate of addition. This operation lasted approximately 2 hours.

After the solution cooled to below 30°C, the terephthaldehyde (65.0 g dissolved in approximately 0.5 litres of T.H.F.) was added dropwise, giving a dark orange solution which was viscous at room temperature. The mixture was refluxed for 2 hours after which it was added to a large excess of acidified cold water. Stirring of this mixture produced a white solution containing $Mg(OH)_2$ which dissolved when more acid was added. The solubility of T.H.F. in water made it necessary to extract with ether until finally the extract was transparent orange. Evaporation of T.H.F. and ether gave an orange precipitate which failed to recrystallize in a 1 : 1 ethanol-water mixture. After several attempts to purify this product it was assumed that the diol had not been recovered and that possibly an excess of acid had been introduced during the work-up which may have facilitated an acid catalyzed dehydration. The preparation was repeated; this time taking particular care to add the acid in small quantities and keep the mixture at ambient temperature during the work up. Recrystallization of the product of the second attempt in a water : ethanol mixture (1 : 4) gave fine white crystals. Yield: 67%; Found: C, 82.6; H, 6.2%; Calculated for $C_{20}H_{18}O_2$: C, 82.7%; H, 6.3%; with correct i.r.

2.4c. Polymer syntheses and further reactions

Irradiations

The monomers used in the following experiments were dried on the vacuum line (ca. 1 day at 10^{-3} m.m. Hg) and the benzene was refluxed over sodium and then distilled prior to use. The following procedures were adopted in the attempted photoreduction of m-dibenzoylbenzene.

(a) Irradiation of meta-dibenzoylbenzene and either 1,3 or 1,4-bis(α hydroxybenzyl)benzene in benzene solution

Equimolar quantities of diketone and bisbenzhydrol were weighed out into irradiation vessels (long pyrex tubes ca. 1 cm. diameter) and sufficient dry benzene added to make solutions 0.1M in each monomer. Only the diketone dissolved completely under these conditions. The mixture was streamed with nitrogen to remove the possibility of residual oxygen quenching the carbonyl triplets; the tubes were stoppered and irradiated in a Rayonet Photochemical Reactor (350 nm lamps). It was hoped, following the precedent of the reported Belgian work, that as the reaction proceeded the diol monomer would dissolve; however, after several days the only observable change was the yellowing of the solution. An analysis by infrared spectroscopy of the solid recovered after evaporation of solvent indicated that no reaction had occurred; it was concluded that the diol monomers were too insoluble to allow the gradual dissolution process reported by the Belgian group (for other monomers) to operate in this case.

In an attempt to obtain homogeneous solutions of both monomers in benzene progressively higher dilutions were examined; however, the dilutions required for solubility (ca. 0.008M) involved inconveniently small quantities of monomer and large volumes of benzene. Even then there was no detectable reaction after irradiating for prolonged (ca. 1 week) periods; for example, the infrared spectrum of the solid recovered after irradiation of a 0.0077M solution of meta-dibenzoylbenzene and 1,3-bis(α hydroxybenzyl)benzene in benzene showed no appreciable consumption of carbonyl.

(b) Irradiation of meta-dibenzoylbenzene and 1,3-bis-(α hydroxybenzyl)benzene in benzene solution at reflux

Since both monomers were found to be soluble in hot benzene, it was decided to attempt the reaction by irradiating the refluxing solution. The apparatus used for these experiments utilized a quartz insertion well in an ordinary 3-necked R.B. flask. The well contained a 125 watt medium pressure mercury lamp.

The first attempt with this technique involved irradiating 1,3-bis(α hydroxybenzyl)benzene (1.45 g) and m-dibenzoylbenzylbenzene (1.43 g) in 250 mls. of benzene at reflux for four days. On cooling the crystals which precipitated were pure unreacted 1,3-bis(α hydroxybenzyl)benzene whereas the material isolated by evaporation of solvent appeared to be a mixture of monomers.

The above experiment was repeated under identical conditions except for the circulation of a filter solution (containing NaBr (74.09 gms.) and $Hg(NO_3)_2$ (0.25 gms.) dissolved in 250 mls) in the outer jacket of the insertion well, this solution cuts out most of the lamp output at wavelengths below ca. 310 nm. Although t.l.c. established the presence of two components other than the monomers, an infrared spectroscopic analysis of the solid product from this reaction indicated an almost insignificant consumption of carbonyl. Attempts to separate the product into its components by column chromatography proved unsuccessful because a suitable solvent could not be found. The reaction between m-dibenzoylbenzene and 1,4-bis(α hydroxybenzyl)benzene was not attempted in view of the failure of the attempt with the meta isomer.

(c) Reactions in acetonitrile as solvent

Acetonitrile was found to dissolve all the monomers involved in this work. The acetonitrile used was distilled from P_2O_5 using a fractionating column (80 cms x 2 cms) containing glass helices.

Two solutions (0.066M and 0.0025M) of the monomers in freshly distilled acetonitrile were prepared in cylindrical reaction vessels fitted with teflon Rotaflow taps. The solutions were degassed on a vacuum line (10^{-3} mm Hg) by three freeze-thaw cycles, after which they were let down to atmospheric pressure under dry nitrogen. The tubes were irradiated in a

Rayonet Reactor (3500 A lamps) for 55 hours and the product recovered by evaporation of the solvent. The infrared spectra of the products indicated that again insignificant carbonyl consumption had occurred. This very disappointing result prompted a check on the experimental technique; irradiation of an equimolar solution of benzophenone and benzhydrol in acetonitrile under the same conditions gave benzopinacol quantitatively.

The disappointing outcome of the attempted polymerizations described above lead to an examination of the optimization of the reductive photopolymerization of meta-dibenzoylbenzene using isopropanol as hydrogen donor.

(d) Photoreduction of m-dibenzoylbenzene in Benzene : Isopropanol Mixtures

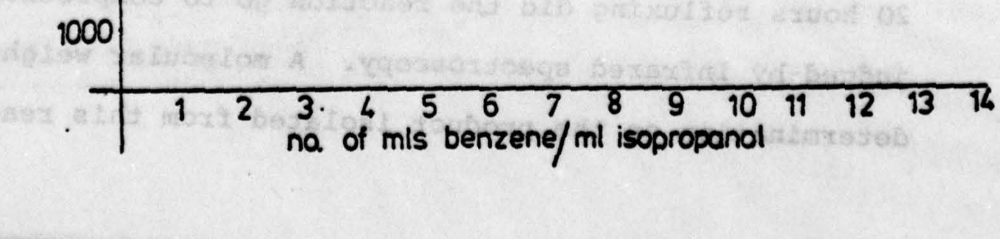
An investigation of the optimum conditions under which a high molecular weight polybenzopinacol may be formed in the presence of isopropanol as a donor was attempted. Six pyrex tubes of approximately 100 mls capacity containing 3 gms. (0.01048 moles) m-dibenzoylbenzene dissolved in mixtures of benzene and isopropanol were made up as shown in the table.

Isopropanol mls	Benzene mls	Ratio isopropanol : benzene	No. of moles isopropanol
2	28	1 : 14	0.026
3	27	1 : 9	0.039
5	25	1 : 5	0.065
6	24	1 : 4	0.079
10	20	1 : 2	0.1308
15	15	1 : 1	0.196

The tubes were placed in a Rayonet 'Merry-Go-Round' and irradiated at 350 nm for one week, at this stage there was some precipitation in some of the tubes and all the solutions were yellow. The precipitation was greatest in the tubes containing the higher concentration of isopropanol and there was a gradual reduction in the amount of precipitate as the isopropanol concentration decreased. The tubes having a 1 : 14 and 1 : 9 ratio showing no precipitation. The precipitates were isolated by filtration and the soluble product recovered by evaporation. The i.r. spectra of all products were virtually the same and showed almost complete carbonyl consumption. The molecular weights determined (Perkin-Elmer-Hitachi Model-115 Molecular Weight Apparatus, $CHCl_3$) for the six products are tabulated below.

Isopropanol:Benzene Ratio (mls)	$\bar{M}_n$	D.P.
1:14	4280	14.8
1:9	4310	15
1:5	4060	14.1
1:4	4750	16.5
1:2	2800	9.7
1:1	2230	7.7

It is clear from the table that as the concentration of isopropanol decreases the molecular weight of the product initially increases and then reaches a plateau value, this trend is more easily seen in the graph below. There are a number of



factors which may control the molecular weight attained; however, it seems probable that the lower molecular weights of the products which precipitated from the solutions having higher isopropanol concentrations result simply from their being removed from solution before completing reaction, that is a simple solubility effect controls the $\bar{M}_n$. On the other hand, the fact that the polymerization tends to a limiting molecular weight of ca. 4350 (i.e. a D.P. ~ 15) may be a result of the ratio of in-cage chain terminating reactions to out-of-cage chain extending reactions; this ratio may be affected by aspects of monomer and solution structure and may well vary from system to system. In view of the limited time available at this stage of the work it was decided not to pursue this matter further but to examine the subsequent steps outlined in 2.4a.

The dehydration of polybenzopinacol (2.4A)

The pinacol-pinacolone rearrangement is a well known reaction; for the model system, benzopinacol to benzopinacolone, the reaction is quantitative. In initial experiments with Polymer 2.4A (d.p. ~ 15) iodine in acetic acid and dimethyl sulphoxide were tried as catalysts since they were known to be effective for the model compound reaction.

Experiment 1. Polybenzopinacol (2.4A - 1 gm.) was refluxed in a mixture of benzene (24 mls), glacial acetic acid (25 mls) and an iodine crystal. Only after 20 hours refluxing did the reaction go to completion as judged by infrared spectroscopy. A molecular weight determination on the product isolated from this reaction showed that extensive degradation had taken place ($\bar{M}_n$ = 706, d.p. = 2.4), t.l.c. indicated the presence of one component only.

Experiment 2. Polybenzopinacol (2.4A - 1 gm.) was refluxed in a 1:1 (v/v) mixture of D.M.S.O. and benzene for several hours after which no reaction had taken place as judged by infrared spectroscopy. The spectrum showed the presence of D.M.S.O. which was very difficult to remove despite prolonged pumping on the vacuum line.

Higgins and coworkers had previously examined the dehydration of the polybenzopinacols resulting from photocondensation of p,p'-dibenzoyldiphenyl ether, p,p'-dibenzoyldiphenylmethane and p,p'-dibenzoyl-1,2-diphenylethane and achieved the desired dehydration using sulphuric acid-dioxane solutions. Their analysis suggested that the rearrangement expected did not take place (i.e. migration of a phenyl group) but instead chain migration took place.

Experiment 3. Polybenzopinacol (2.4A - 5 gms.) was added to a stirred solution (at room temperature) of conc. H_2SO_4 (25 mls) and 1,4-dioxan (150 mls), which was left stirring for 16 hours. The resulting dark-brown solution was then added to iced water, stirred for several minutes, and then filtered. The solid was redissolved in T.H.F. and slowly added to a large volume of water (ca. 2 litres). The product did not precipitate, as expected by analogy with Higgins' work, but formed an emulsion. This emulsion was broken by adding large quantities of dilute HCl after which a precipitate formed. The precipitate was recovered by filtration, washed with Na_2CO_3 solution, then water, and eventually dried on the vacuum line. The infrared spectrum of this product indicated complete consumption of OH function and formation of an intense carbonyl at 1675 cm^{-1}, consistent with the formation of either

2.4E or 2.4F. At this stage in the work the molecular weight apparatus was not functioning and so it was not possible to determine if the dehydration had been accompanied by degradation as in Experiment 1; however, the avoidance of high temperatures in this last procedure gives cause for optimism that it occurred without degradation.

Reduction of polybenzopinacolone 2.4E (polymer and/or 2.4F)

The attempted reduction with sodium borohydride of a toluene solution of the product Experiment 3 (above) was totally unsuccessful as judged by the infrared spectrum of the isolated product. Repetition of the reaction using dioxane as solvent resulted in a product in which the carbonyl function at 1675 cm^{-1} in the infrared spectrum of the starting material was almost completely consumed and replaced by a broad band at 3220 cm^{-1} assigned to hydroxyl; this result being consistent with the formation of polymers 2.4G and/or 2.4H.

Dehydration of polymers 2.4G and/or 2.4H

In order to try and complete the sequence of proposed reactions the product obtained as described in the previous section was refluxed in a mixture of acetic acid, benzene and iodine. After the usual isolation and drying procedure a product was obtained which, if everything had gone according to plan, should have been either 2.4J and/or 2.4K.

However, while the infrared spectra of the product showed that the hydroxyl function had been consumed it also showed overlapping bands in the carbonyl region with the most prominent bands at 1750 and 1685 cm^{-1}. This result poses important questions;

namely it is just the last stage of the sequence which has failed to go according to plan, or was the starting material for the last stage not as originally assumed. It is possible that the carbonyl absorptions observed resulted from the product of esterification of the hydroxyls present in the starting material; acetate carbonyl would be consistent with the band at 1750 cm^{-1}. The strong band at 1675 cm^{-1} might be ascribed to an acetylation product of the aromatic rings, acetophenone carbonyl absorbs at ca. 1685 cm^{-1}, although this explanation seems somewhat unlikely. A further possibility which cannot be discounted is that the result of treating the reduction product of the initial polypinacolone with iodine in acetic acid and benzene is at least in part the regeneration of the polypinacolone; this would not be unreasonable since the reagent is a mild oxidizing agent.

Clearly this final result raises questions which can only be answered by further experiment, unfortunately restricted time at this stage did not allow these experiments to be carried out.

2.4d. Conclusions

The investigation of the photoreductive polymerization of m-dibenzoylbenzene demonstrates some of the difficulties which can be encountered in syntheses of this type. Although it may be possible to improve on the molecular weights obtained for polymer 2.4A in this work by manipulation of reaction conditions the results reported here suggest that such improvements are likely to be small. The factors limiting the attainable molecular weight are not completely clear but are probably complex; on the one hand simple solubility of monomers has been demonstrated to be important and on the other it may be that factors such as steric hindrance of the growing chain and the way in which it is coiled and/or solvated have a marked effect.

A preliminary examination of the proposed sequence of reactions using polymer 2.4A (d.p. ~ 15) as starting material was all that could be carried out in the time available. However, on the basis of these results the first two steps appear to proceed as expected although the single attempt at the third stage was unsuccessful.

If this project is investigated further and brought to a satisfactory synthetic conclusion, the problem of distinguishing between isomeric structures of the possible products remains. However, simple techniques may well be able to provide definitive answers; for example on ozonolysis polymer 2.4J should theoretically be degraded completely to m-dibenzoylbenzene, whereas the isomeric polymer 2.4K should yield benzophenone and a polymeric ketone.

2.5. Irradiations of tere- and iso-phthalaldehydes and Benzaldehyde

The photoreductive polymerization of aromatic diketones is well documented, however, there have been no reports on the irradiations of aromatic dialdehydes in the presence of hydrogen donors. It was decided to investigate the behaviour of two of these dialdehydes, namely tere- and iso-phthalaldehyde, on exposure to ultraviolet light both in the solid state and in solution in the presence of hydrogen donors. It was also decided to attempt a closer examination of the 'photopolymer' formed on irradiation of neat benzaldehyde in the liquid phase in the hope of obtaining some information on the structure of this material which has been the subject of several previous investigations.

2.5a. Results of irradiations of tere- and iso-phthalaldehydes

A summary of experimental procedures and results is given in Table 4. Irradiations were carried out in sealed tubes under reduced pressure in order to exclude oxygen from the system, since terephthalaldehyde is known to yield terephthalic acid on irradiation in the presence of oxygen.[104] Distilled water and perfluoro(methylcyclohexane) were used as the suspending agents for the solid state irradiations since the dialdehydes were not detectably soluble in either of these media at 25°. In both cases efficient stirring and mixing was provided by means of an external mechanical stirrer.

Whereas irradiations in the solid state afforded quantitative recovery of starting materials, irradiations in the presence of a hydrogen donor afforded initially insoluble products which showed both carbonyl and hydroxyl absorptions in the i.r. Irradiations were repeated under the following modifications: (a) the solutions were made as concentrated as possible, (b) H-donor and solvent were very carefully purified before use, (c) solutions were carefully degassed on a grease-free, Hg-free vacuum line and tubes were sealed under lower pressure (ca. 10^{-5} mm Hg), (d) 350 nm radiant source was used instead of the HANOVIA 450-W Hg lamp in an attempt to effect greater overlap between the lamp emission and the carbonyl $n \rightarrow \pi^*$ absorption and to exclude short wavelength photolysis effects, (e) work-up of the solutions after irradiation was modified, the use of DMF or any other high boiling solvent being avoided. The products however were the same as those obtained in the previous experiments.

Table 4

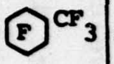
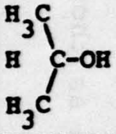
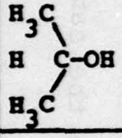
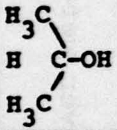
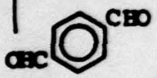
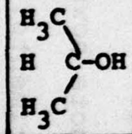
Expt.	Starting Materials		Medium	Concn. (M)	Lamp[d]	Time (Hrs.)	Temp. (°C)	Method[b]	H-donor	Products	Comments
	Carbonyl Compound	H Donor							Solvent Ratio		
1			H_2O	Suspension	A	3	45	A		 quantitatively recovered	c
2				Suspension	A	10	45	A		98% starting materials back	d
3				0.0486	A	26.5	45	A	1:3 v/v	Not characterised	e
4				0.0369	A	15	45	A	1:4 v/v	Not characterised	f
5				0.448	B	330	45	B	1:4 v/v	Not characterised	g
6				0.351	B	61.5	45	B	1:4 v/v	Not characterised	h

Table 4 (cont.)

Footnotes: a. LAMP A: HANOVIA 450-W Hg Lamp.
LAMP B: RUL-350 mm Photochemical Reactor.

b. METHOD A: Irradiations carried out in pyrex tubes; solutions degassed by several freeze-pump-thaw cycles on conventional vacuum lines and sealed under reduced pressure (residual pressure in tube ~ 0.005 mm Hg).

METHOD B: Irradiations carried out in pyrex tubes; solutions degassed by several freeze-pump-thaw cycles on high vacuum grease-free/mercury free vacuum line and sealed under reduced pressure (residual pressure in tubes 10^{-5} mm Hg).

METHOD C: Irradiation carried out in 1L florentine flask; solution nitrogen streamed for 1 hr. and quickly stoppered.

c. Identified by i.r. spectroscopy/recovered material gave one major spot corresponding to therephthalaldehyde on silica t.l.c. examination ($CHCl_3$ eluent).

d. 2% of a yellow material was also obtained (soluble in acetone). ($\bar{\upsilon}_{max}$: 3450, 2930, 2860, 2740, 1700, 1605 cm.$^{-1}$).

e. Product extracted by freeze-drying (112.5% of the terephthalaldehyde used, reaction with donor and/or solvent (?)). Brittle fibres drawn out of the melt. Displayed considerable thermal stability (no change in i.r. after strong heating on bunsen flame). Soluble in DMF, NMP, Pyridine, ethanediol, ethylmethylketone.

Reprecipitation from DMF (solvent)/CCl_4 (nonsolvent) afforded 55% of a yellow material.

f. Product extracted by freeze-drying (116.4% of the isophthalaldehyde used). Brittle fibres drawn out of the melt. Soluble in DMF, NMP, Pyridine, ethylmethylketone.

Reprecipitation from DMF (solvent)/CCl_4 (nonsolvent) afforded 61% of a yellow material.

g. i.r. spectrum of product obtained superimposable with i.r. of product obtained from expt. 3 - similar physical properties.

h. i.r. spectrum of product obtained superimposable with i.r. of product obtained from expt. 4 - similar physical properties.

Treatment of the products with DMF at room temperature for 7 days resulted in substantial degradation and incorporation of DMF into the products, as shown by both i.r. spectroscopy and mass spectrometry. Heating of the DMF-treated products under high vacuum (100°) for 1 day resulted in partial elimination of the DMF peaks from the i.r. spectrum. The products showed considerable thermal stability (no change in the i.r. spectrum after heating at 250° for 10 mins.). Brittle fibres could be drawn from the melt. Comparison of the i.r. spectra of the products with that of polybenzoin prepared according to established route[105] revealed considerable difference in the positions and intensities of the main bands. Both photoproducts were found to be soluble in $(CH_3)_2SO$ giving bright yellow solutions. However, in contrast with the behaviour of polybenzoin[105] no autooxidation was detected, the solutions being still clear after 2 months of standing whereas polybenzoin solutions precipitate polybenzil; precipitation of the photoproducts after 3 months of standing by addition of water yielded unchanged materials.

2.5b. Discussion

The non-reactivity of the dialdehydes in the solid state should not be considered as a surprising result, since the most likely initial product (a benzoin-type structure) would be expected to cleave rapidly,[65] yielding the starting material. The small yield (ca. 2%) of a coloured material obtained from the relatively longer irradiation of isophthalaldehyde in perfluoro(methylcyclohexane) non-solvent could be the result of an out of cage diffusion and dimerization of the radicals resulted from cleavage of the initially formed benzoin structure. The behaviour of the dialdehydes on irradiation in the presence of a H-donor is vastly different. Starting materials disappear completely and new products are formed, the physical characteristics and spectral parameters of which were consistent with their being branched low molecular weight pinacols.

2.5c. The benzaldehyde photoproduct

(i) Introduction

The photopolymer of benzaldehyde has been investigated by several groups of workers over many years.[63,106-118] The photophysical behaviour of benzaldehyde has also been thoroughly investigated.[119] One of the more recent investigations showed that irradiation of benzaldehyde in the gas phase resulted in the formation of a polymeric film with interesting photosensitizing properties.[113] The product was removed from the cells mechanically or by dissolution in various solvents. It was found to dissolve very slowly in tetrahydrofuran, dioxane and methanol at room temperature, and quickly in benzene at 20° and methanol at 60°. The ultraviolet absorption spectrum of the polymer in methanol solution showed a maximum at 234 nm, a shoulder at 248 nm (corresponding to the absorption maximum of benzoin) and a structureless tail out to at least 450 nm. The i.r. spectrum of the polymer was also recorded (KBr disc) and was shown to be different from that of benzoin. Two absorption bands at 1685 and 1723 cm.$^{-1}$ were indicative of two different carbonyl environments. Luminescence excitation spectra of the product (benzene solution, room temperature) taken with 366, 406, and 436 nm excitation were consistent with the presence of two active chromophores in the structure. The polymer film on the cell wall was found to sensitize cis $\rightleftharpoons$ trans isomerization of 1,3-pentadienes and to be active even after long periods of service. Its activity decreased by a factor of 15 after 3 hrs. of irradiation in the presence of 50.7 torr of oxygen; this treatment also caused the disappearance of the yellowish colouration of the polymer. The structure of the benzaldehyde photopolymer was not established in this or any of the earlier investigations.

(ii) Experimental

Purification of benzaldehyde

Technical grade benzaldehyde (300 ml. portions) was washed with 1M K_2CO_3 (aqueous solution, 5 x 200 ml) and dried over anhydrous $MgSO_4$. It was then transferred through a sinter into a 500 mls 3-necked flask (operation carried out under a nitrogen blanket), and fractionally distilled under nitrogen (vacuum jacketed column, 3' x 1", packed with glass helices). Equilibration of the column took about 24 hrs. (pot temp. 178^o, column temp. 210^o, head temp. 170^o - 178^o); head temperature was finally equilibrated at 178^o. Take off rate was kept at approximately 1 : 120; the first 30 and last 50 mls were discarded. Benzaldehyde thus purified was stored under dry nitrogen. No signs of benzoic acid were noticed at the neck of the flask even after several months use.

Irradiations

Benzaldehyde was transferred into dry cylindrical Pyrex vessels under nitrogen, degassed by several freeze-pump-thaw cycles on a conventional vacuum line, and sealed under reduced pressure (10^{-3} mm Hg). In some irradiations a Hg-free, grease-free vacuum line was used and the tubes were sealed under lower pressure (ca. 10^{-6} mm Hg). All irradiations were carried out at ca. 40^o using 350 nm lamps. The reaction was found to be very slow. A yellow colour usually developed after 50 hrs. of irradiation and the initially water white mobile liquid turned into a brown viscous mass after 200 hrs. of irradiation.

Benzaldehyde was initially irradiated for periods of 250 + 360 hrs. In a later experiment four portions of the pure material were irradiated for 100, 350, 660 and 1110 hrs. Contrary to previous reports[63] no crystalline materials were observed on the walls of the tube. The viscous mass formed appeared homogeneous and no signs of water or other immiscible liquids were detected which casts doubts on the validity of earlier arguments.[112]

The tubes were frozen in liquid air before the seal was broken and the open end was immediately connected to a concentrated sulphuric acid bubbler. No pressure was noticed on opening the tubes, even after prolonged irradiations, indicating the absence of non-condensable gases.

Purification of product

The crude products were very viscous masses containing substantial amounts of unreacted benzaldehyde. They were generally purified by repeated precipitations from benzene/60° - 80° petroleum ether. The resultant yellow powders were dissolved in diethylether, washed with dilute aqueous carbonate, then with water and precipitated again using petroleum ether as the non-solvent. Some samples were also precipitated from ethanol/water. In contrast with previous reports it was not possible to obtain white powders even after a great number of precipitations. Concentration of mother liquors did not afford any crystalline compounds. In some early experiments, steam distillation was used as a purification technique; benzaldehyde was the only detectable steam-volatile material. The products were found to be soluble in carbon tetrachloride, chloroform, methylenechloride, toluene, acetone (in cold) and in hot alcoholic solvents; they were insoluble in aliphatic hydrocarbons, aqueous potassium carbonate or methanol/water/potassium carbonate mixtures. On slow cooling of hot concentrated or dilute alcoholic solutions, yellow amorphous powders were obtained. Fairly long (sometimes over 100 cm.) fibres were drawn out of the melt; they were however very brittle. T.l.c. analysis of the precipitated products (benzene/petroleum ether, ethanol/water) showed the presence of one component only, sometimes with a small faint tail which is however not uncommon for polymeric materials (benzene, chloroform, carbon tetrachloride/chloroform 50:50, ethanol/chloroform 50:50, chloroform/methanol/carbon tetrachloride, acetone/methanol/ethanol, ethanol/acetone 50:50, benzene/chloroform, ethanol/acetone/water).

Decolourization of the amorphous material was attempted using activated animal charcoal in hot methanol solution. Repeated treatments gave an off white material (60%) which could not be further decolourized by this method; it had the same spectral characteristics as the yellowish powder obtained from the precipitations.

All products melted between 130° - 140° and elemental analysis figures corresponded to those calculated for benzaldehyde. Photopolymer yields (after precipitation and drying) were found to vary with irradiation time as follows: 32% (100 hrs.), 48% (350 hrs.), 59% (660 hrs.), 68% (1110 hrs.).

(iii) Attempted characterization of the 'photopolymer' of benzaldehyde

The solid state i.r. spectra (KBr discs) and the ultraviolet spectra (methanol) of the photoproducts obtained from irradiations varying in duration from 100 to 1100 hrs. were identical and the same as those reported previously.[113] The ^{1}H n.m.r. spectrum

($CDCl_3$, int. TMS ref.) displayed only one broad peak (δ 7.3). The ^{13}C n.m.r. spectrum showed a peak at δ 198.9 (possibly carbonyl carbon), a singlet at δ 128.3 (aromatic ring carbons) and a singlet at δ 42.38 which is difficult to assign; its value is however close to the one recorded for the sp^3 hybridised carbon in 1,4-dibenzylbenzene (see Fig. 5, p.96). The mass spectrum of the material extended to $^{m}/e$ 930 (d.p. of ca. 9). Determinations of molecular weights in chloroform solution (isopiestic method) gave d.p.'s in the range 9 - 11 for purified samples, independent of irradiation time. The solution phase i.r. spectrum of the photoproduct (carbon tetrachloride, saturated solution) was recorded in the region 4000 to 2500 cm.$^{-1}$ The spectrum showed some alteration on successive dilution and indicated the presence of free hydroxyl (3620 cm.$^{-1}$, sharp), internally hydrogen bonded hydroxyl (3200 - 3500 cm.$^{-1}$, broad and structureless) and aromatic carbon - hydrogen stretching (3030 - 3090 cm.$^{-1}$). A shoulder visible at higher concentrations might arise from intermolecular hydrogen bonding and the band in the region 2800 - 3000 cm.$^{-1}$ displays structure which also alters somewhat on dilution; this band would be expected to arise from aliphatic carbon - hydrogen stretching modes, however the band shape alteration on dilution is puzzling. The solid state i.r. spectrum of the benzaldehyde 'photopolymer' displays two absorptions in the carbonyl region, 1685 and 1723 cm.$^{-1}$; the carbonyl frequencies observed for benzoin benzoate, one of the reported benzaldehyde photoproducts, were 1712 cm.$^{-1}$ (ester carbonyl) and 1698 cm.$^{-1}$ (keto group); it seems unlikely therefore that the benzoin benzoate unit is a part of the photopolymer structure, although it must be admitted that this is not a particularly rigorous argument.

Irradiation of the material (3.0 g) in benzene (20 mls) (nitrogen streamed solution, 24 hrs., 300 nm) effected no change in either the molecular weight or the spectral characteristics.

These usual physical approaches to structure elucidation did not yield a convincing structural hypothesis although it is clear that the product contains hydroxyl, carbonyl and phenyl groups. In view of this fact it was decided to attempt some investigations of chemical reactions on the benzaldehyde 'photopolymer' in the hope that this 'classical' approach might yield some structural evidence. An account of these preliminary studies is given below.

Attempted photoreduction of the 'photopolymer' (3.0 g, benzene/isopropanol 2:3 (50 mls), nitrogen streamed solution, 24 hrs., 300 nm) yielded unchanged starting material as evidenced by i.r. and n.m.r. spectroscopy.

Attempts to obtain crystalline derivatives of the 'photopolymer' via the carbonyl groups by reacting small portions of it with 2,4-dinitrophenylhydrazine in ethanol or hydroxylamine hydrochloride in the presence of either pyridine or sodium acetate gave inconclusive results. The latter experiment afforded recovery of starting material whereas the former resulted in the formation of a material which was unstable and could not be purified.

Treatment of the photoproduct with bromine in carbon tetrachloride solution at room temperature effected no change in the structure of the material as evidenced by i.r. spectroscopy. However on heating the solution at 50° a slow absorption of bromine was observed with simultaneous evolution of an acid gas, possibly resulting from substitution or oxidation reactions. Refluxing the photoproduct (2.0 g) with bromine (1.0 g) in acetic acid (20 mls) for 2 hrs. did not effect incorporation of bromine into the original structure as shown by Lassaigne's test. The operation resulted in the appearance of a new peak in the i.r. spectrum at 1770 cm.$^{-1}$ but no change in the shape or intensity of the hydroxyl band was observed; these later results favour an oxidation process for the reactions with bromine.

Refluxing the 'photopolymer' (5.0 g) with acetylchloride (100 mls) for 3 hrs. under a nitrogen blanket afforded a material whose i.r. spectrum showed a considerably diminished hydroxyl band intensity and a new absorption at 1740 cm.$^{-1}$, presumably due to acetate group(s). No substantial increase in the intensity of the aliphatic carbon - hydrogen absorption was however apparent.

Refluxing the 'photopolymer' (5.0 g) with potassium permanganate (10.0 g) in neutral acetone (750 mls) for 3 hrs. yielded a product whose i.r. spectrum showed no major change from that of the original material.

Pyrolytic decomposition in an inert atmosphere yielded primarily benzaldehyde (> 90%) along with several minor products and an intractable tar. The very high yield of benzaldehyde from this pyrolysis suggests that the unit is not substantially changed on incorporation into the polymer. Attempted examination of the non-volatile residues by t.l.c. on silica (benzene, ethanol, chloroform, acetone, carbon tetrachloride) did not yield definitive results since there were many overlapping components. In contrast with previous reports, it was not possible to isolate hydrobenzoin from this experiment.

Reduction with an excess of sodium borohydride in 1,4-dioxane solution (40 hrs. at reflux) resulted in almost complete elimination of the carbonyl function(s) and increase in the intensity of the hydroxyl bands in the i.r. spectrum. Mass spectral analysis indicated that the molecular weight may have been significantly reduced. On the other hand, reduction with excess Vitride in benzene solution (nitrogen blanket, 18 hrs. at reflux) afforded an almost quantitative recovery of a material whose i.r. spectrum was significantly different from the one obtained from the reduction with sodium borohydride and in this case the carbonyl absorptions were totally eliminated. Such a difference in behaviour might be rationalized if the 'photopolymer' contained ester groups since Vitride reduces them whereas borohydride does not.

Prolonged refluxing of the 'photopolymer' with aqueous sulphuric acid (6N) resulted in a marginal change in the intensity and shape of the hydroxyl bands and a significant change in the number and intensities of the carbonyl bands in the i.r. spectrum. Elemental analysis of the product from this reaction (Found: C, 84.94; H, 5.07%; Calculated for $(C_7H_6O)_n$: C, 79.22; H, 5.70%) was consistent with the overall change being represented as:-

$$(C_7H_6O)_n \xrightarrow{H^+} (C_7H_5O_{\frac{1}{2}})_n$$

That is an apparent loss of one molecule of water for every two benzaldehyde residues in the polymer. The product of this reaction although a solid had an extremely penetrating nauseous smell which precluded further examination.

Treatment of the 'photopolymer' (3.0 g in benzene (80 mls)) with potassium dichromate (20.0 g in water (10 mls)) and concentrated sulphuric acid (15 mls) for 40 hrs. at reflux, resulted in a considerable decrease in the intensity of the bands in the i.r. spectrum associated with hydroxyl and an increase in the intensity and number of bands in the carbonyl region. There was also a significant alteration in the position and intensity of the bands in the aliphatic carbon - hydrogen stretching region. Elemental analysis of the product (Found: C, 64.98; H, 4.56%) was consistent with the overall change being represented as:-

$$(C_7H_6O)_n \xrightarrow{Cr_2O_7^{2-}/H^+} (C_7H_6O_{2.5})_n$$

That is, an apparent incorporation of three oxygen atoms for each pair of benzaldehyde residues in the 'photopolymer'. This experiment, however, was not particularly reproducible and attempts to prepare larger quantities of the product resulted in the isolation of a greenish powder, soluble in organic solvents (ethanol, benzene, chloroform) which was found to contain chromium (6.27%). Treatment of this material with diethylether afforded an ether-soluble material which contained 1.28% chromium. Treatment of both materials with dilute sulphuric acid in ether solution did not effect removal of chromium; these materials were probably chromium complexes of the 'photopolymer'.

The results of the reactions of the 'photopolymer' with acid and oxidizing agents under acid conditions are not amenable to a simple explanation. The hydroxyl diminishing/carbonyl increasing effect of the acid treatment is reminiscent of a pinacol - pinacolone type of reaction and the loss of a molecule of water is, of course, also consistent with such a sequence. An obvious candidate for the oxidation reaction which results in an increase in the oxygen content but no change in the carbon/hydrogen ratio would be oxidation of aldehyde to carboxylic acid units; unfortunately the infrared spectrum did not support such a rationalization and in fact the oxidation process was accompanied by a marked decrease in the hydroxyl intensity.

It has not proved possible, at the time of writing to rationalize the results described above; the possible nature of the benzaldehyde 'photoproduct' and suggestions for elucidation of its structure are discussed below.

(iv) Conclusions

The present experimental work adds to the facts known about the benzaldehyde 'photopolymer' without solving the problem of its structure. It is perhaps surprising that in the light of available knowledge and techniques the problem remains unsolved despite the intermittent attentions of different workers over a period of seventy years. In attempting to set up hypotheses for test it becomes clear that an enormous variety of structures could reasonably be derived by 'paper chemistry' for the product of prolonged irradiation of benzaldehyde.

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The first part of this report describes an attempt to extend earlier work on step-growth photopolymerization leading to polyoxetanes to the synthesis of fluorinated polyoxetanes. This work, which was the primary objective of the-research, was unfruitful. A variety of olefin and carbonyl containing monomers were prepared but all polymerization attempts failed.

The second part of the report describes several topics involving the use of aromatic carbonyl compounds as components of potential step-growth photoreductive photopolymerizations were investigated. Some work was carried out on photoreductive polymerization leading to polypinacols, and the possibility of extending his approach to the synthesis of polymers with pentaphenylglycerol or tetraphenylethanol repeat units was also examined. Finally, preliminary work on the use of aromatic aldehydes as monomers in step-growth photopolymerizations is reported.