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1,3-Dipolar Addition Reactions of Some Bisdiazo Compounds with Mono and Diolefins

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13. ABSTRACT

Bisdiazoterephthalaldehyde, para-bisdiazobenzoylbenzene and meta-bis-diazobenzoylbenzene were synthesized as dicarbene precursors. Simultaneous dicarbene formation and olefinic insertion was attempted. However, what was observed was 1,3-dipolar addition of the bisdiazo compounds and strained olefinic systems such as norbornene and norbornadiene. Nuclear magnetic resonance spectroscopy indicates that the stereochemistry of the adducts formed lead to some large chemical shifts. Polymerization was also attempted between meta-bisdiazobenzoylbenzene and norbornadiene.

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1,3-DiPolar Addition Reactions of Some Bisdiazo Compounds with Mono and Diolefins

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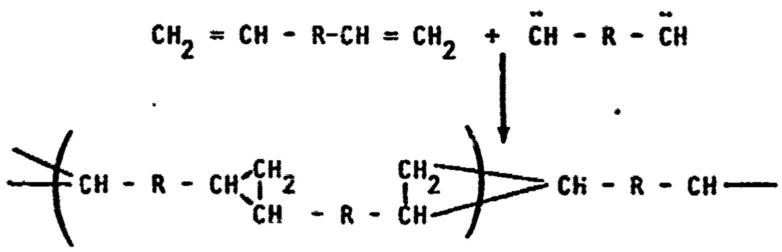
During the past several years, we have been conducting a program of polymer syntheses and characterization.[1-4] Recently, our interest has turned to the synthesis of polymers by means of dicarbene intermediates. No reports have appeared in the literature in which carbene intermediates were utilized in polymer syntheses and, in fact, very little data has been reported dealing with the preparation of bifunctional carbenes.[5-9] The initial objective of this investigation was to form poly-adducts of dicarbenes with dienes by means of the following general reaction:



$$CH_2 = CH - R-CH = CH_2 + \ddot{C}H - R - \ddot{C}H$$

The dicarbene precursors used were the dihydrazones of terephthalaldehyde and meta- and para- dibenzoylbenzene. These dihydrazones, upon conversion to the relatively unstable bisdiazo compounds, were heated with dienes such as

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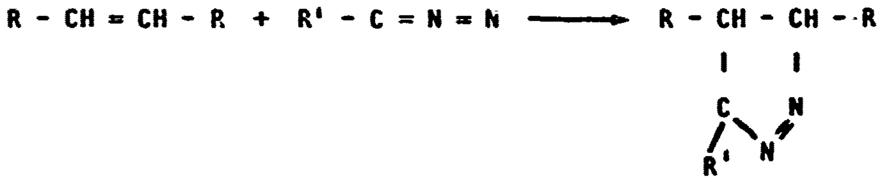
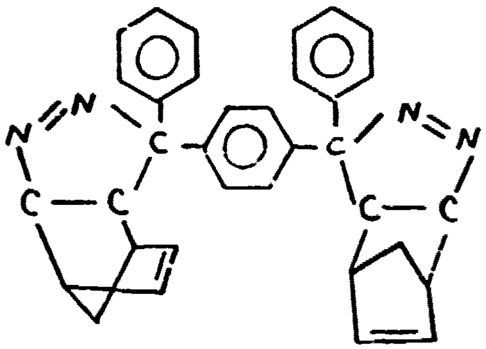
norbornadiene, 1,5-cyclooctadiene and 1,7-octadiene. The formation of adducts between the bisdiazo compounds and mono-olefins such as norbornene and cyclohexene were also attempted. Attempts to synthesize model compounds were also carried out by using excess diene.

It was observed, however, that instead of the bisdiazo compounds eliminating two molecules of nitrogen and forming dicarbenes, nitrogen was not given off and 1,3-dipolar addition of the diazo compounds and the dienes was the predominant reaction in the instances where the dienes contained strained double bonds.



Discussion

In order to form 2:1 adducts, a large excess of norbornadiene was used in reactions with meta- and para- bisdiazobenzoylbenzene. However, instead of obtaining cyclopropyl - containing products which would be formed if dicarbene intermediates were involved, what was obtained were the products of 1,3-dipolar addition reactions. The yields of these products were 81% and 30% for the meta and para isomers, respectively. The postulated structure for the para isomer is



An analagous structure is postulated for the meta isomer. The identity of these structures was confirmed by infrared analysis, nuclear magnetic resonance spectroscopy, mass spectroscopy (meta isomer) and elemental analysis.

Not surprisingly, the more symmetrical para isomer has a high decomposition point and is insoluble in common solvents whereas the meta isomer has a low melting point and is soluble in common solvents such as ethanol and chloroform.

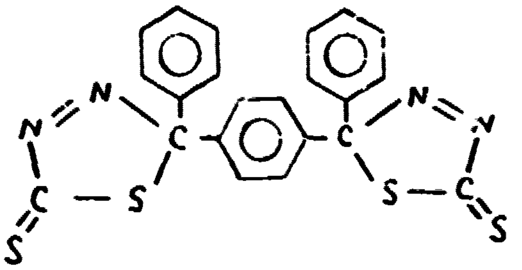
Similar results were obtained when an excess of norbornene was used instead of norbornadiene. The adducts formed were the products of 1,3-dipolar addition reactions. When para-bisdiazobenzoylbenzene was added to norbornene, a solid which decomposed at 277°C and which was insoluble in common solvents was obtained in 33% yield. Its identity was confirmed by infrared and nuclear magnetic resonance spectroscopy. Repeated elemental analyses gave values for percent hydrogen and nitrogen which were consistent with the proposed structure. Carbon, however, analyzed one percent low. We have no satisfactory explanation for this.

The reaction of excess norbornene with meta-bisdiazobenzoylbenzene and with bisdiazoterephthalaldehyde gave the products of 1,3-dipolar addition in 90% and 30% yield, respectively. The meta isomer was a low - melting solid which was soluble in common solvents. A somewhat unstable solid which decomposed at 165°C was obtained from bisdiazoterephthalaldehyde and norbornene The structures of these compounds were confirmed by infrared, nuclear magnetic resonance and mass spectroscopy as well as by elemental analysis.

Synthesis of an adduct between bisdiazoterephthalaldehyde and norbornadiene was attempted. However, a product was obtained which decomposed when isolation was attempted. Nuclear magnetic resonance spectroscopy indicated a similarity between this product and that of the adduct obtained from norbornene and the bisdiazo compound. The major difference was that the norbornadiene reaction product exhibited a peak at 6.2δ which corresponds to the norbornyl protons attached to the carbons of the double bond.

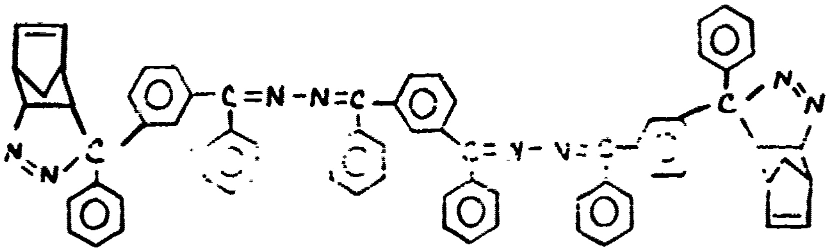
Attempts to synthesize adducts between para- bisdiazobenzoylbenzene and olefins with unstrained double bonds such as cyclohexene, 1,5-cyclooctadiene and 1,7-octadiene were also unsuccessful. All three reactions gave oils which were non-distillable and which could not be fractionated by chromatography. Elemental analyses were poor in all cases. A rationalization for these results is that, unlike the strained bicycloheptene system, these unstrained double-bonded systems are susceptible to side reactions such as hydrogen abstraction and carbon-hydrogen carbene insertion.

A final adduct synthesis was attempted using para- bisdiazobenzoylbenzene and carbon disulfide. The product obtained was unstable but, analagous to the results obtained with norbornene and norbornadiene, the structure is postulated to be

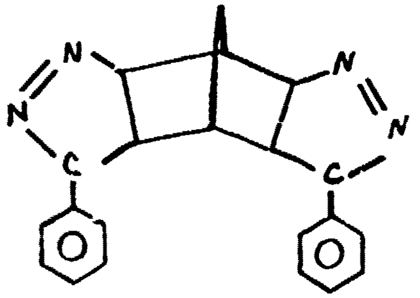


Infrared analysis of the solid material supports the proposed structure since absorption bands are observed at 6.12μ and 8.88μ which can be assigned to $\underset{N}{>}C = S$ and $>C = S$, respectively.[10]

A polymerization reaction was carried out using stoichiometric amounts of meta- bisdiazobenzoylbenzene and norbornadiene in perflourokerosene A yellow product was obtained in 90% yield. Based upon elemental analysis and infrared and nuclear magnetic resonance spectroscopic evidence, this product was postulated to be a diazine trimer of the bisdiazo compound which is terminated on each end by the diene.



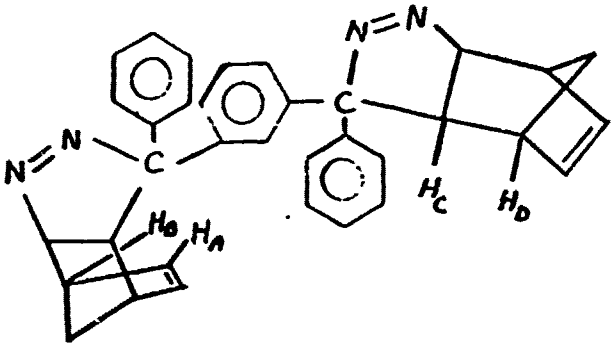
The polymer product that would be formed from alternating 1,3-dipolar addition of the diene and the bisdiazo compound probably did not form because the norbornadiene would have had to be part of a highly - strained tetracyclic system in such a molecule.



No attempts to form polymers with the <u>para</u>- bisdiazo compounds were made since the adducts formed from these compounds were extremely insoluble.

An interesting correlation was observed between the stereochemical configurations of several of these adducts and their nuclear magnetic resonance spectra. Although integrating for the proper proton count, the spectra show some large chemical shifts due to the structures of the compounds. This stereochemical aspect causes some protons to come within the sphere of influence of the aromatic parts of the molecules.

Some extremely large shifts have been calculated by measuring molecular models for normal and in-plane distances from the centers of aromatic rings. Then, from a table compiled by Emsley, *et al.*,[11] chemical shift values for corresponding normal distances (Z) and in-plane distances (P) may be obtained. The largest shift occurred for a vinyl proton in the 2:1 adduct of norbornadiene and meta- bisdiazobenzoylbenzene (II). This was 5.45 ± 0.5 ppm.



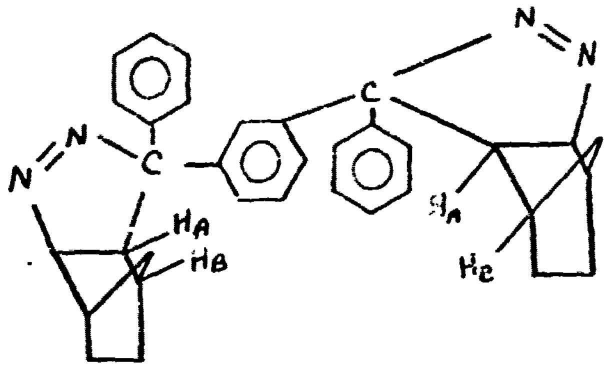
For the endo-exo stereochemical configuration the following shifts were calculated:

Proton	Calculated shift
H_A	5.45 ± 0.5 ppm
H_B	-0.02 ± 0.5 ppm
H_C	-0.39 ± 0.5 ppm
H_D	+0.88 ± 0.5 ppm

The nuclear magnetic resonance spectrum of the compound integrates for three vinyl norbornyl protons (6.2δ). This indicates that the ring junctions are endo-exo since two exo junctions would exhibit four vinyl protons and two endo junctions would exhibit two vinyl protons.

A consequence of this result is that one vinyl proton will be dramatically shifted upfield to 1.05 ± 0.5δ. The H_C, H_D and H_B shifts will not be quite as startling and will tend to be smeared throughout the upfield region. This is what is observed experimentally.

For the 2:1 adduct of norbornene and the meta- bisdiazo compound (IV), the following structure was postulated:



For this exo-exo stereochemical configuration, the following shifts were calculated:

Proton	Calculated Shift
H_A	-0.39 ± 0.5 ppm
H_B	+0.88 ± 0.5 ppm

The nuclear magnetic resonance spectrum obtained was consistent with the proposed structure. If the junctions were endo-exo or endo-endo, then one or two hydrogens would be shifted downfield 2.9 ± 0.5 ppm, which is not the case. A similar analysis led to the conclusion that the 2:1 adduct of norbornene and bisdiazoterephthaladehyde (V) had an endo-endo stereochemical configuration.

Nuclear magnetic resonance spectra of the 2:1 adducts of norbornadiene with para- bisdiazobenzoylbenzene (I) and of norbornene with the para- bisdiazo compound (III) were also obtained. However, due to the extremely low solubility of these adducts in most solvents, no integrable spectra could be obtained. However, the peak locations in (I) were similar to the 1,3-analog (II) and the same is true for (III) and its 1,3-analog (IV).

EXPERIMENTAL

Reagents

Commercial grade terephthaladehyde, mp 114°-116°C, commercial terephthaloyl chloride, mp 82-84°C and commercial isophthaloyl chloride, mp 43-44°C, were used as obtained. Reagent grade norbornadiene, bp 90-92°C, and norbornene, mp 47-48°C were also used as obtained. The benzene used was dried over sodium. Commercial grade hydrazine hydrate, bp 119°C, and commercial grade anhydrous hydrazine, bp 113.5°C, were also used as obtained.

Analytical

Infrared spectra were recorded on a Perkin-Elmer infracord spectrophotometer as Nujol mulls. Nuclear magnetic resonance spectra were run on a Varian HA-60 spectrometer using tetramethylsilane as internal reference. Chemical shifts are given as ppm on the δ scale. Mass spectra were recorded on a Hitachi RMU-7 high resolution mass spectrometer and micro analyses were obtained from MHW Laboratories, Garden City, Michigan. Melting points are uncorrected.

Para-DiBenzoylbenzene

A modified procedure of Volpe, et al.[1] was employed. To a 500 ml two-neck flask equipped with a condensor and stirring bar was added 350 ml of benzene and 20.3 g (0.10 mole) of terephthaloyl chloride. To this mixture was added 28.4 g (0.213 mole) of $AlCl_3$ in small portions over a 45-minute period with stirring. The mixture was stirred an additional 4-6 hrs. at reflux temperature. The yellow solution was cooled, washed with 100 ml of 10% HCL, 100 ml of 40% NaOH, three-100 ml portions of cold water, dried over anhydrous magnesium sulfate, and then the benzene was evaporated off. A tan solid product was obtained which was recrystallized from acetone-hexane (1:1) to yield a white crystalline material, mp 160-161°C (lit. 158-160°C).[1] Identity was confirmed by infrared spectroscopy. Average yield was 77-80%.

Meta-Dibenzoylbenzene

The procedure used for the synthesis of para-dibenzoylbenzene was followed, except that isophthaloyl chloride was used instead of terephtaloyl chloride, and reflux was carried out on a water bath. The crude product was isolated as an oil which solidified upon cooling. It was recrystallized from 95% ethanol to give white fluffy crystals, mp 109°C (lit. 109-110°C).[1] Identity was confirmed by infrared spectroscopy. Average yield was 80-82%.

Para-Dibenzoylbenzene Dihydrazone

A modified precedure of Trozzolo, et al.[7] was used in this synthesis. A solution of 30 g (0.145 mole) of para-dibenzoylbenzene in 50 ml of absolute ethanol was placed in a round bottom flask. Two hundred grams (5 moles) of 99% hydrazine hydrate was added, and the mixture was allowed to reflux for 16-20 hrs. The reaction mixture was cooled and the crude product precipitated. Product purification was accomplished by recrystallization from dioxane. White solid, mp 196°C (lit. 194-200°C)[7] was obtained. Its identity was confirmed by infrared spectroscopy. Average yield was 70%.

Meta-Dibenzoylbenzene Dihydrazone

This procedure was the same as that used for the para compound with the following modification. After cooling the reaction mixture, it was placed on the roto-evaporator until the ethanol was removed, whereupon the product precipitated. It was purified by recrystallization from ethanol to give a yellow white solid, mp 144-145°C. Average yield was 60%. Infrared Analysis: 2.19μ, 3.11μ, (NH_2); 6.4μ ($C{=}N$); 12.46μ (aromatic). Analysis: Calculated for $C_{20}H_{18}N_4$: C, 76.40%; H, 5.80%; N, 17.90%. Found: C, 76.15%; H, 5.77%; N, 17.97%.

Terephthalaldehyde Dihydrazone

A modified procedure of Murray and Trozzolo was followed[6]. A solution of 13.4 g (0.1 mole) of terephthalaldehyde in 100 ml of absolute ethanol was combined with 130 g (4.06 moles) of anhydrous hydrazine for eight days. The ethanol and some hydrazine was removed by means of a roto-evaporator. Upon cooling product was precipitated which was recrystallized from ethanol to give a light yellow solid, mp 159.5°C (lit. 165°C, rapidly taken).[6] Infrared analysis: 2.97μ, 3.15μ, (NH_2); 6.27μ ($C{=}N$). Average yield was 82%.

Bisdiazoterephthalaldehyde

This compound was also prepared by a modified Murray and Trozzolo procedure.[6] To a 500-ml flask equipped with a large stirring bar was added 300 ml of anhydrous ether, 20 g anhydrous sodium sulfate, 21 g (0.1 mole) of yellow mercuric oxide and 3.24 g (0.02 mole) of terephthalaldehyde dihydrazone. Approximately 5 ml of saturated ethanolic potassium hydroxide was then added. The reaction was allowed to continue for 80-90 min. The resulting red solution was filtered and evaporated to dryness by blowing dry air over the solution. A brick-red solid was obtained, mp 57°C (decomposes violently when heated dry!) Infrared analysis: 4.86μ ($C{-}N{\equiv}N$); 6.57μ ($C{=}N{-}$); 10.0μ, 12.15μ (aromatic). NMR (in $CDCl_3$): 7.25(4H,s); 4.8(2H,s). Average yield was 30-35%.

Para-Bisdiazobenzoylbenzene

To a one-liter round bottom flask equipped with a large stirring bar was added 500 ml of anhydrous ether. In addition, 2.5 g (0.0017 mole) of <u>para</u>-dibenzoylbenzene dihydrazone, 7.1 g (0.08 mole) of active MNO_2, and 5 ml of saturated ethanolic potassium hydroxide were added, and the reaction was continued for 2.5 hrs. The red violet solution was then filtered and the filtrate evaporated to dryness at low temperatures (<45°C). The product was a deep purple crystalline solid, which melts with decomposition at 114-116°C (lit. 114-116°C)[7]. Infrared analysis: 4.91μ (C-N=N); 13.28μ, 14.4μ (aromatic). Average yield was 45%.

Meta-Bisdiazobenzoylbenzene

The same procedure for the synthesis of the para isomer was used. The product isolated was a light purple, fluffy solid, mp. 125°C with decomposition. Infrared analysis: 4.94μ (C-N=N); 6.34μ (C=N); 12.19μ, 13.3μ, 14.47μ (aromatic). NMR (in CCl_4): 7.25-7.3 (aromatic). No elemental analysis was obtained, as similar compounds are known to convert to azines upon standing.[12] Average yield was 45-50%.

1,4-Bis(4,7-Methano-3a,4,7,7a-Tetrahydro-3-Phenyl-3(H)-indazol-3-yl) Benzene (I)

To a 100-ml flask equipped with a stirring bar and heating mantle was added 40 ml of norbornadiene. The diene was heated to boiling and 1.6 g (0.005 mole) of para- bisdiazobenzoylbenzene was added with stirring. After the addition the reaction was continued at reflux for one hour, whereupon the solution changed from violet to yellow and a white product precipitated upon cooling. The yield obtained was 20% and the product had a mp of 230°C with decomposition. The product was insoluble in common solvents, and was recrystallized from norbornadiene. Infrared analysis: 6.28μ, 6.45μ, 6.72μ (N═N); 7.13μ, 7.6μ, 8.07μ, 9.75μ, 9.91μ, 11.65μ, 12.1μ, 13.31μ, 14.4μ. NMR (suspension in $CDCl_3$): 7.25, 6.2, 5.1, 4.8, 2.3, 1.4-0.9. Analysis: Calculated for $C_{34}H_{30}N_4$: C, 82.56%; H, 6.11%, N, 11.33%. Found: C, 82.53%; H, 6.24%; N, 11.36%.

1,3-Bis(4,7-Methano-3a,4,7,7a-Tetrahydro-3-Phenyl-3(H)-Indazol-3yl) Benzene (II).

The procedure for the preparation of (I) was followed except meta- bisdiazobenzoylbenzene was used in place of the para compound. The resulting yellow solution was cooled, and the excess norbornadiene was removed by roto-evaporation. A yellow oil remained, which solidified to yield a fluffy, yellow-white solid upon exposure to vacuum for 30-60 min. The yield obtained was 81%. This material was purified either by eluting the product through a 100 g neutral alumina column with chloroform, evaporating the chloroform, and vacuum crystallizing the resultant oil, or by recrystallization from water-ethanol. The product had a mp of 93-94°C and was soluble in most common solvents. Infrared analysis: 6.28μ, 6.45μ, 6.7μ (N=N); 7.55μ, 8.06μ, 9.74μ, 9.91μ, 10.95μ, 11.4μ, 12.42μ, 13.11μ, 14.25μ. NMR (in CCl_4) 7.25 (14H,m), 6.18 (3H,m), 5.1 (2H,m) 3.5 (2H,m), 2.7-0.9 (9H, several peaks). Mass spectrum: (m/e) 438, 373-377, 306-364, 307-312, 62-65. Analysis: Calculated for $C_{34}H_{30}N_4$: C, 82.56%; H, 6.11%; N, 11.33%: Found: C, 82.57%; H, 6.43%; N, 11.14%.

1-4 Bis(4,7-Methano-3a,4,5,6,7,7a-Hexahydro-3-Phenyl-3(H)-Indazol-3yl) Benzene (III).

The procedure for the preparation of (I) was followed, except that norbornene was used in place of norbornadiene. A white product was precipitated as the reaction proceeded. The product was filtered from the warm solution and washed with hexanes to remove any remaining norbornene. It was then recrystallized from ether-ethanol to give a fine white solid which melted at 277°C with decomposition. The yield was 33% and the product was insoluble in common solvents except for slight solubility in ethanol and chloroform. Infrared analysis: 6.26μ, 6.43μ, 6.75μ, 7.74μ, 8.92μ, 9.24μ, 9.33μ, 9.52μ, 9.69μ, 9.75μ, 10.14μ, 10.34μ, 10.72μ, 12.03μ, 13.13μ, 13.88μ, 14.3μ. NMR (dilute solution in $CDCl_3$): 7.25, 4.9, 3.1, 2.4, 1.4-0.65. Analysis: Calculated for $C_{34}H_{34}N_4$: C, 81.89%; H, 6.87%; N, 11.24%. Found: (after repeated recrystallization): C, 80.88%; H, 6.87%; N, 11.14%.

1,3-Bis(4,7-Methano-3a,4,5,6,7,7a-Hexahydro-3-Phenyl-3(H)-Indazol-3yl) Benzene (IV).

The procedure for the preparation of (II) was followed except that norbornene was substituted for norbornadiene. The resulting yellow solution was cooled and then roto-evaporated to give a yellow oil. The oil was exposed to vacuum for 30 min., whereupon it crystallized. The resulting yellow-white solid was purified by the procedures used for the purification of (II). The yield was 90%, and the mp was 96-100°C. The product was soluble in most common solvents. Infrared analysis: 6.27μ, 6.44μ, 6.73μ, 7.74μ, 9.43μ, 9.7μ, 10.4μ, 11.9μ, 12.48μ, 13.1μ, 14.25μ. NMR (in CCl_4): 7.25 (14 H, m), 4.9 (2H,m) 2.9 (2H,m), 2.5-0.7 (16H, several peaks). Mass spectrum: (m/e) 442, 363-366, 257-260, Analysis: Calculated for $C_{34}H_{34}N_4$: C, 81.89%; H, 6.87%; N, 11.24%. Found: C, 81.90%; H, 6.99%; N, 11.19%.

1,4-Bis(4,7-Methano-3a,4,5,6,7,7a-Hexahydro-3(H)-Indazol-3yl)Benzene (V).

In a 100 ml flask, equipped with a nitrogen inlet, was placed 40 ml of norbornene. The flask was heated with stirring and 1.2 g (0.008 mole) of bis-diazoterephthalaldehyde was added under nitrogen atmosphere. The reaction was continued for one hour at reflux temperature and the solution changed from deep red to yellow-orange. The solution was filtered while warm, and the crude product was washed with hexanes to remove any norbornene. The product was recrystallized from chloroform-ether, and was found to decompose in chloroform solution after a number of days.

A yellow crystalline material was obtained with mp 165-168°C (decomposition). The yield was 30%. Infrared analysis: 6.5μ, 6.6μ, 7.75μ, 8.4μ, 9.8μ, 10.28μ, 11.3μ, 12.2μ, 13.3μ. NMR (in $CDCl_3$): 7.12 (4H,s), 5.08 (2H,m), 4.86 (2H,q) 2.9 (2H, m), 2.2 (2H,d), 1.9-0.8 (14H, m). Analysis: Calculated for $C_{22}H_{26}N_4$: C, 76.26%; H, 7.56%; N, 16.14%. Found: C, 76.45%; H, 7.76%; N, 16.25%.

Poly(1,3-Dibenzoylbenzene Azine) VI.

In a 100 ml flask equipped with a magnetic stirring bar and heating mantle was placed 30 ml of perfluorokerosene which was then heated to approximately 90°C. Then 1.36 g (0.004 mole) of meta-bisdiazobenzoylbenzene and 0.41 g (0.0047 mole) of norbornadiene were added with stirring. The reaction was continued for two hours. After the product was filtered and washed with ether, a light-yellow solid was obtained. The yield was 90%. The product was soluble in chloroform and insoluble in ether and its mp was 214-220°C. Infrared analysis: 6.40μ, 7.75μ, 8.6μ, 10.95μ, 13.06μ, 14.4μ. NMR (in $CDCl_3$): 7.2, 1.4-1.0. Analysis: Calculated for $C_{74}H_{58}N_8$: C, 83.90%; H, 5.52; N, 10.58%. Found: C, 83.79%, H, 5.45%; N, 10.71%.

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