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AFML-TR-79-4183
ADB045498

LOW COST ROUTES TO ACETYLENIC INTERMEDIATES

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December 1979

TECHNICAL REPORT AFML-TR-79-4183

Final Report for Period September 1978 to August 1979

AIR FORCE MATERIALS LABORATORY
AIR FORCE WRIGHT AERONAUTICAL LABORATORIES
AIR FORCE SYSTEMS COMMAND
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FOR THE COMMANDER

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REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: AFML-TR-79-4183
2. GOVT ACCESSION NO.:
3. RECIPIENT'S CATALOG NUMBER:

4. TITLE *(and Subtitle)*: LOW COST ROUTES TO ACETYLENIC INTERMEDIATES

5. TYPE OF REPORT & PERIOD COVERED: Final Report for the Period 9/1/78 to 8/31/79

6. PERFORMING ORG. REPORT NUMBER:

7. AUTHOR*(s)*: Dr. J. J. Harrison
Dr. C. M. Selwitz

8. CONTRACT OR GRANT NUMBER*(s)*: F33615-78-C-5141

9. PERFORMING ORGANIZATION NAME AND ADDRESS:
Gulf Research & Development Company
Chemicals & Minerals Division
P. O. Drawer 2038
Pittsburgh, PA 15230

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 24190409

11. CONTROLLING OFFICE NAME AND ADDRESS:
Air Force Materials Laboratory (MBP)
Air Force Systems Command
Wright-Patterson AFB, OH 45433

12. REPORT DATE: December 1979

13. NUMBER OF PAGES: 73

14. MONITORING AGENCY NAME & ADDRESS*(if different from Controlling Office)*:

15. SECURITY CLASS. *(of this report)*: Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE:

16. DISTRIBUTION STATEMENT *(of this Report)*:
Distribution limited to U.S. Government agencies only, test and evaluation; August 1979. Other requests for this document must be referred to the Air Force Materials Laboratory, Polymer Branch, AFML/MBP, Wright-Patterson Air Force Base, OH 45433.

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*:

18. SUPPLEMENTARY NOTES:

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*:
Acetylene terminated sulfone
Halogen displacement

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*:
A number of palladium catalyst systems were prepared and evaluated for their rate of displacement of bromine from bromobenzene by 2-methyl-3-butyn-2-ol. Initial results showed no rate increase over state-of-the-art catalysts. A new approach to the synthesis of 4,4'-di(3-ethynylphenoxy)diphenyl (ATS) was conceived and successfully carried out. The new method is eased upon reaction of 4,4'-di(3-bromophenoxy)diphenyl sulfone, followed by replacement of the bromines by 2-methyl-3-butyn-3-ol and hydrolytic removal of acetone. This method should provide a substantial improvement in cost over the current method which requires the use

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3-hydroxyphenylacetylne.

FOREWORD

This report was prepared by Gulf Research & Development Company, Chemicals and Minerals Division. The work was initiated under contract No. F33615-78-C-5141 "Low Cost Routes to Acetylene Intermediates." It was administered under the direction of the Air Force Materials Laboratory, Air Force Wright Aeronautical Laboratories, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio. Co-authors were Dr. J.J. Harrison and Dr. C.M. Selwitz.

This report covers research conducted from September, 1978 to September, 1979.

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I. INTRODUCTION

This report summarizes our work conducted from September, 1978, to August 30, 1979, on USAF Contract No. F33615-78-C-5141. Our work consisted of two parts. Part I consisting of two months effort was involved with developing new palladium complexes that would catalyze the acetylene displacement of aryl chlorides and deactivated aryl bromides. Our approach was to vary the phosphine ligands around the palladium to promote more facile reaction with aryl chlorides and deactivated aryl bromides.

Part II consisted of ten months effort in the area of synthesis of acetylene terminated sulfones (ATS). We have conceived and successfully carried out a novel synthesis of ATS which avoids the use of the expensive intermediate m-hydroxyphenylacetylene.

II. ACETYLENIC DISPLACEMENT OF ARYL CHLORIDES

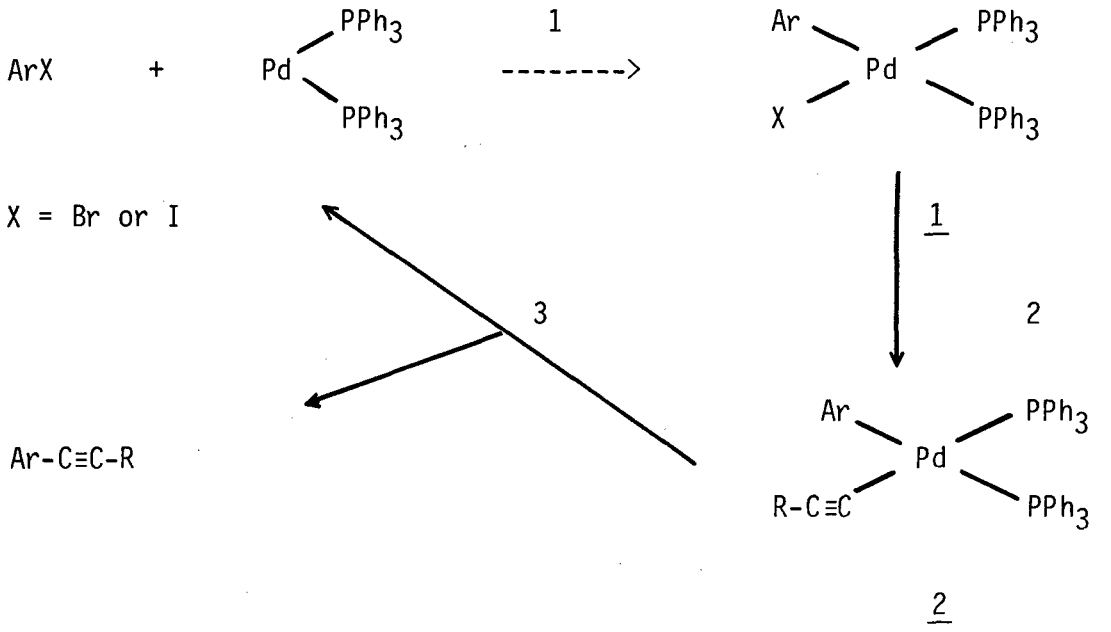
A. Developing a New Catalyst

The problem of catalytic displacement of an aromatic halide with an acetylene unit has been studied by several workers.[1-3,7] Recently, a synthesis of 3-aminophenylacetylene (APA) from 3-bromonitrobenzene using a catalytic displacement of the bromine with an end capped acetylene has been developed. A yield of 85% overall and a catalyst turnover of 5000:1 was observed.[4]

This displacement reaction first reported in the literature by Sonogashira,[2] combined aryl bromines and aryl iodides with an acetylene using dichlorobistriphenylphosphine palladium as catalyst, diethyl amine as solvent and cuprous iodide as cocatalyst (Equation 1).

$$ArX + H\text{-}C{\equiv}C\text{-}R \xrightarrow[\substack{Et_2NH \\ CuI}]{Cl_2Pd(PPh_3)_2} Ar\text{-}C{\equiv}C\text{-}R \qquad (1)$$

Electron withdrawing groups on the aromatic ring generally facilitate the reaction and aryl chlorides react poorly. A postulated mechanism contains the following steps (Scheme 1):



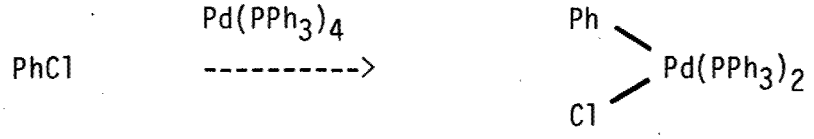
Scheme 1. Proposed Mechanism for Catalytic Cycle

Although aryl chlorides react poorly, by no means are they inert. Cassar[1] reported a coupling reaction of 4-chlorobenzonitrile and an acetylene in 80% yield using sodium methoxide and a palladium catalyst at elevated temperatures.

The reaction of aryl chlorides instead of aryl bromides or iodides is an important area for research because aryl chlorides are more readily available, and generally less expensive than the iodides or bromides.

The poor reactivity of aryl chlorides may be due to two reasons. The first is that aryl chlorides undergo the oxidative addition reaction (Step 1, Scheme 1) at a slower rate than bromides or iodides. The second is that the copper catalyzed displacement of halogen by acetylene (Step 2, Scheme 1) may be slower for chlorides than for bromides.

A literature search revealed that aryl chlorides undergo the oxidative addition reaction to palladium complexes much slower than aryl bromides. For example, chlorobenzene reacted with $Pd(PPh_3)_4$ at 135° to produce 3[5] while bromobenzene reacted with $Pd(PPh_3)_4$ at 80° to produce 4.[6]



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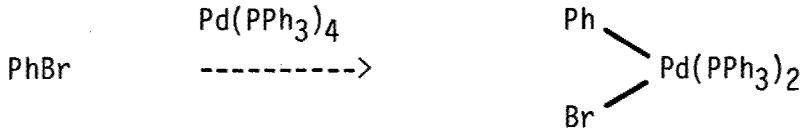

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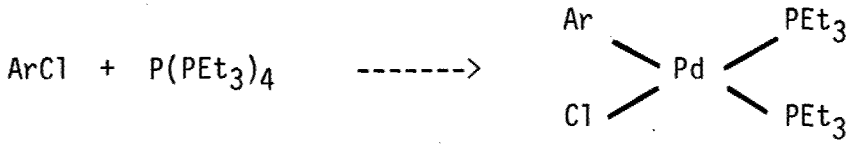
In order to increase the reactivity of aryl chlorides toward the oxidative addition step in the catalytic cycle, we proposed to synthesize novel palladium complexes with activating ligands. Trialkyl phosphines are activating ligands for oxidative addition. For example, tetrakis(triethylphosphine)palladium is known to react with aryl chlorides[8] to produce 5a at much lower temperatures and faster rates than $Pd(PPh_3)_4$ reacts with aryl chlorides.



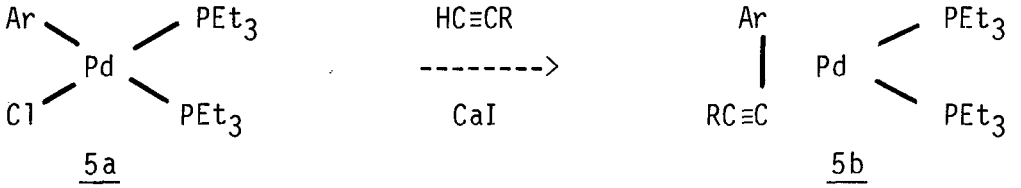
5a

This is perhaps due to difference in steric effects and differences in electronic effects.

The approach of varying the ligand on the palladium to facilitate reaction has been considered by Heck.[9] He found that $(o\text{-tolyl})_3P$ was a much more effective ligand than PPh_3 for the reaction of aryl bromides in the vinylic substitution reaction.

Replacement of a PPh_3 ligand with a PEt_3 ligand can be expected to increase the rate of oxidative addition of aryl chlorides (Step 1, Scheme 1).

However, the presence of PEt_3 ligands in the intermediate 5b might also retard the rate of the reductive elimination step shown below.



5a 5b

$$Ar\text{-}C{\equiv}CR + Pd(PEt_3)_2$$

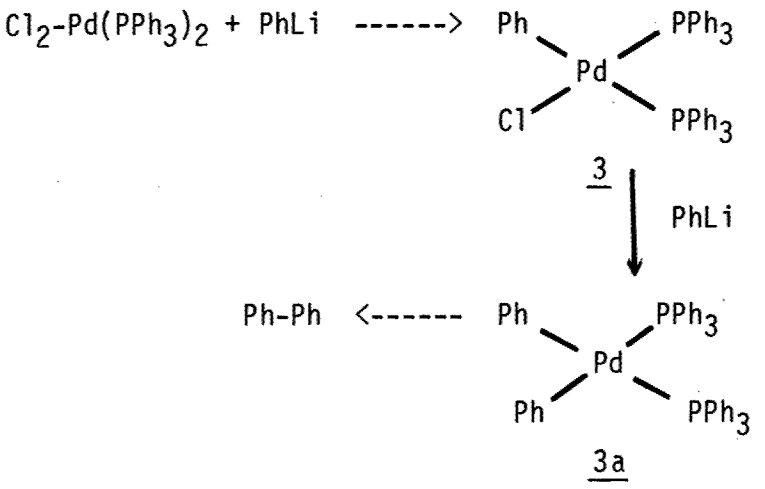
This possibility arises because Cassar has reported [12] that trialkylphosphines stabilize the aryl bonds in nickel complexes. A similar effect may occur in the palladium series. To minimize this effect and still increase the oxidative addition step, phosphines containing both alkyl and aryl groups might be useful ligands.

The effect of the halogen on the copper catalyzed displacement reaction (Step 2, Scheme 1) could not be discerned from the literature search. We therefore, set out to synthesize compounds 3 and 4 and react then under comparable conditions to determine if this step is responsible for the poor reactivity of aryl chlorides.

We now discuss our experimental results pertaining to the synthesis and reactivity of a new palladium catalyst. We begin by a discussion of the synthesis of intermediates in the catalytic cycle.

B. Results and Discussion

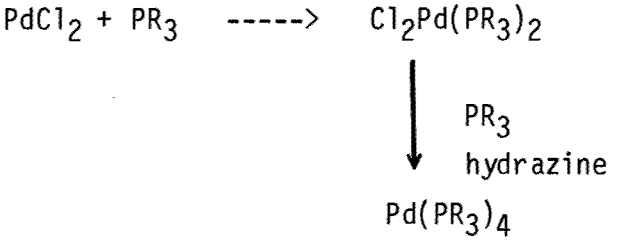
We initially tried to synthesize the intermediates 3 by reacting dichlorobis(triphenylphosphine)palladium with 1 mole of phenyl lithium. Instead of



forming 3, we isolated biphenyl, starting complex and a black palladium residue. We believe that biphenyl is formed through the intermediate 3a which forms rapidly from 4 and phenyl lithium.

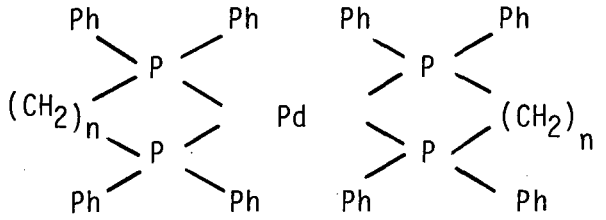
Compounds 3 and 4 were prepared by reaction of $Pd(PPh_3)_4$ with chlorobenzene and bromobenzene, respectively. However, further reaction of these materials with an acetylene and cuprous iodide was not brought to a conclusion because this work was interrupted by work on the ATS system.

We synthesized a variety of catalysts containing different phosphine ligands and investigated their activity on the reaction of aryl halides with acetylenes. The catalysts were synthesized by the following reaction.[10]



This reaction proceeded readily with triphenylphosphine to produce $Pd(PPh_3)_4$.[10] Other phosphines were also reacted according to the same procedure. These were: (dppm) bis(diphenylphosphino)methane, (dppe) bis(diphenylphosphino)ethane, (dppp) bis(diphenylphosphino)propane, (dppb)

bis(diphenylphosphino)butane, and tri-o-tolylphosphine. The structure of the palladium complexes synthesized from products (dppm), (dppe), (dppp), and (dppb) probably can be represented below.

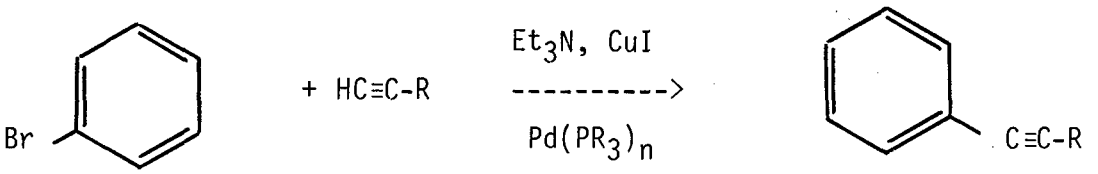


where n = 1-4, respectively.

Careful characterization of these materials was interrupted, however, by the postponement of work in this area and commencement of work in the area of acetylene terminated surfaces which is discussed later. For this reason, an accurate assessment of the structure of these materials could not be made.

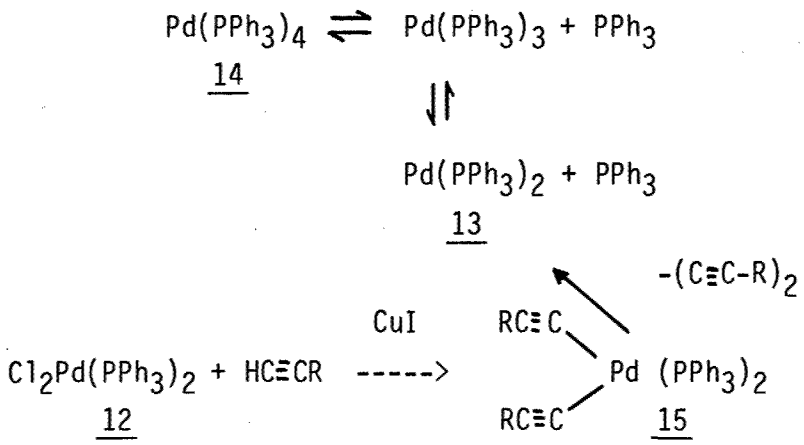
However, we did carry out a qualitative study of the relative rate of reaction of bromobenzene and 3-methylbutyn-3-ol catalyzed by these complexes.

We reacted these complexes with 3-methylbutyn-3-ol and bromobenzene in the presence of triethyl amine and cuprous iodide. At 94°, the production of the substituted phenylacetylene and the disappearance of bromobenzene were examined by GC for each palladium complex studied.



Our results are presented in Tables 1-8. The compounds examined were $Pd(PPh_3)_4$(6), $Pd(dppm)_2$(7), $Pd(dppe)_2$(8), $Pd(dppp)_2$(9), $Pd(dppb)_2$(10), $Pd(o\text{-}tolyl_3P)_4$(11) and $ClPdPPh_3$(12).

The reaction of $Cl_2Pd(PPh_3)_2$(12) is included for comparison. It is immediately obvious that $Pd(PPh_3)_4$ reacts fastest with fewest by-products. Complex $Cl_2Pd(PPh_3)_2$ reacts equally as fast, and this suggests that a common active catalyst is found from both. The active catalyst may be 13 which is formed in the following way:

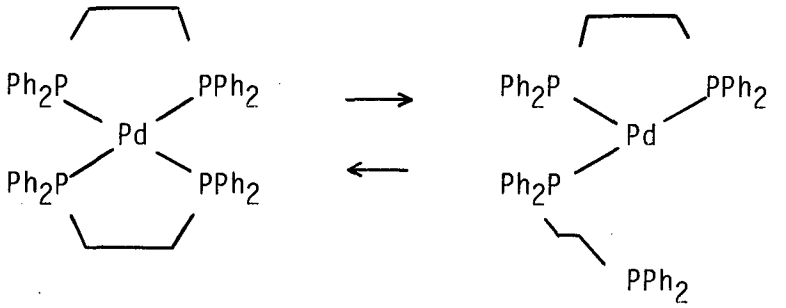


14 may lose triphenylphosphine and 12 may oxidatively dimerize some acetylene to produce 13. Quite disappointing is the result that ligands besides triphenylphosphine fail to accelerate the rate, in fact, they decelerate the rate.

Several catalysts gave measurable yields of by-products amounting from traces for several percent. It appears that the slower the rate the more by-product that is formed. The identities of the by-products has not yet been established in these cases. The reaction of $Pd(PPh_3)_4$ was tried without cuprous iodide. This is reported in Table 8. The rate was remarkedly slower. The cuprous iodide appears to be a cocatalyst in this reaction and is thought to act in catalyzing the addition of the acetylene to an intermediate of the type 1[11] (Scheme 1).

One reason that the palladium complexes substituted with bidentate phosphine ligands react slower may be that complete dissociation doesn't occur readily. If 13 is the catalytic species, then for $Pd(dppe)_2$ breaking of one

phosphorous bond may lead to an intermediate 16 which can very easily re-form the Pd-P bond. A two-coordinate palladium species similar to 13 thus is not easily formed.



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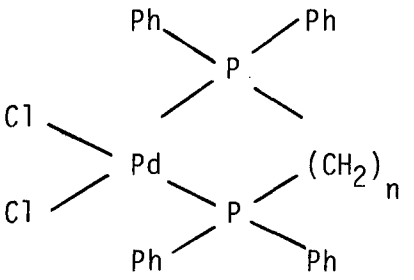
This is in contrast to $Pd(PPh_3)_4$ which may form 13 readily.

To overcome this difficulty complexes such as 17



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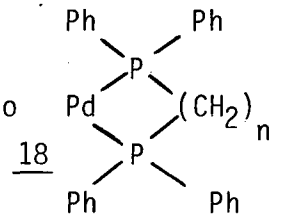
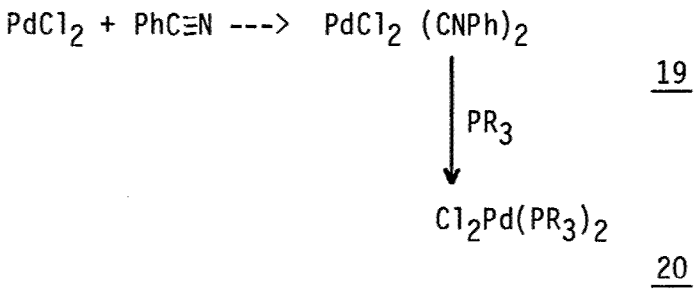
could be synthesized which may then be reduced to  by reaction

18

with 2 moles of an acetylene. These complexes may be effective catalysts. These complexes can be easily synthesized from the following reactions



Before work was halted, we had successfully prepared $PdCl_2(CNPh)_2$[13]

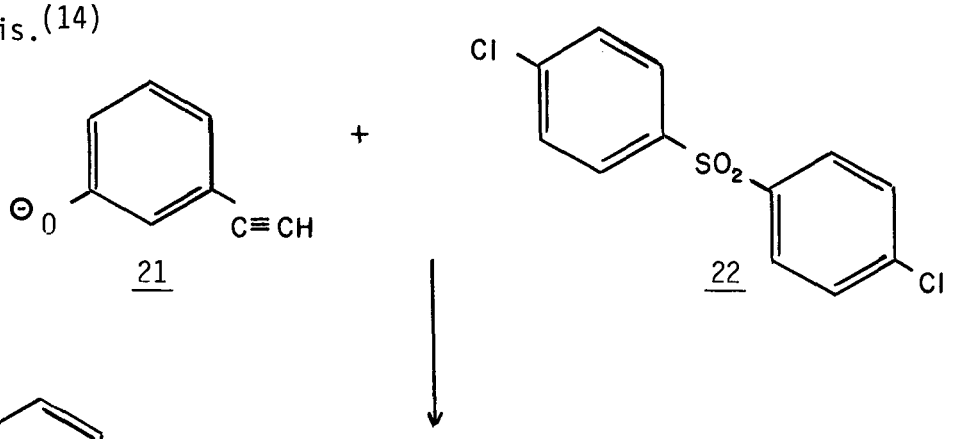
C. Conclusions and Recommendations

It is clear from this discussion that we have only begun to make progress toward the design and synthesis of an active catalyst for aryl chlorides. This work was left incomplete because of the desire by our sponsor to proceed with the investigation into the ATS systems. We believe that a most likely candidate for a successful system is one which contains a phosphine ligand with both alkyl and aryl groups. In this way, we feel that the oxidative addition step may be facilitated by the presence of akyl groups on the phosphine while the reductive elimination step may still proceed. We recommend that further work in this area be continued using this work as a starting point so that ultimately aryl chlorides and deactivated bromides may react in the acetylene displacement reaction.

III. ACETYLENE TERMINATED SULFONES

A. Introduction

Our proposal to this contract, F3354-78-C5141, included ideas for a novel and inexpensive synthesis of acetylene terminated sulfones (ATS). Interest in this idea eventually resulted in cancelling all effort on Part 1 of our proposal. The current synthesis of ATS consisted of the reaction of m-hydroxyphenylacetylene with dichlorodiphenyl sulfone in an Ullmann ether synthesis.(14)



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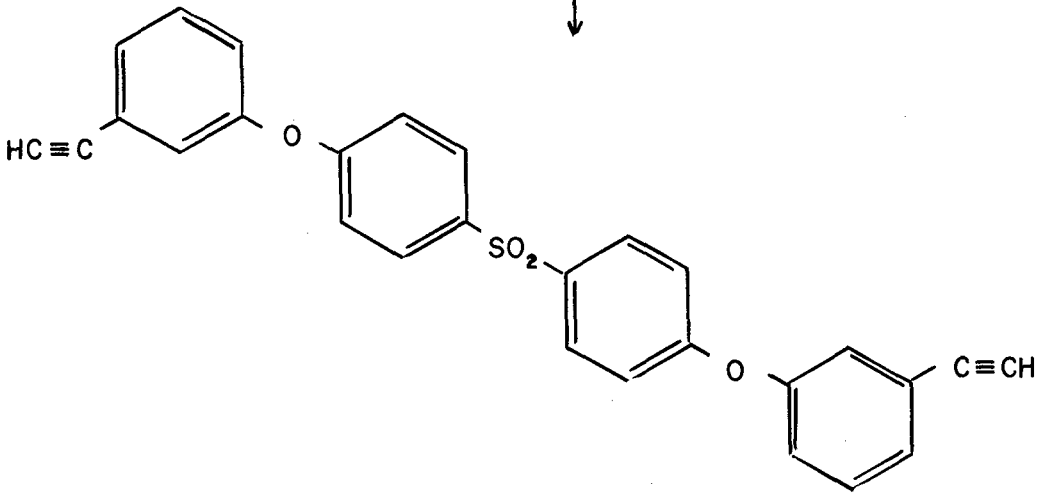
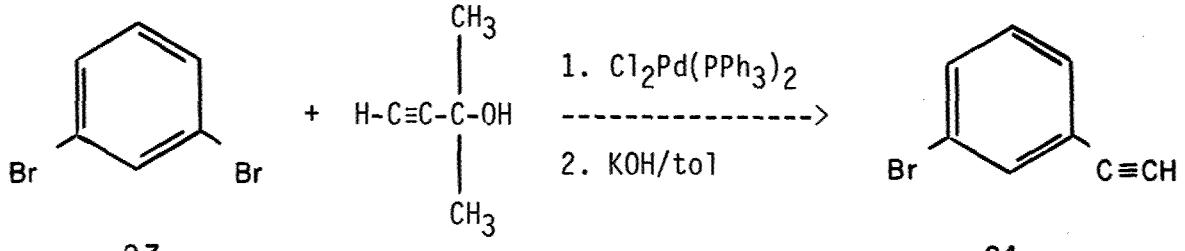


ATS

The disadvantage of this system is the high cost of m-hydroxyphenylacetylene which is produced by a cumbersome procedure.(15)

Our proposal consisted of an alternate route to ATS which avoided completely the use of m-hydroxyphenylacetylene. It consists of using m-dibromobenzene,[16] sulfonyldiphenol and the palladium catalyzed displacement reaction of aryl bromides to give phenyl acetylenes.[4] Our proposed route is shown below. m-Dibromobenzene is reacted with 3-methylbutyn-3-ol and then treated with base to produce 3-bromophenyl acetylene.[4] This then reacts with SDP in Ullmann ether synthesis.[17]



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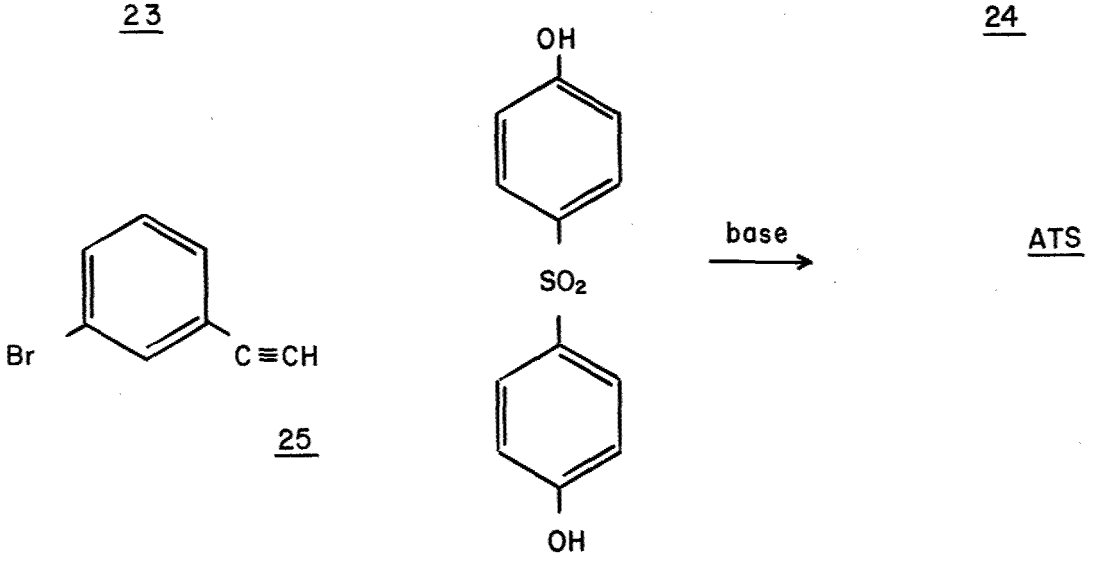

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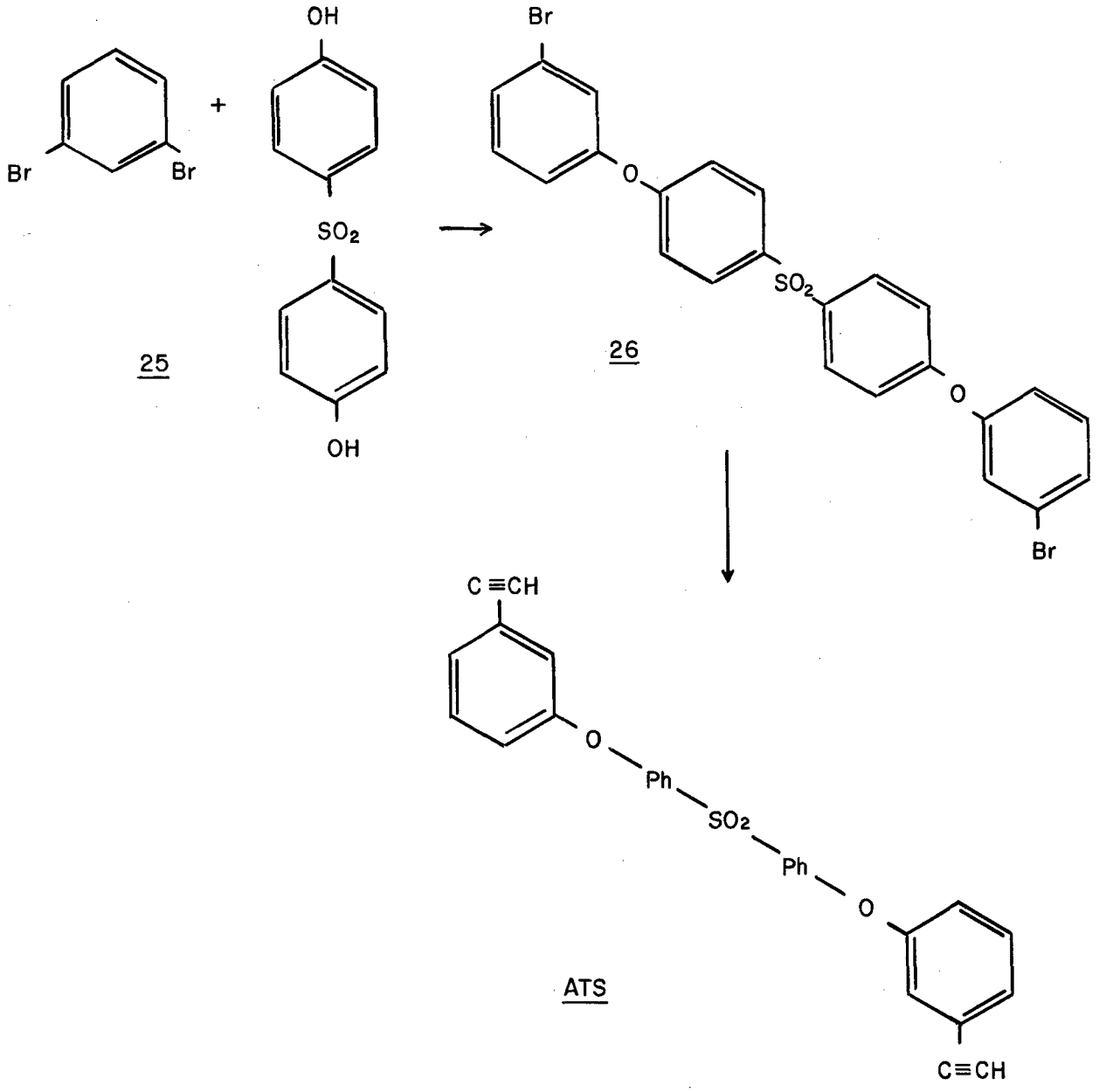
An equally attractive modification of this pathway consists of reacting m-dibromobenzene with SDP in the Ullmann ether synthesis first followed by displacement of the bromine with the acetylene group.



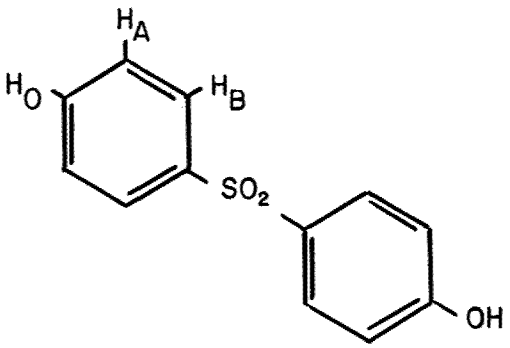
We chose the second alternative for investigation because it was uncertain whether the 3-bromophenylacetylene would survive the Ullmann ether synthesis. The results of our efforts are now reported.

B. Formation of the Potassium Salt of SDP

We have carried out an experiment to measure whether the mono- or dipotassium salt is formed during the reaction of SDP with different bases.

This material is the reactive species in the Ullmann ether synthesis. The experiment consisted of reacting SDP with a base in an NMR tube and measuring the shift of the NMR signal as a function of added base.

The NMR spectrum of SDP consists of two doublets, one assigned to H_B at 314 H_z, the other assigned to H_A at 266 H_z downfield from DMSO.



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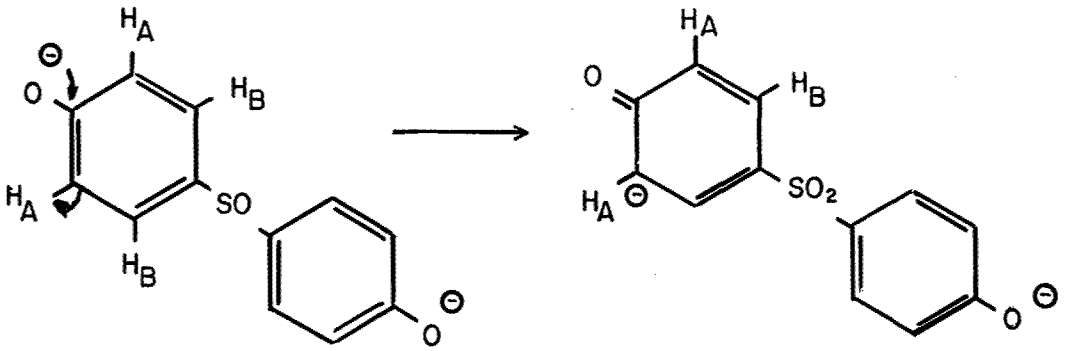
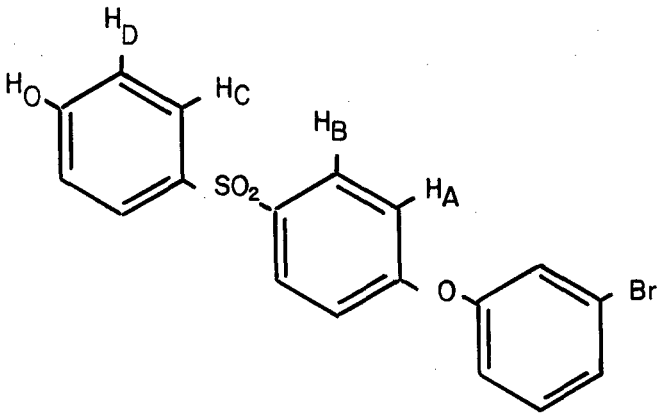
Upon the addition of base, the signals move upfield to different extents. This is shown in Table 9 using KOH as the base. The shift is a function of the amount of KOH added. The assignment of peaks in the spectrum is based on the shift observed ($\Delta\nu$) for the different resourses H_A and H_B and by comparison with the shift predicted by resonance structures shown below.



One resonance structure predicts a high electron density at the carbon bearing H_A. One would therefore predict that H_A would be shift upfield further than H_B. This effect is shown in Table 9.

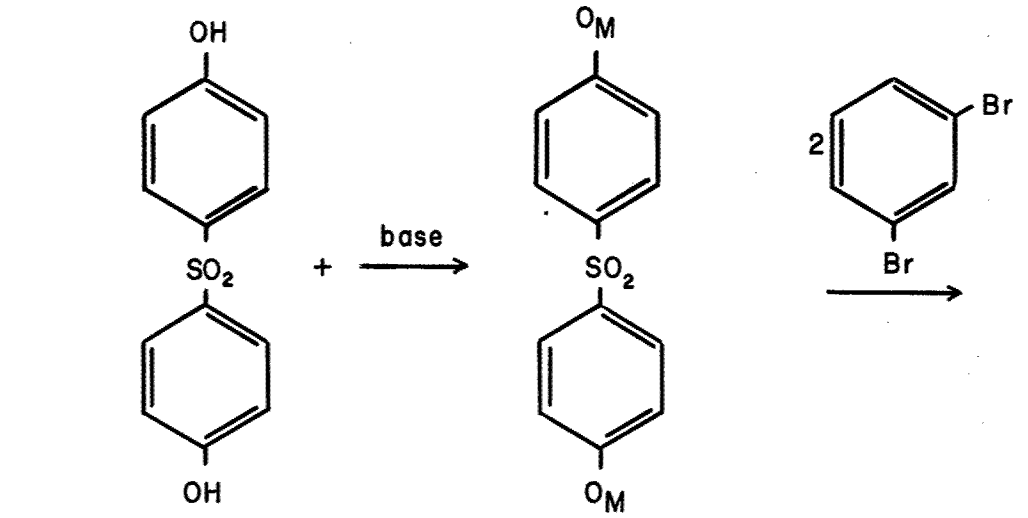
The shift of 34 H_z for H_A and 26 H_z for H_B indicates that, in the case of excess KOH in DMSO, only the monoanion has been formed. This is shown by comparison with the shift observed by reacting excess of KOH with half product 27. Addition of excess KOH in DMSO to half product resulted in a shift of 32 H_z for H_D 23 H_z for H_B and H_C and 21 H_z for H_A. These shifts are comparable to the shift of KOH on SDP and predict formation of monoanion. See Table 10.



Moreover, treatment of SDP with 2 equivalents of a strong base such as potassium tertbutoxide produces a new spectrum where H_A has shifted 54 H_z and H_B 42 H_z. This material which is formed from treatment of SDP with tertbutoxide most likely is the dipotassium salt and this is reflected in the shift of H_A and H_B which is almost twice that of the mono salt. These data indicate that at room temperature potassium hydroxide is not a strong enough base to generate the dianion in DMSO as solvent. However, as will become apparent KOH is an effective base for the condensation reaction of SDP with DBB at elevated temperatures.

C. Ullmann Ether Synthesis

In the early stages of this work, we screened a variety of solvents and conditions to determine what degree of conversion to BPDS could be effected. The reaction sequence (postulated) is shown below.



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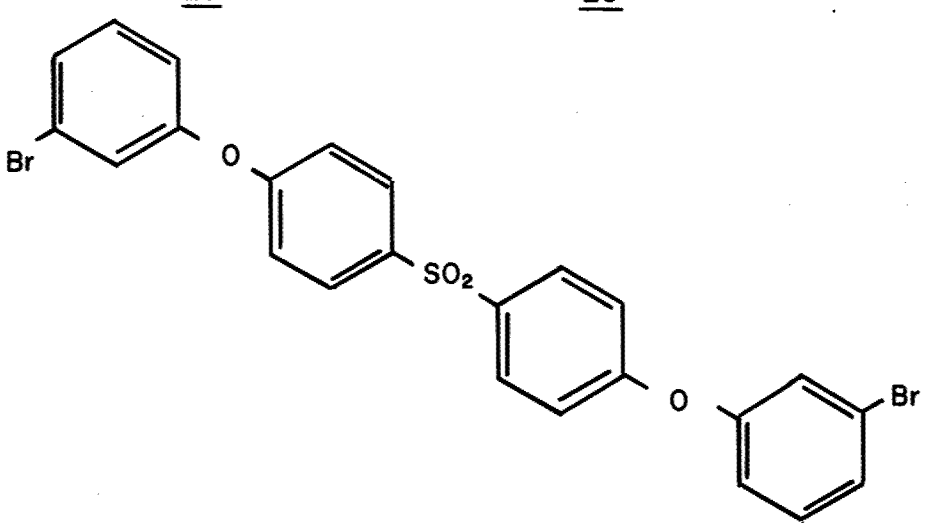
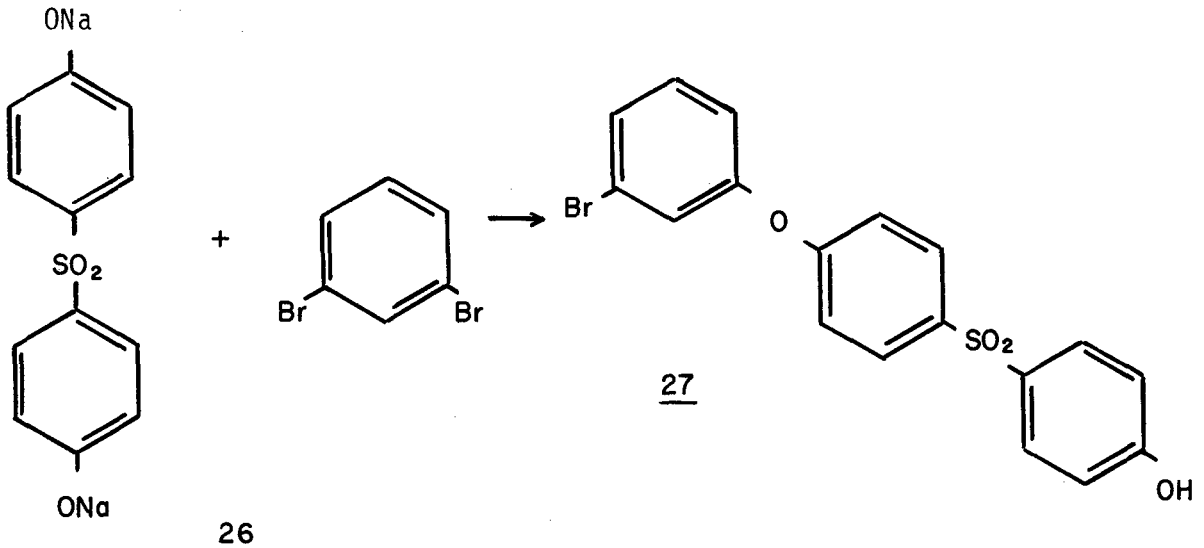


BPDS

Scheme 1

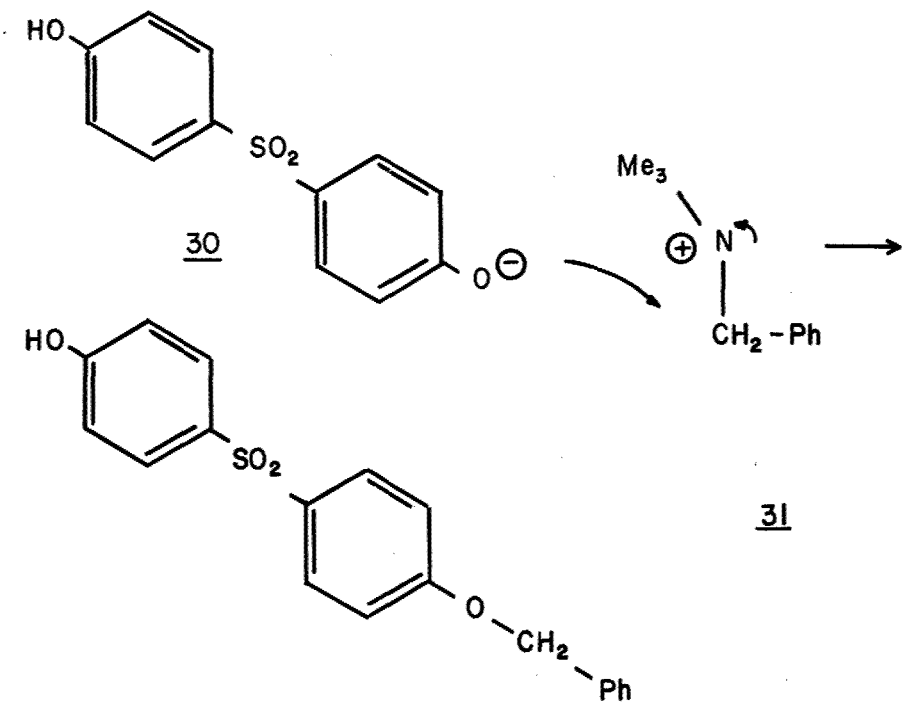
The amount of BPDS was assumed to be equivalent to the weight of material which was not extracted into KOH solution and which was not unreacted m-dibromobenzene. The m-dibromobenzene was typically separated from the BPDS by addition of hexanes or heptanes to the KOH insoluble fraction. The BPDS was insoluble in hexane or heptane and the DBB was soluble. This assumption was later shown to be incorrect due to the presence of oligomers along with BPDS in these precipitates. This will be discussed later.

Our results for a variety of runs is reported in Table 11. The solvents pyridine, DMF, DBB, quinoline, tributylamine all failed to give any reaction whatsoever. This is probably due to the poor solubility of the reagents in these particular solvents. Using NaOMe as the base and either DMSO or NMP as the solvent gave a good yield of half product shown below.



26 27

Interestingly, only half product was formed with the sodium salt even under forcing conditions. This effect may be due to the solubility of sodium salt in the reaction medium preventing further reaction. To overcome this problem we prepared the benzyltrimethylammonium salt 30 of SDP by reaction with benzyltrimethylammonium hydroxide. However, reaction of 30 gave a new product assigned the structure 31 probably formed by attack of $AR\text{-}O^-$ on the reactive benzyl position.



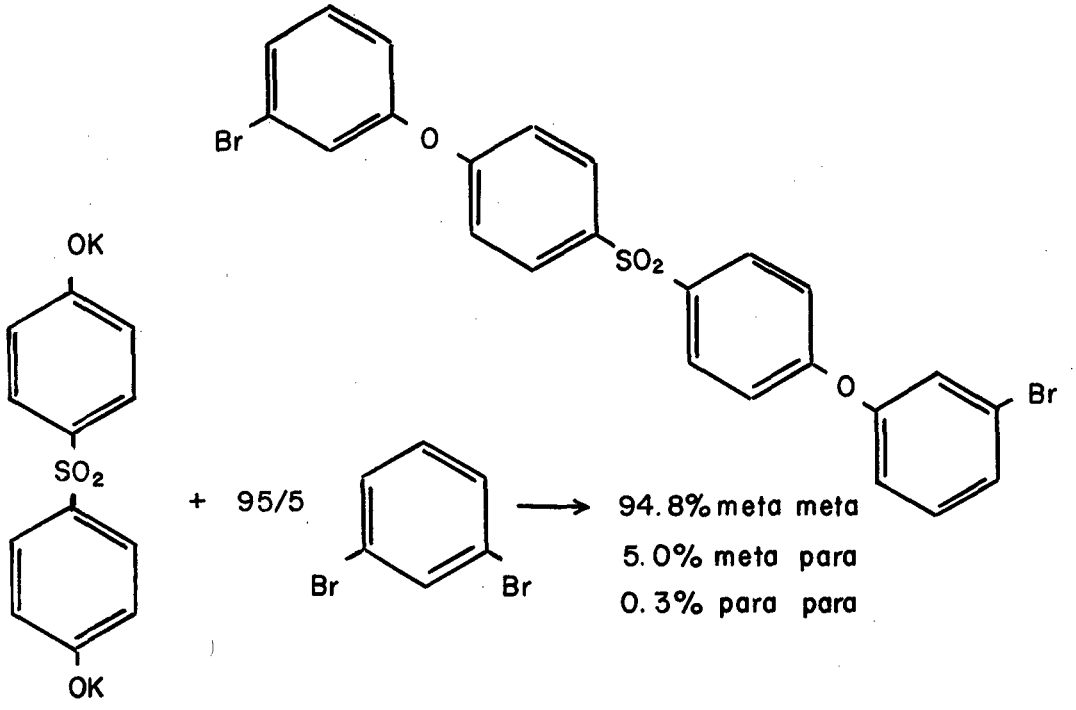
BPDS was finally produced when the potassium salt of SDP was reacted with m-DBB. Potassium hydroxide, potassium in methanol, or potassium tert-butoxide were all shown to be effective bases for the conversion. The greatest recovery of BPDS "appeared" to occur at the highest temperature. The solvents DMSO, NMP, and sulfolane all appeared to be useful for this transformation. Sulfolane was chosen as the best choice because of its stability at elevated temperature and because of its high boiling point relative to DMSO and NMP. Extensive studies were carried out using sulfolane as solvent and are reported later.

Dibromobenzene Isomers

The reaction of SDP dianion with m-dibromobenzene constituted an convenient path to an ATS precursor. The m-dibromobenzene can most economically be prepared as a mixture of meta and para isomers.

The ratio of m- and p-dibromobenzene isomers which could be obtained commercially after purification is 95/5[16] meta/para. For this reason, the synthesis of BPDS which we have attempted to scale up and optimize consisted of a 95/5 meta/para ratio of dibromobenzene as starting component.

Assuming equal rates for the meta- and para-dibromobenzene isomers, with SDP dianion a distribution of products will be obtained shown below.



The assumption of approximately equal rates for the reactivity of meta and para isomers seems to be a valid one. In a related case, Weingarten[18] reported that meta- and para-dichlorobenzene reacted at almost equal relative rates (1.3 to 1.0). We have experimentally tested this by analyzing the mixture of meta- and para-dibromobenzene before and after a typical run recovering unreacted dibromobenzenes. Practically the same meta/para ratio is observed in both cases. See Table 12.

D. Reactions in Sulfolane

General Remarks

Sulfolane was chosen as the solvent of choice for the Ullmann ether synthesis because of its high boiling point and chemical stability.

Initially the base potassium tert-butoxide was used. On a small scale BPDS was produced. However, on scaleup, the potassium tert-butoxide attacked the solvent at 140° giving off a gas and regenerating tert-butanol (Run 563-84). Switching to potassium hydroxide resulted in equally successful reactions 563-88 suggesting that at elevated temperatures even KOH can be used to form the dianion of SDP.

We have verified that potassium hydroxide does produce the dianion in sulfolane by measuring the water released in this reaction by azeotroping water with toluene and measuring the volume. Comparision with the theoretical volume of H_2O indicates that 2 moles of H_2O are produced in reaction of 1 mole of SDP with 2 moles of KOH. See Table 13.

Previous workers[17] have reported that a water free system must be used in the Ullmann ether synthesis. Our results support their work. On several occasions, a run gave no conversion to BPDS and this could be traced to the presence of water is the reaction.

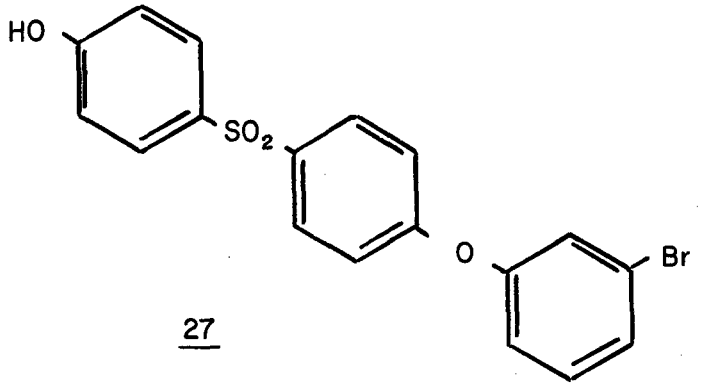
In general, the KOH was added to the reaction as a crushed powder (Method 1) or by dissolving in water (Method 2). Method 2 was more reproducible because we found that on a humid day the crushed KOH would coagulate and not give reproducible results. The water was removed by azeotroping with toluene.

Pyridine is usually a successful solvent for the Ullmann ether synthesis. However, in our case, it is a poor solvent when used alone (see Table 11) and has little effect when added to sulfolane (see Runs 563-88 and 565-38, Table 14).

Cuprous chloride was used as the catalyst for this reaction. In the absence of a copper catalyst, very little reaction occurred (run 565-40). Cuprous acetate was used on one occasion as a replacement for CuCl and little difference could be detected (565-88).

The products which we have isolated during this reaction were separated into two fractions, base soluble (phenolics) and base insoluble

(non-phenolics). The phenolic material consists of two components starting material and half product 27, shown below.



27

Half product is though to arise from reaction of 1 mole SDP with 1 mole DBD. These materials could be separated from each other by extraction into $CHCl_3$ or CH_2Cl_2 which selectivity removes the half product.

We have shown that at the end of the reaction the recovered half product and recovered SDP are present in their protonated form. This indicates that the reaction does not proceed to completion because there is a competitive protonation occurring. The most likely proton source is sulfolane itself.

The non-phenolic products consisted of BPDS, oligomer, and higher oligomers, discussed later. These materials are best recovered by extraction into CCl_4 or dibromobenzene. Other solvents such as ether or $CHCl_3$ gave hard to separate emulsions in some cases.

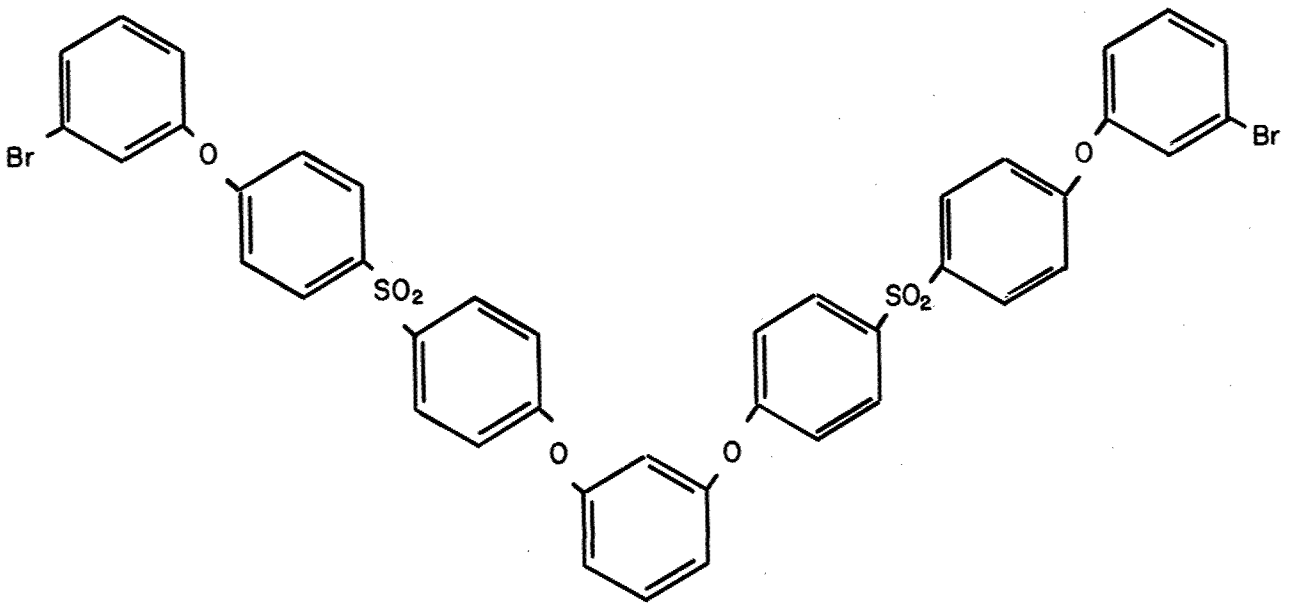
A reaction was carried out using a high ratio of copper (565-84). A poor yield of product was obtained probably because of ion exchange of copper for potassium which was unreactive.

These results are reported in Table 14.

E. Structure Assignment of Products

The results of a series of reactions between SDP and dibromobenzene in sulfolane showed that other products besides BPDS were being extracted by

CCL_4. These non-phenolic materials were shown by TLC to consist of two spots with an R_f lower than BPDS. One of these materials were obtained by careful column chromatography. NMR data for this material and combustion analysis and MW determination indicate the structure shown.

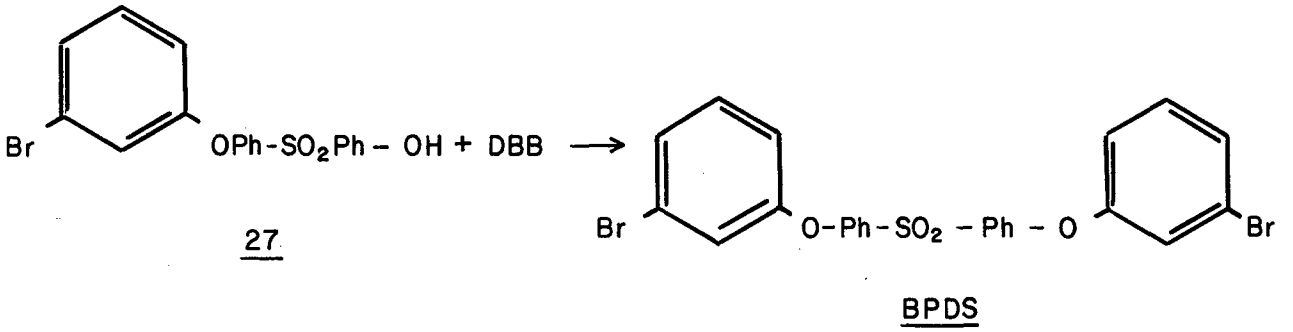


28

This material formally results from further attack of BPDS with 1 mole of half product. This is represented in Scheme 2.

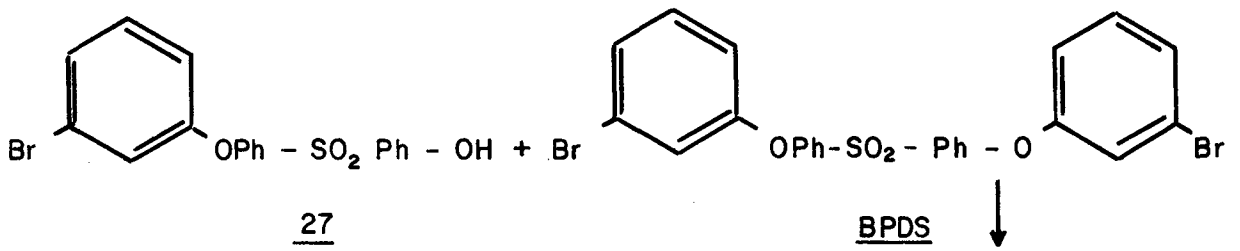
We postulate that the second unknown material with even lower R_f is the higher oligomr 29. This is supported by MW combustion analyses and NMR evidence. This may result from attack of BPDS by 2 moles of 27.

(1)



27

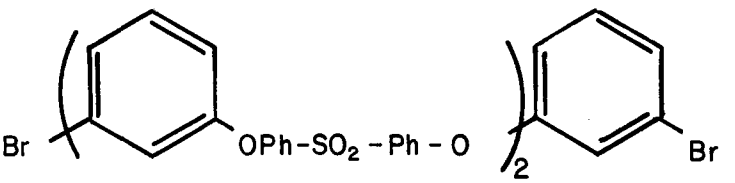
BPDS



27

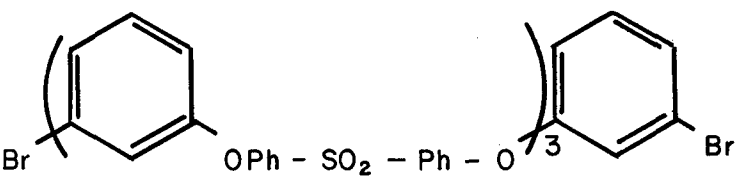
BPDS

(2)



28

(3) 27 + 28 --->

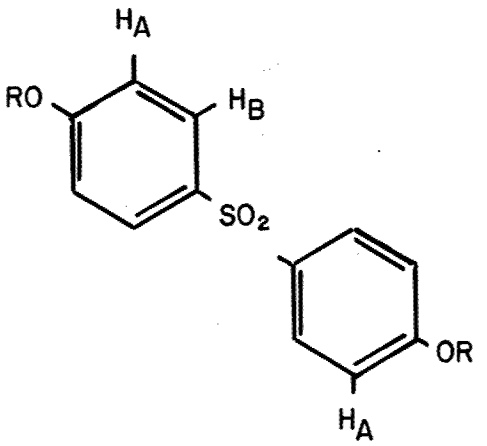


29

(4) 27 + 29 ---> etc.

Scheme 2

Integration of the aromatic signal in the NMR spectrum gave important structural information. For compounds of this type, one signal (H_B) appears at low field



relative to the other. For SDP (R=H) H_A = δ7.00, H_B = δ7.80 (see Table 23). When R = 3-bromophenyl, H_A = 7.05, H_B = 7.90. The resonances for the 3-bromophenyl group (H_C) appears at approximately the position of H_A. Therefore, integration of H_B relative to H_A plus H_C verifies our structure assignment. This is represented in Table 15 for BPDS, 28 and 29 which were separated by column chromatography. (29 could not be completely separated from traces of 28). Elemental analyses and MW determination of these materials are reported in Table 16 confirming their assignments.

F. Reaction with Half Product

The production of oligomer 28 and 29 have been postulated to arise from the reaction of half product with BPDS. We have carried out the reaction of half product with BPDS and have obtained material identical to the oligomer 28 and 29 obtained from SDP plus DBB. This is reported in Table 17. Besides unreacted BPDS and half product 27, we obtained 20% yield of oligomer 28 and 21% yield of oligomer 29. This verifies our structure assignment and lends support to our proposed mechanism for the foundation of 28 and 29 from BPDS and half product.

We have carried out a series of reactions using half product 27 and DBB to examine the effect of DBB/half product ratio on the relative percentage of BPDS and oligomers. These data are reported in Tables 18 and 19.

We have found that as the DBB/half product ratio increases from 1.5/1 to 9.8/1 the % BPDS increases from 35 to 68%. This is consistent with the proposed mechanism involving attack of half product on BPDS. It also indicates that the BPDS/oligomer ratio can be varied by controlling the relative amount of DBB used. The greater the amount of DBB used is the greater amount of BPDS found relative to oligomer. This is an important result since it has been reported by Wright-Patterson AFB testing labs that the presence of oligomer is beneficial. Pure ATS synthesized from our method has been crystallizing during processing. Increased amounts of oligomers is reported to be beneficial to the properties of product. In this respect, it is significant to recall that the dibromobenzene ratio used in this synthesis is 95/5 mixture meta/para. The mixture 95/5 meta/para dibromobenzene is the purity of material obtained by synthesis and purification of crude DBB prepared by a procedure worked out a GR&DC.[16] The crude material before purification has a meta/para ratio of 70/30. This material may be of even more importance in the synthesis to help prevent unwanted crystallization of ATS during processing.

G. Large Scale Runs

We have carried out several 50-100 g scale runs of the BPDS synthesis reacting SDP with DBB. These results are reported in Table 20 with the percent BPDS included. The percent yield of BPDS and of oligomers is reported in Table 21. During several early runs, the temperature varied over the 16-hour period by as much as 40°. We therefore set up temperature controlling device which regulated the temperature to within ±1°. Part of the problem with temperature control is that the reaction is mildly exothermic.

We have investigated the effect of temperature in the yield of the reaction and on the percent BPDS (see Table 20). Little effect occurs as the temperature is varied from 160-180° (see entry 596-8 and 596-6), but at 141°

the yield increases dramatically. This effect may be due to the increased rate of proton abstraction of sulofane by SDP anion as the temperature is raised. Therefore, reaction at lower temperature increases the net overall yield.

The BPDS/oligomer ratio varied only slightly with temperature. However, using a DBB/SDP ratio of 3/1 instead of 6/1 resulted in a decrease of the BPDS/oligomer ratio at the same overall efficiency (Run 596-16). This result demonstrates that an important degree of flexibility in the DBB/SDP ratio exists.

Increasing the amount of copper from 0.01 to 0.04 mole (entries 596-14 and 596-8) resulted in an increase in the yield to 52% (Table 21). This may be due to the fact that a higher copper ratio facilitates reaction of SDP dianion with DBB more than proton abstraction of sulfolane by SDP dianion.

The ratio of sulfolane to DBB is important in the condensation reaction. In one case (Run 565-47), excess of dibromobenzene gave no desired product but instead SDP dipotassium salt precipitated on the walls of the flask. It remained there unreacted. This result demonstrates that importance of using enough sulfolane to keep reacting species soluble.

Early reactions seemed to demonstrate a lower BPDS/oligomer than later runs. This result is rather puzzling and no adequate explanation can be given. Perhaps poor analysis technique can be used to explain these results (analysis of earlier runs was by preparative column chromatograph*) although a column chromatograph separation gave similar results with GPC in the one case examined (Table 22). The other possibility is that traces of metal impurities

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* Toluene could be removed from samples of oligomer only with difficulty and this may explain the relatively high value for oligomer in these runs.

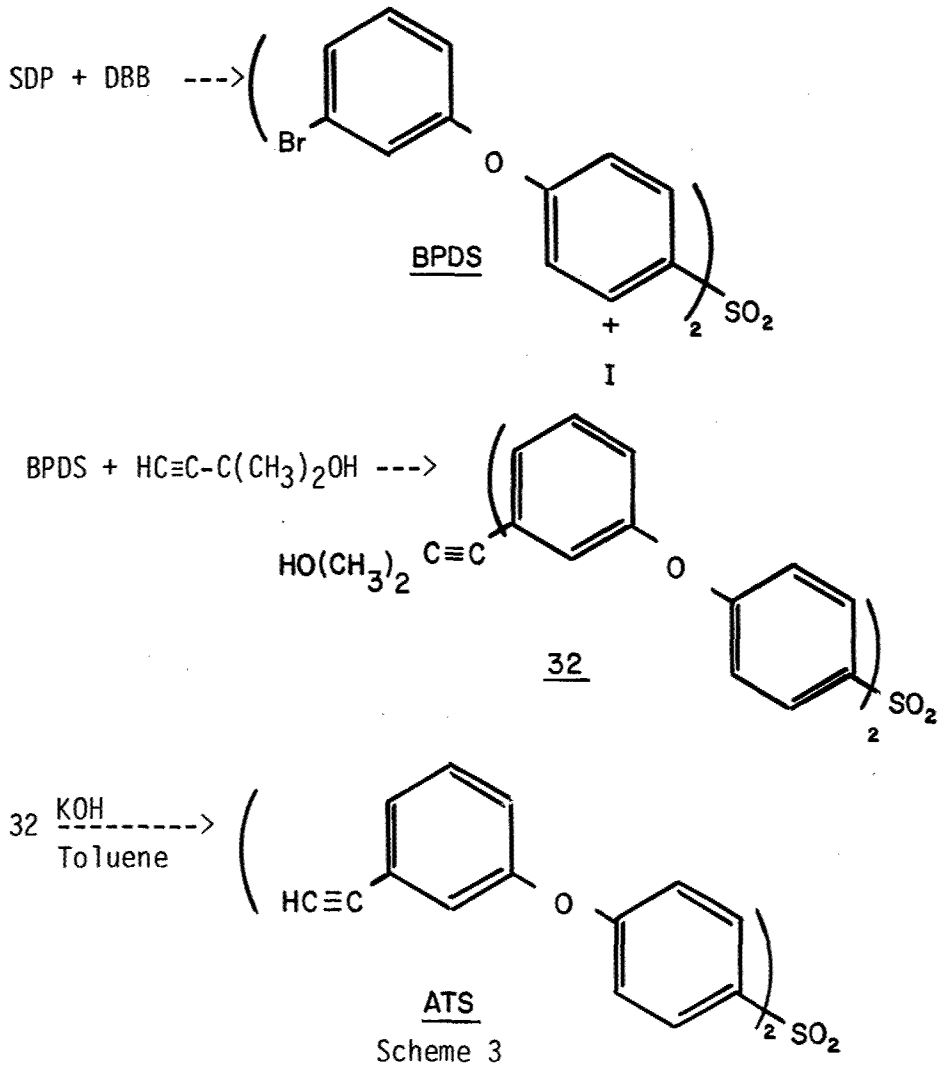
in the sulfolane gave higher oligomer ratios. Runs 596-14 through 596-3 were run with very pure sulfolane mp 21-24°. Earlier runs were made using a technical grade of sulfolane which was slightly colored.

H. Purification of BPDS

In the early stages of this work, pure BPDS uncontaminated with oligomers was desired to prepare ATS for testing. A considerable amount of time was spent to achieve this separation. BPDS could be extracted from samples of BPDS plus oligomer by continuous extraction with heptane. Pure BPDS crystallized from the hot heptane extraction solvent after several days of continuous extraction. Various recrystallization techniques involving ethanol, methanol, isopropanol, toluene, CCl_4, acetic acid, and toluene/hexane mixtures were unsuccessful. The only technique found to successfully separate BPDS from oligomers was column chromatography. Using alumina, BPDS could be eluted from oligomers using toluene. The oligomer 28 was then eluted with CH_2Cl_2 and oligomer 29 with ethylacetate.

I. Synthesis of ATS

Our work has strongly emphasized the first step in our proposed synthesis of ATS, namely, the Ullmann ether synthesis. While we were carrying this out, Wright-Patterson AFB demonstrated the remaining steps of the synthesis of ATS, namely, the displacement of the bromine with 3-methylbutyn-3-ol and caustic cracking to give ATS. This completes the three-step synthesis of ATS which is shown in Scheme 3.



Scheme 3

We have carried out the synthesis of ATS using the BPDS sample prepared from the 95/5, meta/para-dibromobenzene. The butynol(IV) and the ATS, which we synthesized, were identical (NMR, TLC) to samples received from Wright-Patterson AFB.

A curious result was observed when we precipitated the butynol(IV) in water according to the Wright-Patterson procedure. The product which we obtained from water precipitation was thermally cracked with KOH to produce ATS at a significantly slower rate than a sample which was isolated as the crude oil (see experimental section for details).

J. Conclusion and Recommendations

A novel route to ATS has been demonstrated based on a three-step synthesis from methylbutynol, m-dibromobenzene, and sulfonyldiphenol. These raw materials are all under $2 per pound. A 68% yield has been demonstrated for combined ATS and oligomer in the first step. If unreacted and partially reacted sulfonyldiphenol are recycled, the ultimate yield in the first step should be over 90%. We have demonstrated a 91% overall yield for the second two steps on a small scale. On the large scale preparation, the yield in the second two steps was only 55% because trace impurities and color were removed by repeated elution over Fuller's earth in order to make high purity product, and considerable product was lost on the column. If this clean-up is not needed and unreacted material is reused in the first step, the overall three-step yield should be 70-80%. Experimentally, we achieved an overall yield of 33% in the preparation of ATS.

An advantage of our new route to ATS other than cost is the presence of isomers and oligomers which can be produced in this synthesis. A meta/para dibromobenzene ratio of 70/30 or 95/5 is available to produce a variable amount of meta and para isomers.

A certain degree of flexibility in the percent oligomer exists already in this reaction using 95/5 dibromobenzene. We have found that lowering the DBB/SDP ratio from 6/1 to 3/1 increases the percent oligomer from 17% to 27%.

Our standard reaction conditions (Run 596-3, Table 20) produces at 160°, in an overall yield of 47%, product consisting of 83% BPDS and 17% oligomers. Reaction at 140° gives an overall yield of 64%. Another reaction at 160° but using four times as much copper gave an overall yield of 68%. We therefore recommend, as our best procedure, the reaction be carried out at 140° using four times the amount of copper in a standard run.

Scaleup of this process has been proceeding at GR&DC under USAF contract F33615-79-R-5059, "The Synthesis of Polymer Precursors and Exploratory Research Based on Acetylene Displacement Reaction," under the direction of E. T. Sabourin. We strongly recommend that optimum ratio of BPDS and oligomers as well as the best meta/para dibromobenzene ratio be determined so that further optimization of the yield can be carried out.

IV. EXPERIMENTAL

Synthesis of $Pd(PPh_3)_4$ (Reference 10)

To 43.67 g triphenylphosphine (0.167 mol) and 5.91 g palladium dichloride (0.033 mol) under nitrogen was added 400 ml DMSO. This was heated to 143° where components went into solution. To this at 120° was added 4.27 g hydrazine 95% (0.133 mole). A vigorous reaction took place evoling gas. The reaction was cooled to room temperature and stirred overnight. The product, yellow crystals, was filtered and washed twice with 50 ml ethanol and dried overnight under nitrogen. A total of 38.1 g was obtained; 100% yield; mp 92° dec., (lit.[10] 116°); recrystallized from benzene/hexane. Anal. cal. for $C_{72}H_{60}P_4Pd$: C 74.84, H 5.23, Pd 9.21. Found: C 74.91, H 5.42, Pd 9.50; NMR ($CDCl_3$) δ 7.5-7.6 (n, 5H, ring H).

Synthesis of $BrPhPd(PPh_3)_2$ (Reference 6)

To 4.4 g $Pd(PPh_3)_4$ (3.8 mmol) under argon was added 30 ml benzene and 2.0 g bromobenzene (12.7 mmol). This was heated to reflux for 13 hours. The reaction was then cooled and the off-white crystals filtered, washed with 10 ml benzene. A total of 2.50 g was recovered; 84% yield; mp 208° dec. (lit.[6] mp 216-220°); Anal. cal. for $C_{42}H_{35}BrP_2Pd$: C 64.02, H 4.48, Pd 13.50. Found: C 63.45, H 4.91, Pd 13.87; NMR ($CDCl_3$) δ 7.6-7.2 (m. 5 H, ring H).

Reaction of $PdCl_2$ with dppe (Reference 19)

To 1.77 g $PdCl_2$ (0.01 mol) and 9.95 g Bis(1,2-diphenylphosphino) ethane (dppe) (0.025 mol) was added 120 ml DMSO under argon. This was heated to 175° then 1.28 g hydrazine (0.04 mol) was added. After stirring and cooling overnight, the product was filtered, washed with 30 ml ethanol and 20 ml ether. A total of 8.87 g was recovered; 98% yield; mp 188-200° dec. (lit.[19] 234°). Anal. cal. for $C_{52}H_{48}P_4Pd$: C 69.15, H 5.36, Pd 11.78. Found: C 66.33, H 5.78, Pd 13.12; NMR ($CDCl_3$) δ 7.8-7.1 (m, 5H, ring H).

Reaction of $PdCl_2$ with dppm (Reference 19)

To 1.77 g $PdCl_2$ (0.01 mol) and 9.6 g Bis(diphenylphosphino)methane (ddpm) (0.025) was added 120 ml DMSO under argon. This was heated for 72° and 1.28 g hydrazine (0.04 mol) was added. After stirring overnight under nitrogen at room temperature, 7.3 g of orange crystals were obtained; 84% yield; mp 210° dec. (lit.[19] 195-210° dec); NMR ($CDCl_3$) δ 7.8-7.1 (m, 5H, ring H).

Reaction of $PdCl_2$ with dppp (Reference 10)

To 1.77 g $PdCl_2$ (0.01 mol) and 10.35 g Bis(diphenylphosphino)propane (dppp) (0.025 mol) was added 120 ml DMSO. At 55° 1.28 g (0.04 mol) hydrazine was added. After stirring overnight, the product was filtered to give 8.15 g gold crystals; 88% yield.

Reaction of $PdCl_2$ with dppb (Reference 10)

To 1.77 g $PdCl_2$ (0.01 mol) and 10.70 g Bis(diphenylphosphino)butane (dppb) (0.025 mol) was added 120 ml DMSO under argon. At 94°C 1.28 g hydrazine (0.04 mol) was added. After stirring overnight at R.T., 10.0 g crystals were filtered; 104% yield, mp 191-197° dec.

Preparation of $HO - \underset{CH_3}{\overset{CH_3}{C}} - C \equiv C - Ph$

To a 3-necked 100 ml flask equipped wit magnetic stirrer, condenser, thermometer, and N_2 inlet was added 15.7 g bromobenzene (100 mmol), 10.0 g, 3 methylbutyn-3-ol (119 mmol), and 60 ml triethyl amine dried over calcium hydride. To this was then added 0.05 g cuprous iodine (0.26 mmol), 0.05 g dichlorobis(triphenylphosphine)palladium (.071 mmol), and 1.0 g triphenylphosphine (3.8 mmol). This was refluxed for 25 hours, then the run was cooled, filtered to remove triethyl ammonium hydrobromide, and triethyl amine removed

in vacuo. This material was purified by distillation; 7.5 g recovered; bp 120° (10 mm); NMR ($CDCl_3$) δ 7.4 (m, 5H, ring H), 2.48 (1H, 5, OH), 1.62 (6H, 5, CH_3).

Reaction of Dichlorobis(triphenylphosphine)palladium with Phenyl Lithium

To 0.7 g $Cl_2Pd(PPh_3)_2$ (1 mmol) in 18 ml benzene at RT was added 1.8 ml phenyl lithium solution and 1.8 m in benzene/ethyether (1.0 mmol) under argon. A slight temperature increase to 35° was noted and color turned to dark brown. After 4 hours at room temperature, 10% HCl was added and the reaction was extracted with toluene, washed with 10% HCl, and then the solvent dried over anhydrous $MgSO_4$ and toluene removed in vacuo. A brown oil was obtained, 0.979 g, which solidified on standing. This material was identified by TLC, GC, and NMR and by comparison with authentic samples to be a mixture of biphenyl and starting $Cl_2(PPh_2)$ and a black Pd metal residue.

Reaction of Tri-o-tolylphosphine with $PdCl_2$ and Hydrazine

To 15.2 g tri-o-tolylphosphine (0.05 mol) an 1.77 g $PdCl_2$ (0.01 mol) was added 120 ml DMSO under nitrogen. At 95° 1.28 g hydrazine (0.04 mol) was added. This was stirred at RT overnight and the yellow solid was filtered to give 10.9 g material; mp 283-295°C.

Reaction of 3-bromophenol with 3-methylbutyn-3-ol

To 0.1 g $Pd(PPh_3)_4$ (0.09 mmol), 0.05 g cuprous iodide (0.27 mmol), 17.0 g 3-bromophenol (0.098 mol) and 12.0 g 3-methylbutyn-3-ol (0.14 mol) was added 60 ml triethylamine under nitrogen. This was then cooled and filtered. The triethylamine was removed in vacuo. To the residue was added 200 ml ether. This was washed with 10% sodium bicarbonate solution (2 x 200 ml). The ether was then dried over anhydrous magnesium sulfate and the ether removed in vacuo. This material was heated to 164°C 3 mm Hg for distillation but suffered decomposition.

Reaction Procedure for Reaction
of Bromobenzene with Palladium Catalysts

To a 3-necked flask under argon was added 0.1 g of the palladium catalyst to be studied, 0.05 g cuprous iodide, 1.57 g bromobenzene (0.01 mol), 1.2 g 3-methylbutyn-3-ol (0.14 mol) and 10 ml triethylamine. Reaction was heated rapidly to reflux and the progress was monitored by removing 10 µl samples for analysis by GC. A 10-ft OV17 column was used programmed 80°-220°C at 8° per minute. Compounds analyzed for catalytic activity in this way were $Pd(PPh_3)_4$, $Pd(dppm)_2$, $Pd(dppe)_2$, $Pd(dppp)_2$, $Cl_2Pd(PPh_3)_2$, $Pd(dppb)_2$, $Pd(otol_3P)_4$, and $Pd(PPh_3)_4$ without CuI. (Table 1-8)

Preparation of $ClPhPd(PPh_3)_2$ (Reference 5)

To 4.4 g $Pd(PPh_3)_4$ (3.8 mmol) was added 30 ml chlorobenzene under nitrogen. This was heated to 128° for 5 hours. The reaction was cooled to room temperature, filtered, and the crystals washed with ether. A total of 2.90 g product was obtained; 100% yield; mp 270° dec (lit. mp 240.5° dec).

Preparation of $Cl_2Pd(PhCN)_2$ (Reference 13)

The preparation of $Cl_2Pd(PhCN)_2$ was carried out according to the method of Kharasch.[13]

Preparation of BPDS - Oligomer Mixture (Run #596-3), Table 20)

To 800 ml sulfolane, and 300 ml toluene was added 100 g sulfonyldiphenol (0.4 mol) under nitrogen. To this was added 52 g potassium hydroxide (87% KOH by weight) (0.8 mol) dissolved in 28 ml H_2O. Then 566 g m-dibromobenzene (5% para) (2.4 mol) was added. The mixture was heated with stirring and toluene/H_2O azeotrope was collected. After all the toluene/H_2O had been removed, 45 ml H_2O recovered, the mixture was cooled and 2.0 g CuCl (0.02 mol) was added. This was heated at 160° $\pm$ 1° for 16 hours. The reaction mixture was then allowed to cool and to it was added 1 liter 10% potassium hydroxide solution.

The mixture was then extracted with hexane (3 x 500 ml) and combined. Slowly a precipitate formed which was filtered to give 11.6 g almost pure BPDS contaminated with some sulfolone. The aqueous layer was then extracted with CCl_4 (3 x 500 ml). The 11.6 g of crystals were dissolved in the CCl_4 and the total was washed with water (3 x 400 ml). The CCl_4 was dried with anhydrous magnesium sulfate and the CCl_4 removed in vacuo. The residue was triturated with hexane, filtered and dried to a constant weight under vacuum. A total of 106.5 g was recovered. This material analyzed by gel permeation chromatography was 82.8% BPDS and 17.2% oligomer. The remaining aqueous layer was acidified with conc HCl to pH 1.5 and then extracted with ether. The ether was washed with water and then dried over anhydrous magnesium sulfate and the ether removed in vacuo. A total of 33.0 g of unreacted SDP and half reacted product was recovered. NMR indicated that this material was contaminated with sulfolane.

Preparation of Half Product 27 (Run #536-114, Table 11)

To 16 ml dimethylsulfoxide (DMSO) under nitrogen was added 2.5 g sulfonyldiphenol (0.01 mol). To this, at 38°C, was added 4.6 ml sodium methoxide solution (25% in methanol) (0.02 mol). The mixture was heated to 120° and 3.0 ml methanol was distilled. To this was added 10 ml pyridine and the temperature was increased to 145° removing an additional 2.5 ml methanol and 4.5 ml pyridine. Then 0.10 g cuprous chloride (1 mmol) and 9.4 g m-dibromobenzene (0.04 mol) was added. This was heated to 150° for 6 hours. Then 100 ml 10% HCl was added and the product extracted into ether. The ether was extracted with 10% KOH, the KOH was acidified and extracted with ether. The ether was removed in vacuo to give 5.0 g of crude material. This was purified on a column of silica gel using chloroform as solvent to give 1.8 g half product; 44% yield. See Table 23 for NMR data.

Reaction of SDP with KOH in DMSO d_6

To 0.05 g sulfonyldiphenol (0.2 mmol) was added 0.5 ml DMSO d_6 in NMR tube. To this at intervals was added four 0.125 ml portions of 0.22 g KOH (4 mmol) dissolved in 0.5 ml D_2O. NMR spectra were recorded after each

addition. The chemical shift as a function of added base is reported in Table 9.

Reaction of Half Product (27) with KOH in DMSO d_6

To 0.162 g half product (27) in 0.5 ml DMSO was added KOH, 0.22 g (4 mmol) in 0.5 ml D_2O in four 0.125 ml portions. The NMR spectrum was recorded after each addition and is reported in Table 10.

Reaction in DMF (Run #563-8, Table 11)

To a 50 ml flask equipped with a thermometer, magnetic stirrer, and distilling head was added 16 ml dimethylformamide dried over CaH_2 and 2.5 g (0.01 mol) sulfonyldiphenol. The mixture was warmed to 45°C where material dissolved. Then 4.6 ml 25% sodium methoxide in methanol (0.02 mol) was added. The temperature was increased to 100° and a fraction bp 65°C was recovered (5.5 ml). This fraction was mostly methanol with a small amount of dimethylamine dissolved in it. The reaction was then cooled and pyridine, 10 ml, was added. A solid precipitated at this point, which did not dissolve upon heating. The reaction was cooled and 0.1 g CuCl and 9.4 g dibromobenzene (0.06 mol) was added. This was then heated at 140°C overnight. The product was cooled, diluted with 10% HCl and extracted with ether. The ether was then extracted with 10% KOH and then dried over anhydrous magnesium sulfate and the ether removed in vacuo to yield 8.6 g product which was identified as m-dibromobenzene by NMR. TLC showed a trace of authentic BPDS was formed. The KOH was then acidified with concentrated HCl and extracted with ether to yield 2.7 g of material which was mostly sulfonyldiphenol by NMR. Some half condensed product 27 was also formed as indicated by NMR and TLC.

Reaction in NMP (Run # 563-10, Table 11)

In a 3-necked flask under nitrogen was added 16 ml NMP (technical grade) and 2.5 g sulfonyldiphenol (0.01 mol). After warming to dissolve the sulfonyldiphenol, 4.6 ml (0.02 mol) sodium methoxide solution 25% in methanol was added. This was heated to reflux and 5.5 ml methanol bp 65°C was

recovered. Then 10 ml pyridine, 0.1 g CuCl, and 9.4 g m-dibromobenzene was added, and the reaction was heated at reflux 198° for 48 hours. The reaction was then cooled and worked up in the normal manner to yield 5.9 g m-dibromobenzene and 2.2 g of half product 27. Very little desired BPDS was formed.

Reaction with Potassium Metal in DMSO (Run #563-12, Table 11)

In a 3-necked flask under nitrogen was added 10 ml of dry methanol and 0.79 g potassium metal (0.02 mol). When the potassium had dissolved, 2.5 g sulfonyldiphenol (0.01 mol) was added, and then 16 ml DMSO. Reaction was heated to reflux and CH_3OH bp 65° was distilled and recovered. (9.6 ml was recovered.) Then 10 ml pyridine was added, and 0.1 g CuCl and 9.4 g m-dibromobenzene. The mixture was heated at 110°C to 140°C overnight and then worked up in normal manner. We isolated 7.6 g of a mixture of m-dibromobenzene and BPDS from which 0.5 g BPDS crystallized mp 140-148°C. A total of 2.9 g of half condensed product 27 was also formed.

Reaction with Sodium Metal in DMSO (Run #563-14, Table 11)

In a 3-necked flask under argon was added 10 ml methanol and 0.46 g (0.02 mol) sodium metal. To this was then added 2.5 g (0.01 mol) sulfonyldiphenol and 16 ml DMSO. This was heated and fraction boiling at 65°C was recovered (9.8 ml). 10 ml pyridine was added, then 0.1 g CuCl and 7.4 g (0.06 mol) m-dibromobenzene. This was heated at 140°C overnight. After usual work-up, we recovered 7.5 g m-dibromobenzene and 3.6 g half condensed product 27.

Reaction with Potassium
Hydroxide without Solvent (Run #563-18, Table 11)

To a 3-necked flask was added 2.5 g sulfonyldipehnol (0.01 mol) and 50 ml pyridine. Then 1.12 g potassium hydroxide (0.02 mol) was added. The mixture was heated and 40 ml pyridine and H_2O were removed by distillation. a solid precipitate formed which did not dissolve with further heating. The reaction was cooled and 0.1 g CuCl and 7.4 g (0.06 mol) m-dibromobenzene was

added. The temperature was increased to 150°C by distilling off the remaining pyridine and heated overnight. After work-up, we isolated 9.9 g of unreacted m-dibromobenzene and 1.82 g of unreacted SDP.

Reaction with Potassium Hydroxide in DMSO (Run #563-24, Table 11)

To a 3-necked flask under nitrogen was added 50 ml toluene, 2.5 g (0.01 mol) sulfonyldiphenol, and 1.12 g (0.02 mol) potassium hydroxide crushed pellets. The mixture was heated and toluene/water azeotrope plus toluene was collected by distillation. Then DMSO (10 ml) was added and the temperature increased to 122°C and the rest of toluene removed. Then 0.1 g CuCl and 9.4 g (0.06 mol) m-dibromobenzene was added. This mixture was heated at 130° for 4 days, then worked up. Large amounts of decomposition by-products of DMSO complicated work-up. We isolated 8.0 g of product which was a mixture of BPDS and m-dibromobenzene. A total of 0.4 g of BPDS crystallized out. The rest of the material was discarded.

Reaction of SDP with Triton B (Run #563-58, Table 11)

To 20 ml NMP was added 2.5 g SDP (0.01 mol) under nitrogen. To this was added 8.35 g of benzyltrimethylammonium hydroxide (40% solution in methanol) (0.02 mol). Toluene (10 ml) as added to azeotrope, the H_2O, and the methanol. The reaction was then cooled and 0.1 g CuCl and 9.4 g m-dibromobenzene (0.04 mol) was added. This was heated to 195° overnight. The reaction was worked up in the usual manners to give 10.1 g DBB and 2.7 g of a new product which was assigned the structure 31; 80% yield; NMR ($CDCl_3$) δ 8.0-6.8 (1's, m, ring H's), 5.03 (2H's, S, $\underline{CH_2}Ph$).

Reaction of SDP in
Sulfolane using $(CH_3)_3\ O^-K^+$ as Base (Run #563-78, Table 11)

To 20 ml sulfolane was added 2.25 g potassium tert-butoxide and the mixture was heated to help it dissolve. Then 2.5 g and 5.0 ml toluene were added. The toluene/t-butanol azeotrope was removed by distillation, then 1.0 ml pyridine, 9.4 g DBB, and 0.1 g CuCl was added. This was heated to

185°C for 16 hours then to 200°C for 5 hours. After cooling to room temperature, the reaction was then diluted with 100 ml 10% HCl and extracted with ether (three times 50 ml). This was washed with KOH and dried over anhydrous magnesium sulfate and yielded 9.6 g material which crystallized in hexane to give 3.2 g desired product (57% yield). The KOH was then acidified and ether extracted to yield 2.1 g half product II (50% yield).

Reaction of SDP with
DBB with Excess Copper (Run #565-84, Table 14)

To a 3-necked flask under nitrogen was added 100 ml sulfolane, 100 ml toluene and 5.0 g sulfonyldiphenol (20 mmol). This was heated to 55° to dissolve the reagents and 18.8 g 95% metadibromobenzene (80 mmol) was added and 2.6 g potassium hydroxide (40 mmol). This was heated to remove water/toluene azeotrope. Then 1.0 g cuprous chloride (10 mmol) was added. The reaction was heated to 155° overnight. After work-up in the usual way, we recovered unreacted m-dibromobenzene and unreacted SDP.

Reaction of SDP with
DBB Using Cupric Acetate (Run #565-88, Table 14)

To a 3-necked flask under nitrogen was added 100 ml sulfolane, 100 ml toluene, and 5.0 g SDP (20 mmol). Then at 55° 2.6 g KOH (40 mmol) and 18.8 g (80 mmol) DBB was added. After removing the water, the reaction was cooled and 0.05 g cupric acetate (0.25 mmol) was added. This was heated to 150° overnight. In the morning, the temperature had risen to 202° indicating loss of temperature control during the night. After normal work-up, we obtained 2.0 g of material which consisted of BPDS, oligomer, and higher oligomer. Relative percentage of these materials was not determined.

Reaction of SDP at 156° for 6 Hours (Run #565-90, Table 20)

To a 3-necked flask under nitrogen was added 800 ml sulfolane, 200 ml toluene, 100 g sulfonyldiphenol (0.4 mol), 52 g potassium hydroxide (0.8 mol) and 566 g 95% m-dibromobenzene (2.4 mol). The water was removed and then 2.0 g cuprous chloride (20 mmol) was added. The reaction was heated to

156° and kept there for 6 hours. The product was worked up in the usual way to give 50.7 g of BPDS plus oligomers. This material was sent for HPLC and gel permeation chromatographic analysis. Results are reported in Table 20.

Reaction at 160° (Run #565-97, Table 20)

A reaction identical to the one above was carried out at 160° overnight. In the morning, we found that the temperature had decreased to 120° indicating no temperature control during the night. Work-up yielded 93.4 g of BPDS plus oligomers. This was also sent for HPLC and GPC analysis.

Reaction of 27 with DBB

To a 250 ml 3-necked flask equipped with a magnetic stirrer, thermometer and distilling head was added 8.3 g half-product 27 (20 mmol), 100 ml sulfolane, 100 ml toluene, 14.8 g DBB (94% meta, 5% para) (63 mmol) and 1.3 g potassium hydroxide (20 mmol) under nitrogen. This was heated to remove the water, toluene azeotrope, then 0.1 g CuCl was added. The reaction was heated at 160° for 16 hours, then cooled. To this was added 10% KOH (200 ml) and the mixture was extracted with hexanes (3 x 200 ml). This removed unreacted DBB. The mixture was then extracted with carbon tetrachloride and the CCl_4 removed. This materials were separated on a column of alumina using toluene to elute BPDS, methylene chloride to elute 28 and ethyl acetate to elute 29. Results are reported as a function of DBB/27 ratio in Table 18. The KOH solution was acidified to pH 1.0 with conc HCl. Then extracted with ethyl ether to recover unreacted 27. See Table 18.

Preparation of Oligomers 28 and 29

We reacted 27 (20 mmol) with BPDS (20 mmol) according to the above procedure substituting BPDS in place of DBB. The CCl_4 soluble product was purified by column chromatography to give 3.6 g 28 (20% yield) and 2.5 g 29 (21% yield).

The result of this reaction was reported in Table 17. NMR data are reported in Table 23.

Synthesis of BPDS (Run #563-92, Table 20)

To a 1-liter, 3-necked flask was added 400 ml sulfolane and 50 g sulfonyldiphenol (0.2 mole) under nitrogen. To this was added 22.0 g KOH (86.6% pure) (0.34 mole). Toluene 100 ml and dibromobenzene was a 95/5 mixture of m-dibromobenzene and p-dibromobenzene. The mixture was heated with stirring to remove the water by toluene azeotrope. After the water was removed, the reaction was cooled to 70°C then 20 ml pyridine and 1.0 g CuCl was added. The reaction was then heated to 175°-180° overnight. The reaction was then cooled and to it was added 750 ml water followed by extraction with CCl_4 (3 x 750 ml). The CCl_4 was extracted with KOH (3 x 750 ml) 10% solution then with water (3 x 750 ml). The CCl_4 was then dried over anhydrous magnesium sulfate and the solvent removed in vacuo. A total of 165.0 g of dark oil was recovered. This was then distilled at 15 mm to remove the excess dibromobenzene. The recovered dibromobenzene was analyzed by GC to give essentially the same ratio of isomers with which we started meta/para = 95/5 (Table 1). The residue from dibromobenzene distillation 50.6 g was purified by column chromatography over silica gel using toluene or more conveniently over alumina using toluene to give a total of 33.4 g of BPDS mp 133°-140°. NMR was practically identical to BPDS prepared from 100% m-dibromobenzene. NMR data is reported in Table 23. Combustion data is reported in Table 16.

Synthesis of BPDS (Run #565-30, Table 14)

To a 100 ml, 3-necked flask under nitrogen was added 20 ml sulfolane, 2.5 g (0.01 mol) sulfonyldiphenol, 1.3 g (0.02 mol) potassium hydroxide, 10 ml toluene, and 9.4 g (40 mmol) dibromobenzene (meta/para = 95/5). This was heated and water removed azeotropically with toluene. Then 0.05 g cuprous chloride (0.5 mmol) was added and the reaction was kept at 175° for 16 hours. The reaction was cooled, diluted with water and extracted with hexane (3 x 80 ml). The hexane was then removed in vacuo to give 5.4 g of DBB. The aqueous phase was extracted with carbon tetrachloride (CCl_4). Then the CCl_4 was extracted with 10% KOH. The CCl_4 was then dried over anhydrous magnesium sulfate and removed in vacuo. The residue was then purified through a column of alumina using toluene to give 2.13 g of BPDS 38% yield.

Preparation of Butynol 32

To a 3-necked flask, 50 ml flash under nitrogen was added 20 ml toluene, 5.6 g BPDS (10 mmol), and 2.0 g 2-methyl-3-butyn-2-ol (23 mmol). Then, 0.05 g cuprous iodide, 0.05 g dichlorobistriphenylphosphine palladium and 0.1 g triphenylphosphine was added. Finally, 10 ml triethylamine was added and the reaction heated to reflux. After five hours, the reaction was cooled and filtered to remove the triethylammonium bromide (3.97 g recovered). The solvent was removed in vacuo. A total of 9.6 g of crude product approximately 70% pure (contaminated with toluene) was recovered; NMR ($CDCl_3$) δ 6.8-8.0 (m, aromatic H's), 2.9 (2H, brs, OH), 1.60 (12H, S, CH_3).

Reaction of Butynol-32 with Hydroxide in Toluene

The above butynol (IV) 5.0 g, 70% pure (6.2 mmol), was dissolved in 50 ml toluene and to this was added one KOH pellet which had been crushed. Using a dean stark trap, 20 ml of toluene/acetone was removed in two hours. The crude product was then filtered through alumina, then the solvent removed in vacuo. Purification through a column of alumina, using toluene, gave 1.78 g of ATS as a dark yellow oil; 64% yield; NMR ($CDCl_3$) δ 6.8-8.0 (m, aromatic H's), 3.0 (S, 2H, C=CH).

Preparation of Butynol-32 - Water Precipitation Work-up

The synthesis of butynol (IV) was carried out as previously described from 29.9 g BPDS. The crude product obtained after solvent removed was then dissolved in 160 ml methanol, decolorized with norit, and slowly added dropwise with stirring to 1.5 ℓ H_2O. A tan solid precipitated and was filtered with difficulty through filter paper. Using a sintered glass funnel was unsatisfactory because the funnel became easily clogged. The product 29.5 g was identifical (TLC and NMR) to alternate procedure.

Thermal Base Cracking Behavior of Butynol from Water Work-up

Butynol (IV), 29.5 g, obtained as a precipitate from water was dissolved in 200 ml toluene and to it was added two crushed KOH pellets. The solution was heated to boiling and with a dean stark trap 6 ml water, and 30 ml toluene was removed. More potassium hydroxide was added and more toluene was added periodically. Finally, after about 16 hours of heating, the reaction was still incomplete by TLC and by NMR. The reaction was then discontinued.

Purification of BPDS by Column Chromatography

A sample of BPDS, 28 and 29 26.3 g was dissolved in a minimum of toluene and passed through a column of alumina activated at 100° overnight. BPDS was eluted with toluene 14.5 g recovered. Fractions were analyzed conveniently by TLC. Methylene chloride was then used to elute 28, 4.9 g recovered. Ethyl acetate or acetone was then used to elute 29, 2.5 g recovered. Total recovery 21.9 g 88% recovery.

Hot Heptane Extraction of BPDS

A crude product mixture (337.4 g) containing DBB BPDS, 28 and 29 was distilled at 15 mm Hg 94°C to recover the DBB (90 ml). To the solid residue was added 300 ml heptane in a liquid liquid extractor. The system was warmed to melt the solid residue which was then continually extracted for twenty four hours with heptane. A total of 61 g of pure BPDS crystallized out from the hot heptane.

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Table 1

Displacement of Bromobenzene Using $Pd(PPh_3)_4$ as Catalyst[a]

Time	Temperature	% Bromobenzene[c]	% A	% Phenylacetylene	% Dimer
0[b]	95	4	-	96	-
60	95	0.3	-	99.7	-

(a) 0.1 g $Pd(PPh_3)_4$, 10 ml, Et_3N, 0.001 g CuI, 1.57 g bromobenzene, 1.00 g 2-methyl-3-butyn-2-ol were used.

(b) reaction took 30 minutes to reach 95°.

(c) relative percentage by GC area.

Table 2

Displacement of Bromobenzene Using $ClPd(PPh_3)_2$ as Catalyst[a]

Time	Temperature	% Bromobenzene[c]	% A	% Phenylacetylene	% Dimer
0[b]	93	6	tr	94	tr
55	91	3	tr	97	tr

(a) 0.1 g $Cl_2Pd(PPh_3)_2$, 10 ml, Et_3N, 0.001 g CuI, 1.57 g bromobenzene, 1.00 g 2-methyl-3-butyn-2-ol were used.

(b) reaction took 65 minutes to reach 93°.

(c) relative percentage by GC area.

Table 3

Displacement of Bromobenzene Using $Pd(dppm)_2$ as Catalyst[a]

Time	Temp., °	% Bromobenzene[c]	% A	% B	% Phenylacetylene	% Dimer	Other
0[a]	95	85	8	3	3	1	-
60	95	66	18	5	10	1	-
120	95	62	17	tr	20	1	-
180	95	62	17	tr	20	1	-
240	95	62	17	tr	21	1	-
420	95	52	20	tr	28	tr	-

(a) 0.1 g $Pd(dppm)_2$, 10 ml, Et_3N, 0.001 g CuI, 1.57 g bromobenzene, 1.00 g 2-methyl-3-butyn-2-ol.

(b) reaction took 30 minutes to reach 95°.

(c) relative percentage by GC area.

Table 4

Displacement of Bromobenzene Using $Pd(dppe)_2$ as Catalyst[a]

Time	Temperature	% Bromobenzene	% A	% Phenylacetylene
0[b]	93	99	-	1
60	95	97	tr	3
120	95	95	tr	5
180	95	90	tr	10
240	95	86	1	13

(a) 0.1 g $Pd(dppe)_2$, 10 ml, Et_3N, 0.001 g CuI, 1.57 g bromobenzene, 1.00 g 2-methyl-3-butyn-2-ol.

(b) reaction took 30 minutes to reach 93°.

Table 5

Displacement of Bromobenzene Using $Pd(dppp)_2$ as Catalyst[a]

Time	Temperature	% Bromobenzene[b]	% A	% Phenylacetylene	% Dimer
0	95	99.7	-	0.3	-
60		94	-	6	-
120		89	-	11	tr
170		82	tr	18	tr
240		77	tr	21	2
300		64	tr	33	3

(a) 0.1 g $Pd(dppp)_2$, 10 ml, Et_3N, 0.001 g CuI, 1.57 g bromobenzene, 1.00 g 2-methyl-3-butyn-2-ol.

(b) reaction took 30 minutes to reach 93°.

Table 6

Displacement of Bromobenzene With $Pd(dppb)_2$ as Catalyst[a]

Time	Temperature	% Bromobenzene[b]	% A	% Phenylacetylene	% Dimer
0	94	99.6	-	0.4	-
60	95	83	3	14	tr
120	93	75	5	20	tr
180	94	65	6	27	2

(a) 0.1 g $Pd(dppb)_2$, 10 ml, Et_3N, 0.001 g CuI, 1.57 g bromobenzene, 1.00 g 2-methyl-3-butyn-2-ol.

(b) reaction took 30 minutes to reach 93°.

Table 7

Displacement of Bromobenzene With $Pd(p\text{-}tol_3P)_4$ as Catalyst[a]

Time	Temperature	% Bromobenzene[c]	% A	% Phenylacetylene	% Dimer
0[b]	96	89	tr	9	1
60	94	79	tr	19	2
120	94	79	tr	19	2
180	94	75	tr	22	2
240	93	73	tr	24	2

(a) 0.1 g $Pd(p\text{-}tol_3P)_4$, 10 ml, Et_3N, 0.001 g CuI, 1.57 g bromobenzene, 1.00 g 2-methyl-3-butyn-2-ol.

(b) reaction took 30 minutes to reach 96°.

(c) relative percentage by GC area.

Table 8

Displacement of Bromobenzene Using
$Pd(PPh_3)_4$ as Catalyst Without CuI as Cocatalyst

Time	Temperature	% Bromobenzene[c]	% A	% Phenylacetylene	Other[d]
0[b]	94	96	-	1	3
60	94	79	-	7	13
180	94	65	-	13	22

(a) 0.1 g $Pd(PPh_3)_4$, 10 ml, Et_3N, 0.001 g CuI, 1.57 g bromobenzene, 1.00 g 2-methyl-3-butyn-2-ol.

(b) reaction took 30 minutes to reach 94°.

(c) relative percentage by GC area.

(d) peak unknown GC retention time 18.00 minutes.

Table 9

Chemical Shift[a] of SDP Plus KOH in DMSO - d_6

Sample	Amt KOH	νH_B	νH_A
563-38-1	0 ml	314	266
563-38-2	0.125 ml	303	254
563-38-3	0.125 ml	300	249
563-38-4	0.125 ml	299	243
563-38-5	0.125 ml	298	243
563-38-6	heated	289	233
$\Delta \nu$		25	33
505-98-C	potassium t-butoxide	272	288
$\Delta \nu$		42	54

[a] Shift in cps downfield from DMSO-d_6 signal.

Table 10

Chemical Shift[a] of Half Product Plus KOH in DMSO

Sample	Amt KOH	νH_A	νH_B	νH_C	νH_D
563-39-1	0 ml	328	319	280	269
563-39-2	0.125 ml	316	306	266	255
563-39-3	0.125 ml	307	296	254	242
563-39-4	0.125 ml	307	296	256	237
563-39-5	0.125 ml	309	296	257	237
$\Delta \nu$		19	23	23	32

[a] Shift in cps downfield from DMSO-d_6 signal.

Table 11

Reacting 0.01 mol SDP, 0.02 mol Base, 0.04 mol DBB, 0.1 g Copper Catalyst

Run No.	Base	Solvent	Catalyst	Time, hr	Temp, °C	Wt, BPDS[c]
536-108	NaOMe	pyridine	$Cu(OAc)_2$[b]	16	115°	0
536-111	NaOMe	pyridine	CuCl[b]	72	115°	0
536-114	NaOMe	DMSO pyridine	CuCl[b]	5	150°	0[a]
536-116	NaOMe	DMSO pyridine	CuCl[b]	16	178°	0[a]
563-8	NaOMe	DMF pyridine	CuCl	16	140°	0
563-10	NaOMe	NMP pyridine	CuCl	48	198°	0[a]
563-12	KOMe	DMSO pyridine	CuCl	18	110-140°	0.5
563-14	NaOMe	DMSO pyridine	CuCl	16	140°	0[a]
563-18	KOH	DBB pyridine	CuCl	24	150°	0

[a] half product produced.

[b] 0.01 g catalyst added.

[c] mixture of BPDS, 28, and 29

Table 11 (Cont'd)

Run No.	Base	Solvent	Catalyst	Time, hr	Temp, °C	Wt, BPDS[c]
563-24	KOH[a]	DMSO pyridine	CuCl	96	130°	0.4
563-27	KOMe	DBB pyridine	CuCl	96	140°	0
563-25	KOH	NMP pyridine	CuCl	72	150°	0.6
563-32	KOH	NMP pyridine	CuCl	72	195°	2.3
563-36	KOH	BMEDE	CuCl	72	200°	1.8
563-42	KOH	quinoline	CuCl	72	165°	0
563-47	KOMe	NMP	CuCl	48	130-140°	1.5
563-50	benzyl trimethyl ammonium hydroxide (BTMAH)	pyridine	CuCl	72	125°	0[b]
563-54	KOMe	tributylamine	CuCl	16	197°	0
563-56	BTMAH	BMEDE	CuCl	16	190°	0[b]
563-58	BTMAH	NMP	CuCl	16	190°	0[b]
563-78	$(CH_3)_3COK$	sulfolone pyridine	CuCl	17	200°	3.2

[a] H_2O removed by toluene azeotrope

[b] New product 31 formed.

[c] mixture of BPDS, 28, and 29.

Table 12

Meta/Para Ratio of Recovered DBB

Meta/Para Charge[a]	Meta/Para Recovered Material[a]	Run
94.2 / 5.0	93.4 / 4.9	25 g
94.2 / 5.0	92.7 / 5.7	50 g
94.2 / 5.0	92.5 / 6.0	100 g

[a] Monobromobenzene also present in small amounts.

Table 13

Water produced in RXN of SDP with KOH

Run No.	Moles SDP	External ml H_2O Added[a]	Predicted[b] ml H_2O	Actual
596-6	0.2	16.7	23.9	24
596-3	0.4	31.3	45.7	45
596-8	0.2	16.7	23.9	24

[a] amount of water used to dissolve KOH.

[b] assuming sulfolane is water free (sulfolane purity mp. 21-24°C)

Table 14

Reactions in Sulfolane

Run	Sulfolane, ml	SDP, g	KOH, g	Pyridine, ml	DBB, g	CuCl, g	Temp, °C	Time, h	BPDS, g[d]
563-84	200	25	22.4[a]	10	94	1	190-210	60	0[b]
563-88	200	25	11.0	10	94	1	171-178	16	16.7
565-38	40	2.5	1.3	-	9.4	0.05	169-175	16	3.3
565-40	40	2.5	1.3	-	9.4	-	174-180	16	tr
565-88	100	5.0	2.6	-	18.8	0.05[c]	185-202	16	2.0
565-84	100	5.0	2.6	-	18.8	1.0	155°	16	0
565-30	20	2.5	1.3	-	9.4	0.05	175°	16	2.1[e]

[a] $(CH_3)_3$ COK used instead of KOH.

[b] base was destroyed in reaction with sulfolane.

[c] cupric acetate was used instead of CuCl.

[d] obtained as a mixture of BPDS plus 28 and 29.

[e] obtained pure.

Table 15

NMR Integration of Products

Name	n		H_B	$H_A + H_C$
BPDS	1	theory	4	12
		actual	4	13
Oligomer 28	2	theory	8	20
		actual	8	21
Higher Oligomers 29	3	theory	12	28
		actual	12	27

Table 16

Analysis of Products

Name		% C	% H	% Br	MW
BPDS	Calc.	51.45	2.88	28.53	560
$C_{24}H_{16}Br_2O_4S$					
n = 1	Found	52.34	3.18	29.68	600
Oligomer 28	Calc.	57.03	3.19	18.07	885
$C_{42}H_{28}Br_2O_8S_2$					
n = 2	Found	56.73	3.59	17.74	835
Higher Oligomer 29	Calc.	59.61	3.34	13.22	1209
$C_{60}H_{40}Br_2O_{12}S_3$					
n = 3	Found	59.37	4.07	13.5	1350

Table 17

Reaction of Half Product (27) with BPDS

Run No.	BPDS/Half Product[d]	% Yield[e] Half Product 27	Oligomer 28	Higher[b,c] Oligomer 29	Material Balance
565-71	1/1	43	20	21	84%

a yield determined as $\frac{\text{g product} \div 885}{0.020} = \%$ yield

b yield determined as $\frac{\text{g product} \div 1209 \times 2}{0.020} = \%$ yield

c other oligomers also present (n > 3).

d 20 mmoles half product used.

e 8.0 g BPDS unreacted was recovered.

Table 18

Reaction of Half Product (27) with DBB

Run No.	DDB/Half Product[c]	% Yield[d] Half Product 27	BPDS	[a,b] Oligomer 28 and 29	Material Balance
565-66	1.5 / 1	42	10	23	75%
565-61	3 / 1	34	30	20	84%
565-64	4.8 / 1	40	35	20	95%

a yield calculated as $\frac{\text{g product} \div 885 \times 2}{0.020} = \%$ yield

b higher oligomers were also observed which were not separated.

c 20 mmoles half-product used.

d excess DBB recovered in all cases.

Table 19

Relative Percentage of DPDS and Oligomers as a Function of DBB

Run No.	DBB/half product	% BPDS[c]	% Oligomers[b,c]
565-66	1.5 / 1	35	65
565-61	3.1 / 1	65	35
565-64	4.8 / 1	68	32
505-106	4 / 1[a]	64	36
565-52B2	6 / 1[a]	70	30

[a] DBB / SDP ratio.

[b] mixture of 28 and 29.

[c] calculated as weight percent.

Table 20

Runs in Sulfolane

Run No.	SDP mole	DBB mole	CuCl mole	Sulfolane ml	Time hr	Temp. °C	CCl_4 Extract g	BPDS/BPDS+ Oligomer[d]
596-16	0.2	0.6	0.01	400	16	160[a]	54.3	72.5
596-14	0.2	1.2	0.04	400	16	160[a]	75.3	80.8
596-12	0.2	1.21	0.01	400	16	141[a]	69.5	82.5
596-8	0.2	1.2	0.01	400	16	160[a]	53.9	86.3
596-6	0.2	1.2	0.01	400	16	180[a]	52.6	83.4
596-3	0.4	2.4	0.02	800	16	160[a]	106.5	82.8
565-97	0.4	2.4	0.02	800	16	120-161	93.4	93.1
565-90	0.4	2.4	0.02	800	5	150-156	50.7	92.9
565-52	0.4	2.4	0.02	800	16	160-166	89.6[f]	70[e]
565-18	0.4	2.4	0.01	800[b]	16	170-187	99.2	77[e]
563-92	0.2	0.8	0.01	400[c]	16	178-184	50.6	66[e]
565-47	0.4	4.0	0.02	600	16	133-152	0[g]	-

a Temp. $\pm$ 1°

b Contained 40 ml pyridine

c Contained 20 ml pyridine

d Determined by GPC

e Determined by prep. column chromatography

f Portion of material lost due to spillage

g SDP salt crystallized out

Table 21

Yield of Reaction SDP Plus DBB

Run No.	Yield, BPDS[b]	Yield Oligomers[a]
596-16	32	15
596-14	52	16
596-12	51	13
596-8	37	7
596-6	37	10
596-3	37	10
565-3	37	10
565-97	36	3
565-90	19	2
565-52	28	15
565-18	34	13
563-92	30	19

[a] $\frac{\%\ \text{oligomers} \times \text{weight} \times 2 \div 885}{\text{mole SDP}}$ = yield oligomers

[b] $\frac{\%\ \text{BPDS} \times \text{weight} \div 560}{\text{mole SDP}}$ = yield BPDS

Table 22

Comparison of Analytical Techniques on 585-P12

Technique	% BPPS	% Oligomer	% Higher
GPC	70	24	6
Prep. Column Chromatography	66	25	9

Table 23

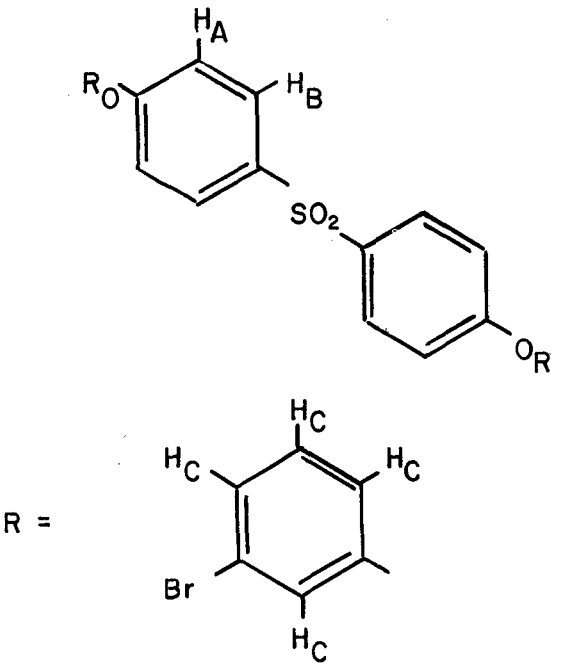
NMR Spectra of ATS Intermediates[a]

Compound	Chemical Shift (δ)	Multiplicity	Assignment[c]
SDP[b]	7.80	4H, d ($J=8H_z$)	H_B
	7.00	4H, d ($J=8H_z$)	H_A
27	7.77	2H, d ($J=8H_z$)	H_B
	7.83	2H, d ($J=8H_z$)	H_B'
	7.00	2H, d ($J=8H_z$)	H_A
	6.90	2H, d ($J=8H_z$)	H_A'
	7.7 - 6.9	4H, m	H_C
BPDS	7.90	4H, d ($J=8H_z$)	H_B
	7.05	4H, d ($J=8H_z$)	H_A
	7.4 - 6.8	8H, m	H_C
28	7.90	8H, d ($J=8H_z$)	H_B
	7.5 - 6.7	20H, m	$H_A + H_C$
29	7.90	12H, d ($J=8H_z$)	H_B
	7.5 - 6.7	32H, m	$H_A + H_C$

[a] samples in $CDCl_3$ in δ downfield from TMS.

[b] in acetone-d_6

[c] see Figure 1 for assignments



R = H

Figure 1. Structure Assignment of NMR Spectrum

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