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THE SYNTHESIS OF POLYMER PRECURSORS AND EXPLORATORY
RESEARCH BASED ON ACETYLENE DISPLACEMENT REACTION

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Final Report   for Period 1 June 1979 – 30 May 1980.

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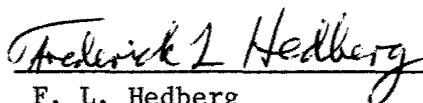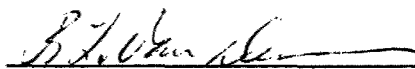
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20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*
This report summarizes the work involved in the development of synthetic procedures suitable for scale-up of acetylene terminated sulfone resins. Several acetylene terminated resins were delivered in one-pound quantities periodically throughout the contract.

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I. INTRODUCTION

This report summarizes our work conducted from June 1, 1979, to May 30, 1980, on USAF Contract No. F33615-79-C-5059. The work involved optimization of synthetic procedures amenable to scale-up and the preparation of several pound quantities of various acetylene terminated sulfone resin compositions. Several pounds of a benzil end-capped acetylene terminated phenylquinoxaline resin were also prepared and the synthetic sequence evaluated.

II. ACETYLENE TERMINATED SULFONES

A. Background

The compound 3,3'-diethynyldiphenyl sulfone (ATS) developed at Wright-Patterson Air Force Base has shown considerable promise as a composite matrix. The original synthesis involved the reaction of m-ethynylphenol with dichlorodiphenyl sulfone in an Ullmann ether synthesis.[1] The disadvantage of this synthesis is the high cost and lack of availability of the m-ethynylphenol which is made by an arduous, multistep sequence.[2]
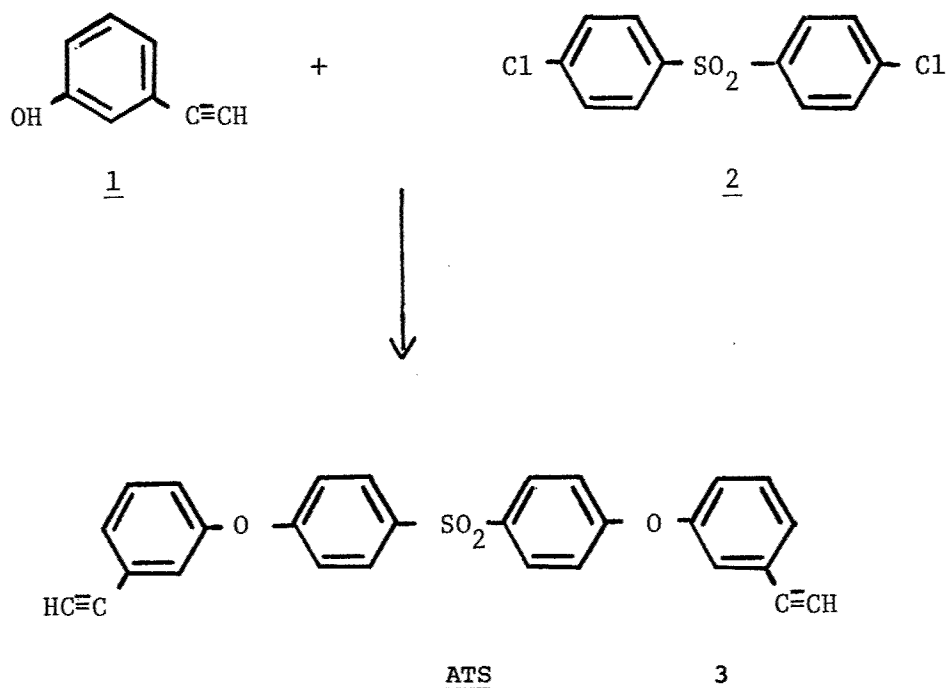
In an earlier contract to this laboratory (F33615-78-C-5141), a new synthetic sequence to ATS was discovered which employed readily available starting materials. This three-step sequence, depicted below, consists of an initial Ullmann ether synthesis with sulfonyldiphenol (SDP) and two moles of dibromobenzene followed by displacement of the remaining bromines by 2-methyl-3-butyn-2-ol and a final cleavage of acetone to give the free ATS.[3]
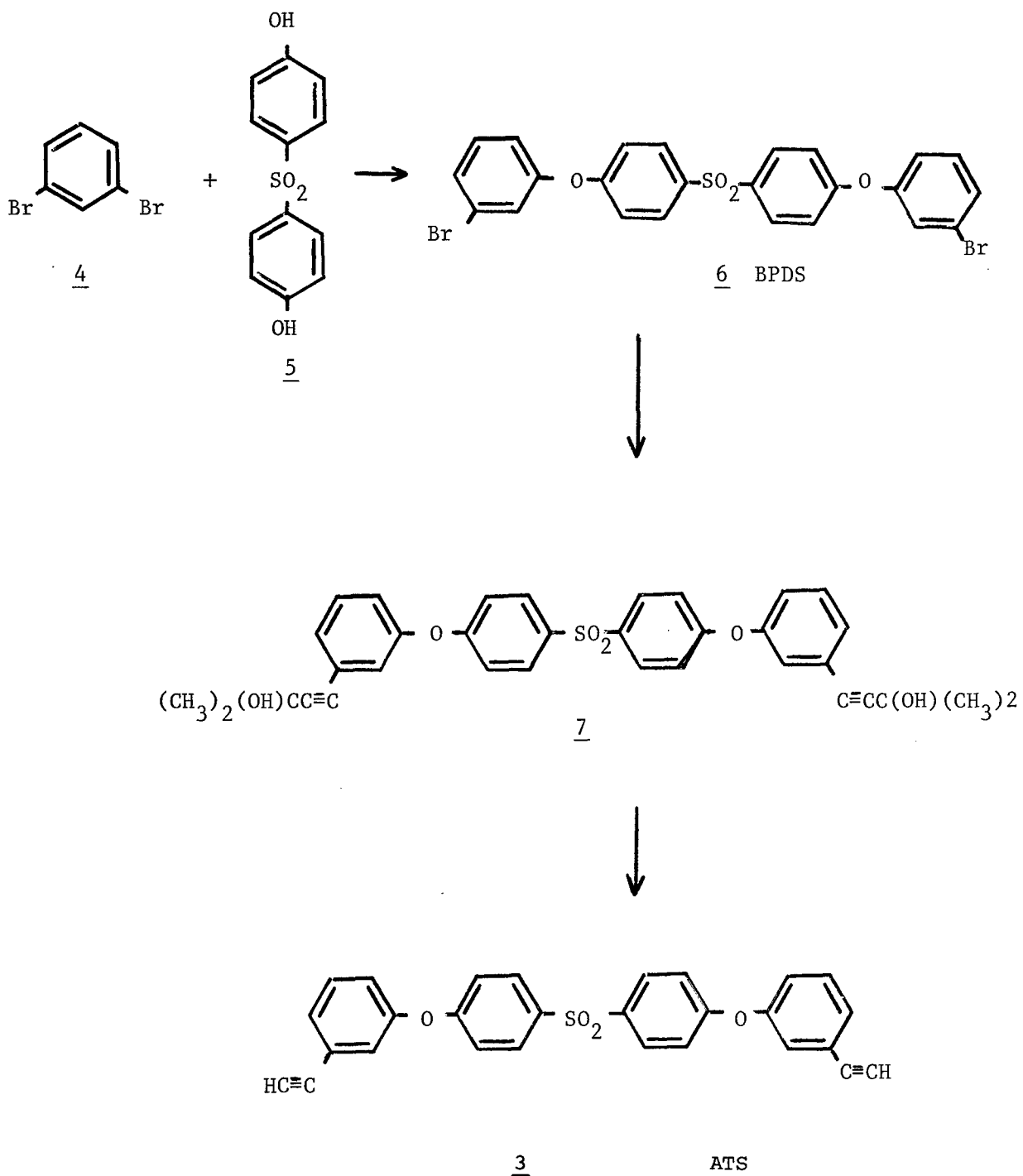
This route presented such promise that the present contract was started immediately to provide several pounds of material for evaluation. During the overlap period of this contract and the previous contract, two

factors arose which complicated the project. The first was mainly an economic consideration. While pure m-dibromobenzene is available, its cost is disproportionately high compared to material containing moderate amounts (~5%) of the para isomer. Use of an isomer mixture leads to a mixture of three products. Since the isomers are of almost equal reactivity, the composition of the BPDS isomers is readily calculated.

90.3% m,m-BPDS   6

SDP

+

95/5 m/p DBB   ⟶

9.5% m,p-BPDS   8

0.2% p,p-BPDS   9
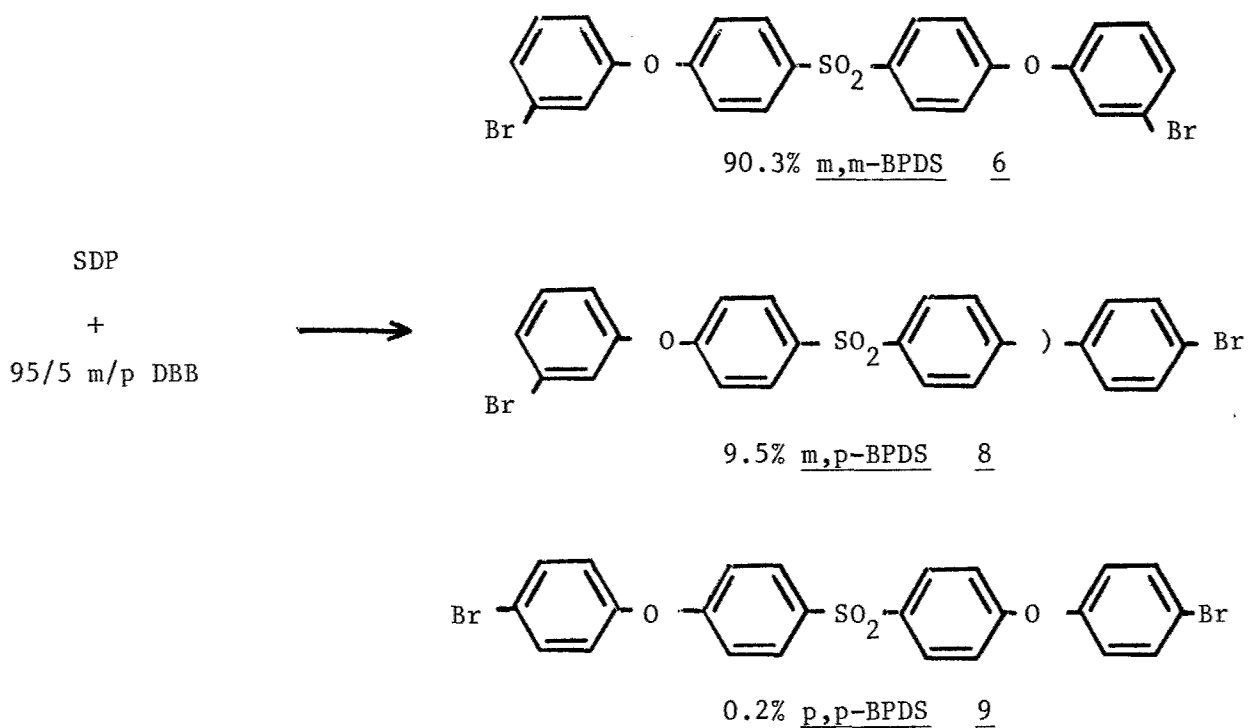
The second factor was strictly a chemical problem. It was discovered that, in spite of using a large excess of dibromobenzene, a significant amount of oligomeric material formed. Some possible reaction sequences are shown in Scheme 1. This meant that we would have to learn to separate BPDS from the oligomers and learn how to control the amount of oligomer formed.

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SDP + DBB

Br—⦿—O—⦿—SO₂—⦿—O⁻ ... (structure **10**)

$\underline{10}$

DBB

BPDS

SDP

BPDS

$\underline{11}$

DBB

$\underline{9}$

BPDS ⟶ Next higher oligomer

$\underline{12}$
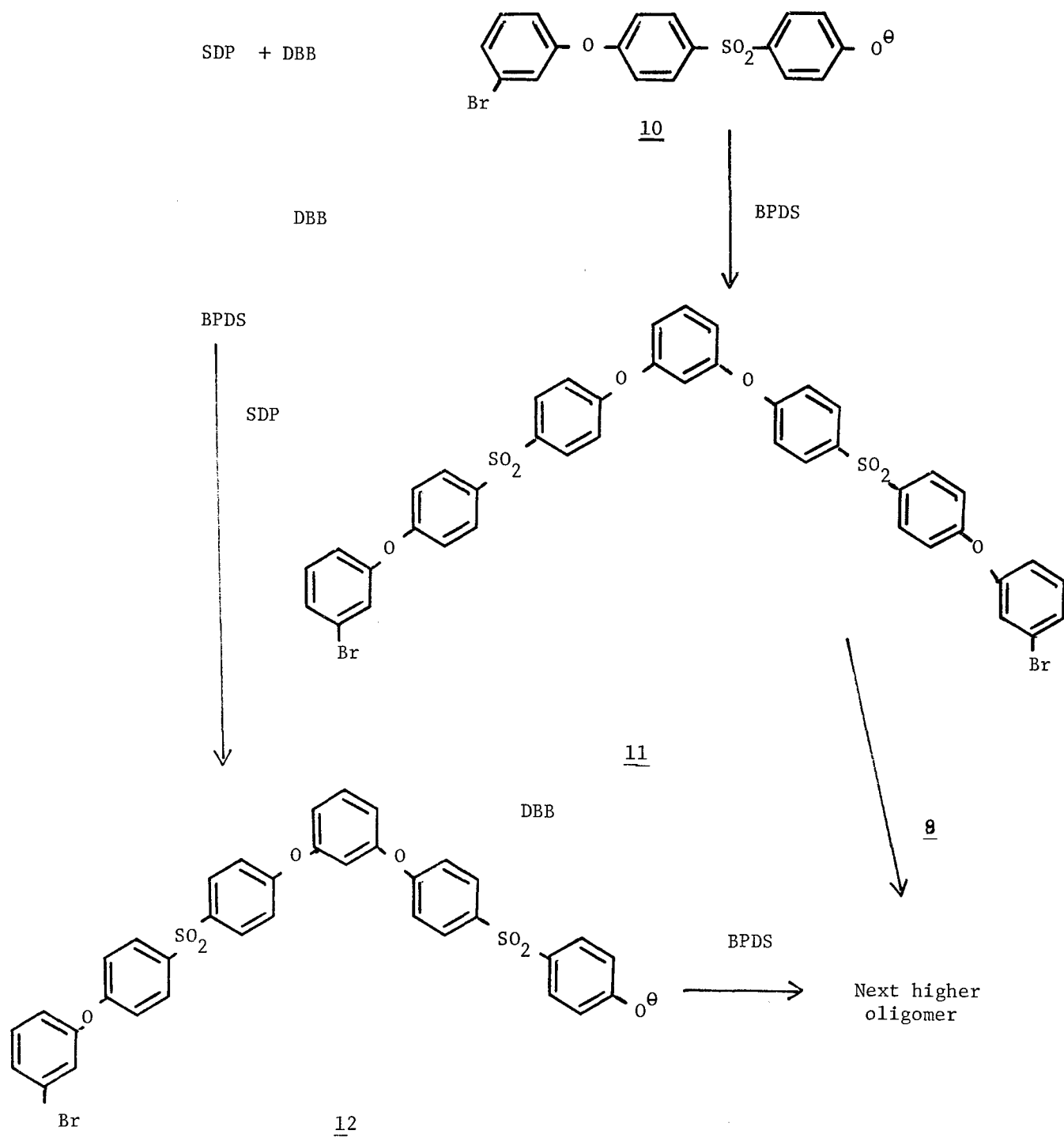
Scheme 1. Possible Route to Oligomers

5

Serendipitously, it was found that neither the presence of isomers nor oligomers had any deleterious effects. In fact, their presence appeared to be beneficial.[1] Therefore, it was decided that the program would include preparation of the main constituents in pure form so that evaluation of blends could determine the optimum content of each.

B. Preparation of Blending Stocks

The preparation of the isomeric blending stocks was the first task undertaken. Because separation of BPDS from the oligomers would be necessary, no optimization to control oligomer content was undertaken at this time. This resulted in rather high oligomer content and considerable delay in purifying materials. After several small-scale runs made to determine that formation of the dianion from potassium hydroxide or potassium methoxide made no difference in the course of the reaction, three runs employing 1 kg of SDP each and pure m-DBB were made. No quantitative data were obtained from the first run, as a variety of separation techniques was explored. Several types of continuous extraction apparatus were tried as well as a number of solvents (heptane, cyclohexane, isopropanol, methanol, toluene and heptane-DBB mixtures) without success. Recrystallization efforts with toluene, halomethanes, dichlorobenzene and their mixtures with hexane, dioxane, tetrahydrofuran, acetone, acetic acid and their mixtures with water all failed. The only significant improvement was attained by boiling with isopropanol, decanting and allowing an oily mixture of ca. 1:1 BPDS:oligomers to settle out, then decanting again and waiting for slow crystallization of BPDS containing only a faint trace of oligomer by thin layer chromatography (TLC). Finally, it was decided to isolate the materials by column chromatography. On small runs, clean separations of BPDS and the first oligomer could be attained, and this was the basis for analysis. On the larger scale, column chromatography is quite impractical as it requires a minimum of 4-5 kilograms of alumina per kilogram of pure BPDS isolated. Even then a considerable portion of BPDS had to be left in the oligomer fraction to obtain reasonably pure material. In order that proper blending could be accomplished, it was necessary to develop a rapid and accurate analysis of the product mixture. It was found that gel permeation chromatography (GPC) gave results comparable to those obtained by column chromatography. Table 1[*] shows some typical analyses of the early runs.

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[*] Figures and tables are located at end of report.

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In the preparation of m,m-ATS, the methylbutynylation of over-kilogram quantities went smoothly in about 2 to 3 hours even though the BPDS is only partially soluble in the triethylamine solvent. The intermediate product was not isolated. Cleavage was accomplished in 6 hours in refluxing toluene with a catalytic amount of sodium hydroxide. The solution produced had a very dark red color which was removed by passage through fuller's earth. The crude product also contained a small amount of oligomeric acetylene terminated sulfones (OATS) which had to be removed by column chromatography on silica gel. The use of large quantities of adsorbents led to large losses. The overall yield of OATS-free ATS was only 46%. An additional 10% yield of material contaminated with 8% OATS was also obtained. In addition to material lost by adsorption, some material appeared to react on the columns. Small-scale reactions had shown that passage of ATS over silica gel produced small amounts of material not shown to be present by TLC in the original product. The ratio of acetylene to aromatic protons by NMR for this material indicated reaction through the acetylene groups.

Preparation of the OATS with completely-meta orientation was carried out with a mixture containing 17% BPDS and 83% of the analogous oligomers. The use of N-methyl-pyrrolidinone as a cosolvent was employed. The intermediate, 13, was not isolated. The crude OATS mixture was passed through fuller's earth to remove color. The resulting product, 14, was shown by GPC to contain 24% ATS and 76% OATS. This probably indicates that some of the OATS was held up on the adsorbent, but it could also mean a preferential reaction of the OATS on the adsorbent.

The preparation of m,p-BPDS was accomplished by the two-step sequence, shown below, in which SDP is reacted with m-DBB in dimethylsulfoxide to give selectively 4-hydroxy-4-(3-bromophenoxy)diphenyl sulfone (HBPDS) in 78% yield. The HBPDS is then reacted with p-DBB in sulfolane to produce m,p-BPDS and the analogous oligomers. Analysis by GPC indicated the crude product contained 62% m,p-BPDS. A pure material was isolated by elution from alumina.

HO —⟨benzene⟩— SO$_2$ —⟨benzene⟩— OH

NaOCH$_3$/DMSO
m DBB

↓

Br—⟨benzene⟩— O —⟨benzene⟩— SO$_2$ —⟨benzene⟩— OH

HBPDS   15

KOH/sulfolane
p DBB, 160°C

↓

Br—⟨benzene⟩— O —⟨benzene⟩— SO$_2$ —⟨benzene⟩— O —⟨benzene⟩— Br

m,p-BPDS   8

+

oligomers
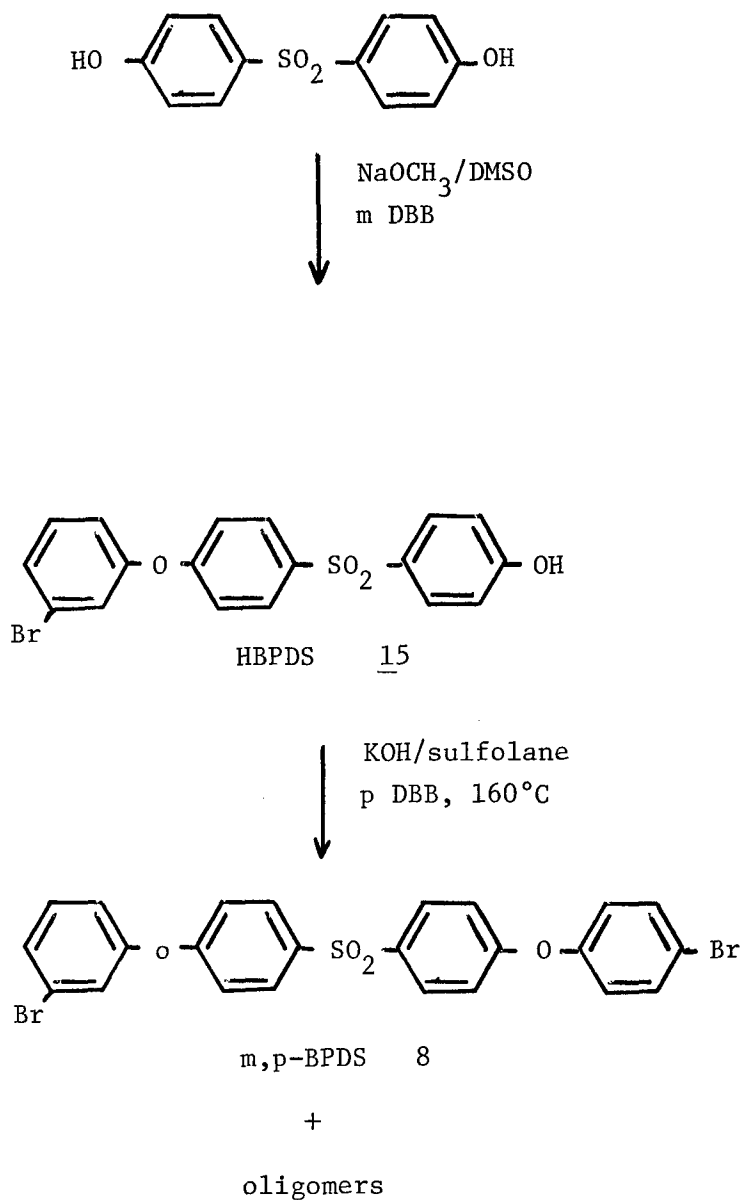
Conversion to the corresponding methylbutynol derivative, 14, and subsequently to m,p-ATS, 15, occurred without incident in 74% yield. The NMR spectral data for the bromo intermediates, the methylbutynol intermediates and and the acetylene terminated products are given in Tables 2, 3, and 4 respectively. Physical data and analyses are listed in Table 5.

$(CH_3)_2C(OH)C\equiv C$ —[structure]— SO_2 —[structure]— O —[structure]— $C\equiv CC(OH)(CH_3)_2$

<u>16</u>

$HC\equiv C$ —[structure]— O —[structure]— SO_2 —[structure]— O —[structure]— $C\equiv CH$

<u>17</u>

m,p-ATS
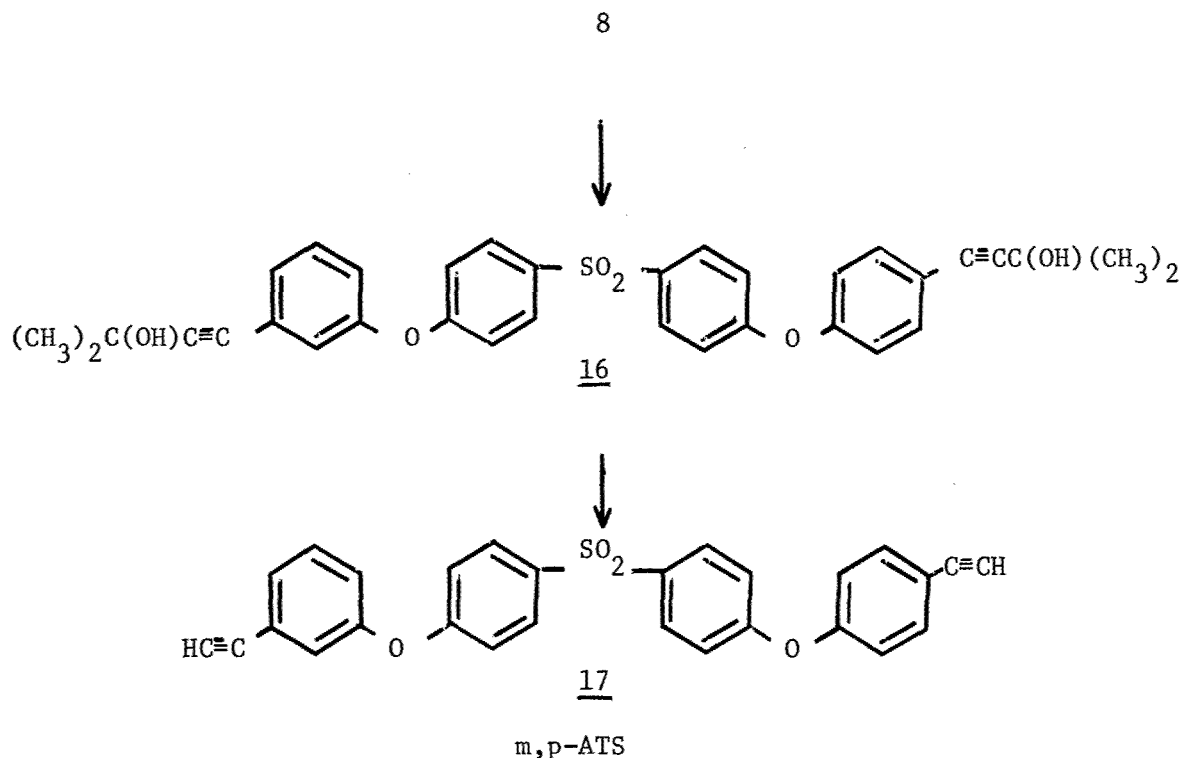
C.   BPDS Preparation - General Considerations

Based on evaluation of early materials, it was decided to prepare a pound sample of BPDS containing 20% oligomers and having 95-5 meta-para orientation.[1]   During the preparation of this material, sufficient problems arose to indicate that many subtle variables can influence the course of the reaction.   A number of small-scale runs were also made to try to elucidate some of the trouble spots.   The following discussion gives our current thoughts on various aspects of the synthesis.

During scale-up runs, we attempted to use the highest concentrations possible to boost volume productivity.   This led to the usual problems of difficult stirring and formation of hard nodules which fail to react.   More importantly, it also seems to have led to higher ratios of oligomers (see Figure 1).   The dipotassium salt of SDP is only slightly soluble in sulfolane, even at reaction temperature.   Once the potassium salt of the half-product, 4-hydroxy-4(3-bromo-phenoxy)diphenyl sulfone, <u>10,</u> has been formed, it is totally soluble in the concentration range of interest.   Likewise, BPDS and

DBB are soluble. Therefore, if the ratio of BPDS to oligomers was only dependent upon the competitive reaction of 10 with either BPDS or DBB, changing the total concentration in the solvent while maintaining a constant ratio of DBB to SDP should have no effect on the product ratio. On the other hand, the presence of large amounts of the dipotassium salt of SDP represents a surface on which adsorption-desorption equilibria probably occur. A preferential adsorption of BPDS relative to DBB would lead to a localized increase in concentration of BPDS at the surface. This would lead to significant quantities of intermediate 12 (Scheme 1) which is subsequently converted to oligomers. This assumes that reaction can take place either in the solid phase or shortly after dissolution while BPDS is still in the solvent shell. If true, anything leading to lower solubility of the dipotassium salt would cause an increase in oligomer. Thus, residual toluene not removed after the azeotroping step could lead to small differences. This could also explain the relatively small effect on the oligomer ratio when the SDP/DBB ratio is changed. The extra DBB forces more salt out of solution. When reacting soluble 10 with DBB, much larger shifts were noted.[3] In Figure 1, the points with the cross indicate runs made on the 500-1000 g of SDP scale. The other points are all 10 g runs. The small scale, unfortunately, does not cover a wide enough range to confirm the trend shown on the larger scale. Furthermore, they show a significant degree of scatter. Better, and variable, stirring rates in the small scale runs leading to more rapid dispersion of localized concentrations could wipe out the effect. It is realized that the paucity of data makes the entire argument quite speculative.

A number of small-scale runs were made to test some of the reaction variables. In the case of temperature (Table 6) two different temperatures were checked. The first, defined as stripping temperature, is the temperature to which the mixture is taken to remove water produced in the formation of the dipotassium salt of SDP. The second is the actual reaction temperature. To attain maximum activity, the stripping temperature needs to be at least 160°C, and preferably 170°C. Higher temperatures do not appear to offer any advantage. Run temperatures of 140°C appear to be the minimum. Again, 170°C seems to be optimum, but repeat runs still show enough scatter to prevent choice of an absolute optimum.

Several runs were made to check the effect of different potassium bases and the mode of addition. These runs are shown in Table 7. While potassium carbonate has found some success in this reaction at WPAFB[1], its use alone in Run 34 produced no reaction in sulfolane. Preforming the dipotassium-SDP, and adding the powder, showed no effect on the ratio of BPDS to oligomer. Because unreacted SDP and half-product have been found as the free rather than the salt form at times,[3] it was attempted to add additional base after several hours of reaction hopefully to attain overall higher yields of product. When anhydrous potassium carbonate was used, the yield did jump significantly. However, the amount of oligomers also increased dramatically. The insoluble carbonate may provide another site for surface adsorption. Additional potassium hydroxide also caused a shift in the product ratio but without a significant yield increase. To circumvent the addition of solids, a soluble base, potassium 2,6-dimethylphenoxide was tried. It was felt that the two ortho-methyl groups would sterically hinder the reaction of this species in the Ullmann reaction; but it should be capable of transferring the potassium to SDP. The NMR of the product shows no methyl groups substantiating the first assumption. Failure to obtain increased yields, however, suggests that the latter assumption was not correct. Furthermore, a distinct orange coloration was imparted to the product indicating the introduction of impurities.

Several runs were made incorporating small amounts of other solvents. Several runs were made with pyridine which is known to be an excellent solvent in many Ullmann reactions.[4] It showed no effect on the product ratio. Runs 32 and 33, which were identical except for pyridine, may indicate that pyridine can help mask small amounts of water which might remain when the stripping temperature is too low. The other additive checked was polyethylene glycol, which WPAFB indicated was effective in some systems.[1] In the sulfolane system, it reduced reactivity so that only traces of BPDS were detected.

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While cuprous chloride is the standard catalyst for this reaction, we did try several others including copper stearate, cupric ethylacetoacetate and cuprous bromide. In the latter case, a trace of copper powder was added to minimize disproportionation of the cuprous ion. Cuprous chloride appeared to be the most effective catalyst.

D.   Acetylene Displacement and Cleavage Reactions

Because of our experience in displacing bromine with 2-methyl-3-butyn-2-ol in a wide variety of aromatic systems and then cleaving off acetone to give the free acetylene,[5,6] we anticipated very little difficulty with the ATS system. For the most part this proved to be correct. Only three difficulties were encountered, two of which were very minor.

The limited solubility of BPDS, and especially the oligomers in triethylamine, was a cause for some concern. This was circumvented initially by the use of a cosolvent, N-methyl pyrrolidinone. While this improved the reaction rate, it proved difficult to remove all traces of it from the product. It was decided to use only triethylamine and accept the slower rate and the presence of solids which slowly dissolved, reacted and then usually stayed in solution as the derivative.

A second minor problem was the problem of determining when complete reaction occurred during the cleavage step. While TLC can readily show the disappearance of the bis-butynol adduct, the monobutynol adduct is difficult to distinguish from higher oligomers. The use of HPLC with a reverse phase column allowed easy monitoring because the order of elution is reversed; i.e., bis-butynol, mono-butynol-BPDS, bis-, mono-oligomer is the sequence.

The only other problem turned out to be very troublesome. ATS is meant to be used as a thermally-cured material curing at temperatures well above 100°C. If all the palladium and copper used as catalysts in the butynylation reaction are not removed, catalytic curing can occur at lower temperature making the resin unprocessable. In the preparation of low molecular weight acetylenes by this route, no problems occur because the

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acetylene can be distilled or crystallized away from the trace metals at low temperatures where curing is negligible. Even ATS itself can be cleaved by this method and freed from the metals effectively by chromatography. However, when a mixture of ATS and OATS is desired, premature curing is the rule. Sometimes it even takes place during the cleavage step (refluxing toluene) if a large volume of solvent is not used and care taken to avoid hot-spots on the heating surface. Because of this last possibility, we looked for metal removal methods which were applicable at the bis-methylbutynol stage. The approach used was to make a standard displacement run which would contain a total of 1200 ppm copper and 500 ppm palladium if it all remained in the product. Aliquots of this were then subjected to various treatments. The bis-methylbutynol adduct was isolated and analyzed by atomic adsorption analysis for metals content. It was somewhat surprising to note that little, if any, of either metal was removed by acid washing. Neither silica gel nor alumina treatment were effective. This is probably due to the polar butynol groups deactivating the adsorption sites. Sparging with air, either directly after reaction in triethylamine solution or in the neutral toluene solution, failed to render the metals insoluble and removable by filtration. Washing with the tetrasodium salt of ethylenediamine tetra-acetic acid, pH 11, or the disodium salt, pH 4, proved ineffective for palladium removal, but the tetrasodium salt did remove copper. Dilute caustic or ammonia (10%) give excellent removal of copper and partial removal of palladium. Concentrated ammonia may be slightly more effective than dilute ammonia, but does not effect complete removal of palladium. A hydrochloric acid wash prior to the ammonia treatment appears more effective than sulfuric acid. This may indicate that chloride ion has access to the palladium complex while sulfate does not. Several hydrochloric acid washes are not more effective than one. Unfortunately, repeated ammonia washes do not further reduce the palladium content unless the temperature is elevated. While somewhat more effective at 60°C, foaming due to ammonia evolution makes it troublesome. Addition of a chelating diamine such as ethylenediamine to a toluene solution and stirring 15 min at room temperature before washing with water reduces the palladium to 30 ppm. If the temperature is raised to 60°C, the value is lowered to

14

18 ppm. Without a prior hydrochloric acid wash, this treatment is also ineffective. Figures 2 and 3 summarize the actual results of the various metal removal schemes attempted.

An alternate approach to removal of Pd from the product after reaction would be to fix the metal on a support to prevent it from getting into solution in the first place. To test the efficacy of this approach, we prepared a catalyst from polystyrene-supported triphenylphosphine (see Experimental). Several initial runs were made with 4-bromonitrobenzene to ascertain the relative reactivity of the supported catalyst versus the homogeneous catalyst. The supported catalyst was less active by a factor of about 130. Among other factors, this might be attributable to the fact that the polymer-supported catalyst is not strictly analogous. The active homogeneous catalyst has been proposed to be the bis-triphenyl-phosphine species, A. The supported catalyst, however, most likely has only one

$$\left[(C_6H_5)_3P \right]_2 \quad Pd$$
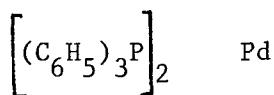
A
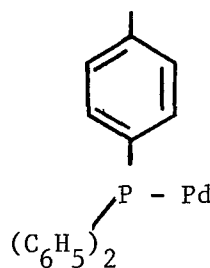
B

phosphine ligand per Pd atom, except in the very fortuitous case where two phosphines are in the precisely correct position in the polymer chain to allow bonding to the same Pd atom. A more appropriate (but still not exact) model would be polymer-bound DIPHOS. Such a material is known, but the preparation is quite laborious.[7]

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To come to a closer model, a run was made in which an equivalent of triphenyl phosphine was added to the reaction mixture, hopefully to provide a catalyst, C. This resulted in a 5-10 fold increase in rate.

$$(C_6H_5)_2P - Pd - P(C_6H_5)_3$$

C
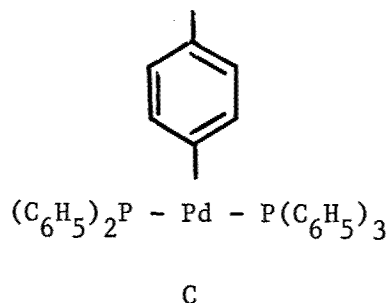
Furthermore, it was demonstrated that the catalyst could be recovered and reused in another batch. However, catalyst C could suffer loss of Pd from the support by dissociation of the polymer phosphorous-palladium bond. To check this, a run was made with BPDS.

It took 138 hours to convert 14 g of BPDS; the last 66 hours were needed to convert the last traces of monobutynylated material. The product was isolated with no effort to extract any solubilized palladium. Analysis showed 24 ppm. This indicates that some of the palladium is going into solution when free triphenylphosphine is present.

E.   Conclusions and Recommendations

The intermediate scale-up of this novel three-step route to ATS using readily available, moderately priced starting materials has confirmed the earlier findings. While all aspects of the mechanism of the first step are not yet clear, reproducible BPDS/oligomer ratios can be attained. By observing temperature minimums in both the dehydration of the dipotassium salt of SDP and the reaction itself, combined yields of BPDS + oligomer of 60-70% can be routinely obtained. Recycling of unreacted or partially reacted SDP would raise the yield to over 90%. The use of dibromobenzene as the extraction solvent for isolation of the BPDS was demonstrated. This is recommended for any larger scale operation, as it will simplify recycle operation.

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The combined second and third steps have been shown to give a yield of 93%. Problems of premature curing of the product leading to discoloration and increased viscosity have been circumvented by use of an ethylenediamine extraction of residual metals in the workup procedure of step two. This has been shown to reduce the level of copper to less than 5 ppm and palladium to less than 20 ppm.

While the overall procedure contains many unit operations, such as extractions and washes, it appears that the process can be reasonably scaled to larger quantities.

III. BENZIL END-CAPPED ACETYLENE TERMINATED PHENYLQUINOXALINES (BATQ's)

A. Introduction

A number of BATQ resins of the general structure shown below have shown promise as moisture-insensitive adhesive and matrix materials.[8]
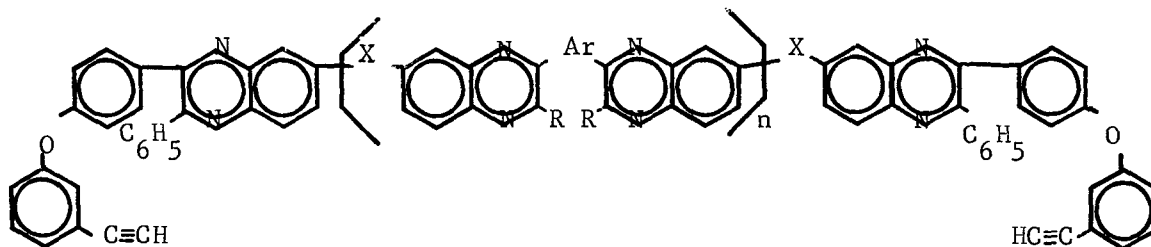
BATQ

x = 0 or single bond

Ar = variety of aromatic moieties

n = integer from 0 to about 4

The purpose of this portion of the contract was to produce several pounds of BATQ-H, x = single bond, Ar = bis-1,4(4-phenoxybenzene), and evaluate the synthetic sequence.

Preparation of BATQ-H requires three components - 3,3'-diaminobenzidine, 4-(3-ethynylphenoxy)benzil, and 1,4-bis-(4-benziloxy) benzene. The reaction sequence is depicted below.

2 18

19

20

2 21

22

BATQ-H
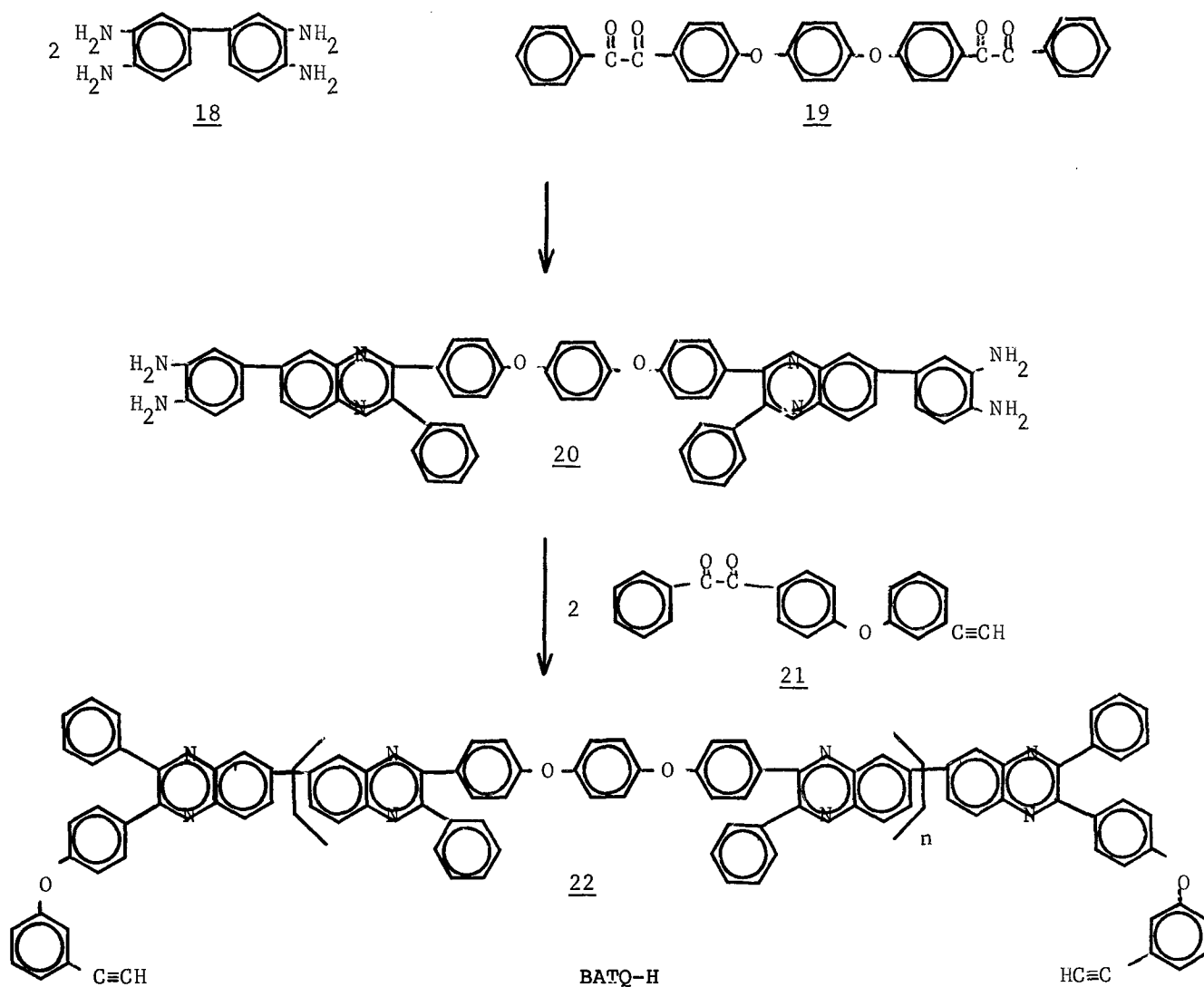
Of these three, only the first can be purchased at any price. The other two each require several steps from the first available starting material. The actual synthetic sequences employed are shown below.

23 → 24

24 → 25

25 + NaO—⟨ ⟩—ONa → 19

26

H₂N—⟨ ⟩—C≡CH → HO—⟨ ⟩—C≡CH

27   28

28 + 25 → 21

20
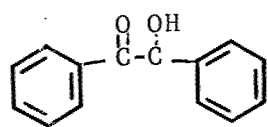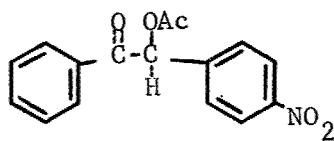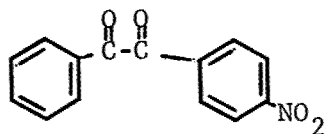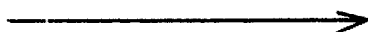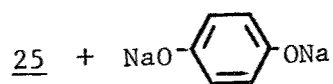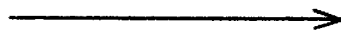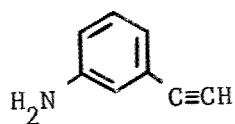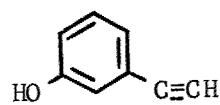
B.   Discussion of Results

1.   4-Nitrobenzoin Acetate, 24

The procedure supplied by WPAFB[1] indicated that nitration of benzoin 90% nitric acid in acetic anhydride gives a quantitative yield of 24. In our hands, a nearly quantitative yield of nitrobenzoin acetate was obtained, but as a mixture of all three nitro-isomers. Moreover, direct crystallization from the nitration media could not be induced even by seeding. The desired isomer was isolated from the gummy crude product in 98%+ purity only after three recrystallizations from methanol. The yield of purified material was a disappointing 31%.

2. 4-Nitrobenzil, 25

The conversion of 24 to 25 by hydrolysis and oxidation with 70% nitric acid proceeds very smoothly. Only one caveat should be made. When working with pure 24, 25 crystallizes from the reaction media as soon as the exotherm stops. The temperature must be monitored very closely so that the hot reaction can be poured over ice when the temperature falls one degree from the maximum. If it is allowed to fall two degrees, the entire reaction mass crystallizes forming a solid mass which must be dug out of the flask. Since the mass still contains large amounts of nitric acid and nitrogen oxides, this is a tedious and dangerous operation. In larger equipment where transfers would be made through valves and other piping restrictions, this propensity to crystallize could be very troublesome. The yield in this step was 87.5%.

3. 1,4-bis(Benziloxy)Benzene, 19

This was essentially a scale-up of the Relles' procedure.[9] It works reasonably well, but hot ethanol wash and three recrystallizations to obtain material of suitable purity to carry on, make it less desirable. The 59% yield might be improved if the recrystallization technique improved sufficiently to reduce the number of recrystallizations.

4. 3-Ethynylphenol, 28

3-Ethynylphenol is a key intermediate in the synthesis of a number of acetylene terminated resins. Small-scale preparations via m-bromophenol were successful, but the scale-up reaction was very sluggish, and the catalyst kept dying. Large amounts of an undetermined by-product were formed. This route was abandoned as needing further development.
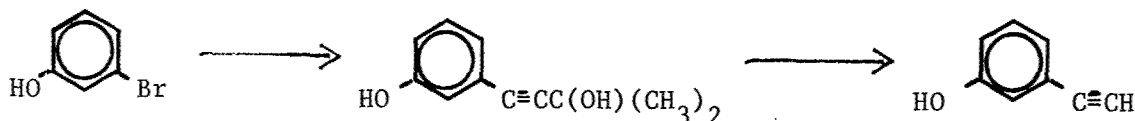
Instead, we chose to prepare the ethynylphenol by diazatization of aminophenylacetylene.[5] This reaction gives a crude product in nearly quantitative yield. The crude product, however, contains considerable amounts of heavy materials not eluting from the gas chromatograph. Internal standards indicate the actual product content of about 52-55%. Vacuum distillation gives pure product in yields of 45-48%.

5. 4-(3-Ethynylphenoxy)Benzil

On the small scale (about 0.2 mole), it was possible to obtain yields of 70%. Upon about 25-fold scale-up, the yield fell to 40%. The principal problem was failure to find a suitable recrystallization technique. Purification had to be accomplished by column chromatography. On a large scale this is economically unfeasible.

6. BATQ-H

This procedure scaled-up very well to give 76% yield of product containing mainly components where n = 1, 2 and 3 in successively decreasing amounts. The need for four precipitations to remove impurities presents the only problem in this step.

C. Conclusions

The excessive number of steps, the difficulty of purifying intermediates, and the relatively low yields suggest that commercial development of this material is very unlikely.

IV. EXPERIMENTAL

Small-Scale Preparation of m,m-BPDS (Run 585-6, Table I)

Potassium metal (3.12 g, 0.04 mole) was dissolved in 50 ml of methanol in a 500 ml 3-nrb flask equipped with a mechanical stirrer,

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Dean-Stark trap, thermometer, heating mantle and a nitrogen inlet-outlet. SDP (10.0 g, 0.04 mole) and 80 ml sulfolane (previously dried by azeotroping with toluene) were added with vigorous stirring. Benzene (50 ml) was added. Methanol and benzene were distilled out (nitrogen sweep) with the pot temperature held below 100°C. Cuprous chloride (0.4 g, 0.004 mole), pyridine (10 ml), and DBB (57.0 g, 0.24 mole) were added and the temperature was raised to 160°-170°C. Excess pyridine was accumulated in the Dean-Stark trap. Temperature was maintained for 4 hours. The mixture was allowed to cool with stirring (overnight in this case). Aqueous 10% potassium hydroxide (200 ml) was added, and the mixture was extracted with carbon tetrachloride (3 x 100 ml). The extracts were washed with 5% HCl (2 x 100 ml) and water (1 x 100 ml), then dried over magnesium sulfate, filtered and stripped. Hexane (300 ml) was added to the residue. Filtration gave 12.5 g of solid which was dissolved in 175 ml of toluene and passed over 50 ml of alumina in a 1-inch diameter column. Elution with toluene (1500 ml) produced pure BPDS (10.51 g, 0.019 moles). Elution with methylene chloride (500 ml) gave pure oligomer (1.33 g, 0.0015 moles). Elution with acetone (150 ml) gave pure oligomer (0.64 g, 0.005 mole). The hexane was stripped from the filtrate and the residue was distilled to give DBB (38.5 g, mole) and some additional oligomer (1.5 g, 0.0017 mole).

The original aqueous portion was acidified with HCl and extracted with ether (2 x 100 ml), washed with NaCl solution, and dried over magnesium sulfate. Stripping gave a gummy residue which was triturated with methylene chloride. Filtration gave recovered SDP (2.0 g, 0.008 mole). The solvent was stripped to give half-product (2.14 g, 0.005 moles).

Large-Scale Preparation of m,m-BPDS (Run 585-8)

A 12-1 rb flask equipped as in the previous run was employed. Sulfonale (5 1), SDP (1000 g), potassium hydroxide (512 g 87% assay dissolved in 200 ml water) and 400 ml toluene were charged to the reaction flask. The total water azeotroped off in a total of 8 hr was 540 ml compared to 486 predicted based on water added, water in solvent and reactants, and water

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produced by salt formation. Toluene was distilled from the system through the Dean-Stark trap, pot temperature 160°C. DBB was added; the temperature was then 120°C. Cuprous chloride (20 g) and pyridine (100 ml) were added and the temperature brought to 160-170°C. A slow exotherm caused the temperature to rise to ca. 185°C even with cutting back of the heat supply. The exotherm subsided after 3 to 4 hours, but the temperature was maintained at 170°C for a total of 20 hours. After cooling, 2 l of 10% aqueous KOH was added. The mixture was divided in half at this point to facilitate workup. Each half was charged to a 12-l flask with a bottom draw-off and diluted with 4 l of water. The DBB layer which settled out was drawn off. The aqueous portion was extracted with carbon tetrachloride (2 x 1 l) and the extracts added to the DBB layer. The aqueous layer was acidified with HCl and extracted with ether (2 x 1 l). The ether extracts were water washed (3 x 500 ml), dried over magnesium sulfate, filtered and stripped to give 80.2 g of oil. Trituration with methylene chloride produced 59 g SDP. Stripping the filtrate gave 20.6 g of half-product. This seemed low, so the aqueous portion was re-extracted with ethylacetate. This produced an additional 160 g of SDP, but no half-product. The organic layer was washed with 5% HCl (2 x 2 l) and NaCl solution (1 x 2 l). The carbon tetrachloride was removed by distillation. The DBB was then vacuum distilled until the residue was too thick to allow good heat transfer (2945 g DBB overhead). Hexane (3 l) was added to the residue, and the resulting solids were filtered and washed with hexane. Stripping the hexane produced an additional 907 g crude DBB. The crude product after remaining in the vacuum filter overnight weighed 1654 g. TLC showed large amounts of oligomer and higher oligomers. This material was used to test crystallization and extractive purification schemes.

Preparation of m,m-BPDS and Oligomer (Run 585-12 Table I)

Dry sulfolane (5 l) and SDP (1000 g) were added to the 12-l reaction vessel equipped as in the previous experiment containing potassium methoxide prepared from 312 g potassium in 2 l methanol. Methanol was distilled. Toluene (400 ml) was added and distilled. DBB was added, and the remaining reagents were added after the temperature cooled to ca. 100°C. The

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temperature was raised to 160-185°C, held for 4 hours, then allowed to cool overnight. Workup proceeded as in Run 585-8 with the following exceptions. DBB itself was used as the extraction solvent to eliminate the need to separate the carbon tetrachloride. Ethyl acetate was used as the extraction solvent to recover SDP and half-product. In the product recovery step, sufficient DBB was left in the pot to maintain a very mobile fluid which was added to a well-stirred resin kettle containing 4 l of heptane. The resulting mixture was filtered to produce 1678 g of crude product. The filtrate was stripped of heptane and the remaining DBB distilled. A pot residue was washed with heptane to give an additional 175 g of product. Analysis of a small portion of the crude product showed 54% BPDS; 27% oligomers, and 19% entrained DBB. The crude product was freed of DBB by high speed blending with hexane and filtration. The filter cake was dissolved in 12 l of toluene and refluxed with a Dean-Stark trap to remove traces of water. After cooling, the solution was passed sequentially through four 2-l burrettes each containing 1 kg of 80-200 mesh Fisher alumina. The columns were washed with an additional 3 l of toluene. The toluene was stripped in vacuo and filtered periodically when solids would accumulate. The combined filter cakes were dried to constant weight to give 898 g BPDS, TLC pure, 40% yield. The residue from the last filtration, about 0.5 l, was combined with a solution obtained by washing the column with 8 l of methylene chloride. Stripping gave 337 g of BPDS-oligomer mixture. Further washing of the alumina with 6 l of ethyl acetate gave 128 g of oligomers (see Table I). Run 585-16, which followed the same procedure, is also summarized in Table I.

Preparation of m,m-ATS (Run 585-23)

Each of two 12-l flasks equipped with mechanical stirrers, heating mantles, condensers, and nitrogen inlet-outlets, were charged with 1150 g BPDS, 430 g 2-methyl-3-butyn-2-ol, 12.5 g triphenylphosphine and 7.5 l triethylamine. The system was purged with nitrogen. Bis-triphenylphosphine palladium chloride (2.5 g) and cuprous iodide (2.5 g) were added and the temperature raised to reflux with vigorous stirring. The heats were cut back once the reaction started because of the exothermic neutrallization of HBr.

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After about 2.5 hr the exothermicity was over. Reflux was maintained for 6 hr. The mixture was cooled to room temperature and filtered. Triethylamine was stripped under reduced pressure, and the residue from both pots taken up in toluene (6 l) and combined. The toluene solution was washed with 10% sulfuric acid (1 x 2 l), water (1 x 2 l), saturated sodium bicarbonate (1 x 1 l), and water (1 x 2 l). The organic layer was dried over magnesium sulfate, filtered, and charged to a 12-l pot with 10 g sodium hydroxide pellets. The pot was stirred vigorously with a mechanical stirrer, and heated to reflux. A toluene-acetone mixture was distilled slowly over 6 hr, until the acetone content of the overhead was less than one percent. The hot solution was filtered through celite and cooled to room temperature. The dark red colored solution was passed through 6 gal of 8-14 mesh fuller's earth and eluted with an additional 10 gal of toluene to give a yellow solution. This was passed through silica gel columns, 500 g in 2-l burrettes, to remove small amounts of OATS. The eluent was monitored by TLC and the column replaced when OATS broke through. A total of 6 kg of silica gel was used. Stripping the toluene produced 820 g, 46%, of ATS. Washing the fuller's earth with 4 gal of methylene chloride produced an additional 178 g of ATS which contained 8% OATS by gel permeation chromatorgraphy.

Preparation of m,m,m-OATS (Run 585-27)

A mixture containing 17% BPDS and 83% of the analogous oligomers (1038 g) obtained from Runs 585-12 and -16 was charged along with 1850 ml NMP, 3 l triethylamine, 400 g methylbutynol, 12.5 g triphenylphosphine, 2.5 g bis-triphenylphosphine palladium chloride, and 2.5 g cuprous iodide to the apparatus used in the previous example. The reaction was carried out as above. Unfortunately, about half of the material was lost when a flask broke during workup. The crude OATS solution after cleavage was passed through 1 kg of fuller's earth to remove color and stripped to give a yellow solid. The material could be ground to a powder, but it usually caked upon standing. Gel permeation chromatography indicated the material was 24% ATS and 76% OATS. Traces of toluene remained in the material even after vacuum drying for 48 hr.

Preparation of 4-Hydroxy-4-(3-Bromophenoxy)Diphenyl Sulfone (Run 585-17)

To a 5-1 3-nrb flask equipped with a distillation head, nitrogen-inlet-outlet, mechanical stirrer, and a thermometer were added 1950 ml dimethylsulfoxide (dried over molecular sieves), 375 g SDP, and 690 ml of 25% sodium methoxide in methanol. The mixture was heated for 2 hr under nitrogen (pot temperature 124°C) collecting overhead at 66°C. After cooling below 100°C, 150 ml pyridine was added and the reaction mixture was heated to reflux, collecting fractions and checking for methanol in the overhead by GLC. When methanol no longer came overhead, the reaction was cooled and cuprous chloride (15 g), and m-DBB (1425 g) were added. The mixture was heated to 150°C for 6 hr (nitrogen atmosphere). The mixture was cooled and 3 1 of 10% HCl was added and solution extracted with ether (2 x 1000 ml). The ether was extracted with 10% KOH (2 x 1000 ml). The ether layer was dried over $MgSO_4$ and stripped to give 1101.7 g crude recovered DBB. The KOH extracts were acidified with HCl to pH 1 and extracted with ether (2 x 1000 ml). The extracts were dried and stripped to give 515 g crude product. Methylene chloride, 1000 ml, was added and brought to reflux. Upon standing overnight, 12 g SDP crystallized. Stripping the solvent first on a rotary evaporator and finally at high vacuum gave 471 g HBPDS.

Preparation of m,p-BPDs (Run 585-21)

The HBPDS prepared above, 471 g, in 3 1 of sulfolane was charged to a 12-1 rb flask equipped with a mechanical stirrer, nitrogen inlet-outlet, a Dean-Stark trap, thermometer, and condenser along with 74.8 g potassium hydroxide (87% assay) in 100 ml water and 350 ml toluene. The water was azeotroped from the mixture. Toluene was then distilled out and the mixture allowed to cool overnight. p-Dibromobenzene, 823 g, and cuprous chloride, 10 g, were added and the temperature brought to 160°C and held for 6 hr. After cooling, 10% aqueous KOH, (2 1), was added and the mixture stirred for 20 minutes. After dilution with 3 1 of water, the mixture was extracted with carbon tetrachloride (3 x 1000 ml). The organic layers were washed with 10% HCl (1 x 1000 ml) and water (2 x 1000 ml), dried over $MgSO_4$ and stripped.

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Unreacted p-DBB was removed by extraction with hot hexane to give 322 g crude product. The aqueous portion was acidified with HCl and extracted with ethyl acetate (3 x 1000 ml). The extracts were washed with water (3 x 1000 ml) dried over $MgSO_4$, and stripped. Sulfolane was distilled from the residue at 1 mm to give 188 g recovered HBPDS. Analysis by GPC showed that the crude product contained 184 g of m,p-BPDs. The crude product was dissolved in toluene and passed over 1000 g of alumina. Elution with more toluene produced 132 g pure m,p-BPDS. Elution with ethylacetate gave 162 g of a mixture of BPDS and oligomer.

Preparation of m,p-ATS (Run 585-30)

m,p-BPDS prepared as indicated above, 130 g, (NMR in Table II) was charged under nitrogen with 1200 ml triethylamine, 0.25 g triphenylphosphine, 50 g methylbutynol, 0.2 g bis-triphenylphosphine palladium chloride and 0.2 g cuprous iodide. The reaction was allowed to run 16 hr at reflux. The amine salt was filtered and the triethylamine stripped. The residue was taken up in toluene (3 l) and washed with 5% HCl (2 x 500 ml) and water (2 x 500 ml). An aliquot was taken, stripped to give a heavy oil which was placed on 50 ml silica gel. Elution with ethyl acetate gave a pale yellow oil which solidified under high vacuum to a white solid, mp 66-68°C. The NMR appears in Table III. The toluene solution was then filtered through 25 ml silica gel and refluxed in the presence of 10 g of sodium hydroxide. The mixture was filtered hot through celite, cooled to room temperature, and eluted through 500 g silica gel. The column was washed with 2 l of toluene. Stripping the solvent gave 76.9 g (74%) of m,p-ATS. Figure 5 shows the NMR.

Small-Scale BPDS Reaction Variable Studies (Tables VI-IX)

A 500-ml 3-nrb flask equipped with a nitrogen inlet-outlet, temperature controller, mechanical stirrer, and a distillation head was charged with 10.0 g SDP, 100 ml sulfolane, and heated under nitrogen to 90°C. Then 5.12 g 89% assay KOH dissolved in 4 ml water and 20 ml toluene were added. The water was azeotroped out and the toluene stripped from the system at the desired

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temperature. The mixture was cooled slightly, 56.7 g dibromobenzene added followed by 0.2 g cuprous chloride. The temperature was then raised to the desired level and the reaction allowed to run overnight. After cooling, 40 ml of 10% KOH were added and the mixture extracted with hexane (3 x 40 ml). (Upon standing, the hexane extract produced 0.4-0.6 g crystals which were recovered and added to the product.) Water (80 ml) was added. The mixture was extracted with carbon tetrachloride (3 x 40 ml). The extract was washed with water (3 x 40 ml), dried over magnesium sulfate, filtered, and stripped. Traces of DBB were removed by hexane washing. Products were analyzed for oligomer content by HPLC and/or GPC.

The runs employing different catalysts employed identical procedures. The runs using different bases eliminated the azeotroping and toluene stripping steps.

Metals Removal (Figure 2 and 3)

Several displacement reactions of slightly varying size were run as BPDS became available. A typical reaction procedure follows. A 250-ml 3-nrb flask equipped with a nitrogen inlet-outlet, magnetic stirrer, condenser, and heating mantle was charged with 14.0 g BPDS, 0.25 g triphenylphosphine, 0.05 g bis-triphenylphosphine palladium dichloride, 5 g methylbutynol, and 50 ml triethylamine. After purging with nitrogen, 0.05 g cuprous iodide was added and the mixture heated to reflux. When HPLC of samples indicated the reaction was complete, triethylamine hydrobromide was removed by filtration. The filtrate was stripped and the residue taken up in 150 ml toluene. Washes as defined in Figures 2 and 3 were 50 ml in volume. Solutions were dried over magnesium sulfate. Passage through adsorbents was accomplished by putting the adsorbent (roughly 1-to-1 weight relationship with product) in a small fritted funnel, topping with a layer of celite, and gravity filtration and solvent wash. Toluene was removed under vacuum, and the light yellow powder submitted for analysis.

Preferred Procedure for BPDS-Oligomer Preparation from 95-5 m-p Dibromobenzene (Run 585-48)

To a 12-1 pot was charged 500 g SDP and 5 1 sulfolane. A nitrogen atmosphere was established, and the mixture was heated to 90°C. Potassium hydroxide, 256 g of 89% assay dissolved in 200 ml water was added. After 15 minutes of stirring, 1 1 of toluene was added and the water azeotroped from the system via a Dean-Stark trap. After the water was removed, the toluene was stripped from the mixture - final pot temperature 175°C. Addition of 2830 g of 95-5 m-p DBB dropped the temperature to 152°C. Cuprous chloride (40 g) was added, and the temperature rose to 167°C even with no added heat. Removal of the insulation allowed the temperature to fall back to 160°C. After about 30 minutes, the heat could be restored and the reaction was maintained at 160°C for 16 hr.

The mixture was cooled and 2 1 of 10% aqueous KOH was added. After extraction with hexane (4 x 1 1), 4 1 of water was added and the mixture extracted with CCl_4 (3 x 2 1). Crystals which formed in the hexane were filtered and added to the CCl_4. The CCl_4 extracts were washed with water (3 x 1 1), dried over $MgSO_4$, and stripped. After thoroughly washing with hexane the product was dried to constant weight in a dessicator under vacuum to give 700.3 g. The hexane washes and extracts were stripped and the DBB distilled to give an additional 12.0 g of product. GPC showed BPDS/BPDS + oligomer equal to 0.81. (Note: On a larger scale which incorporates recycle streams, DBB itself would be the best choice for the extraction solvent.)

Preferred Procedure for Preparation of ATS-OATS Mixture (Run 585-59)

A mixture containing 81% BPDS and 19% of the oligomeric analogous (23.0 g) was charged along with 2-methyl-3-butyn-2-ol (8.6 g), 150 ml tri-ethylamine, and triphenylphosphine (0.25 g) to a 250-ml flask equipped with a thermometer, magnetic stirrer, nitrogen inlet-outlet and a condenser. A nitrogen atmosphere was established and bis-triphenylphosphine palladium chloride (50 mg) and cuprous iodide (50 mg) were added. The mixture was brought to reflux for 6 hr. The mixture was filtered and the filter cake

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washed with a little triethylamine. The filtrate and wash were stripped and the residue taken up in toluene (ca. 300 ml). The solution was washed with 15% hydrochloric acid (1 x 100 ml) and water (1 x 100 ml). Ethylenediamine (3 ml) was added and the solution brought to 60°C for 30 minutes to complex traces of palladium. The solution was washed thoroughly with water. Analysis by atomic absorption at this point indicated less than 20 ppm Pd on a solvent-free basis. Several pellets of sodium hydroxide were added to the toluene solution, and the mixture was refluxed while removing acetone as it formed. When the formation of acetone ceased, the hot solution was treated with 2 g of charcoal and filtered through a layer of celite. Stripping the solvent gave an orange oil (16.8 g, 91%). Gel permeation chromatography indicated 79% ATS and 21% OATS.

Preparation of Polymer Supported Catalyst (Run 578-70)

Polymer-bound triphenylphosphine (5.0 g) 0.46 meg/g (20% cross-linked polystyrene puchased from Strem) and palladium dichloride (0.42 g) were charged along with 50 ml benzene and 100 ml absolute ethanol under nitrogen to a 500-ml 3-nrb flask equipped with a magnetic stirrer, condenser, and a heating mantle. The mixture was refluxed for 16 hr during which the red color disappeared. The solvent was decanted. The yellow beads were slurried with absolute ethanol and the liquid decanted four times to remove a small amount of black fines (Pd metal?). The beads were slurried once more in 100 ml absolute ethanol. At room temperature, 95% hydrazine (2.0 g) was added. Stirring was continued for three hours. During this time the beads became black. The beads were removed by filtration under a nitrogen blanket and placed in a vacuum dessicator.

Methylbutynylation of Bromonitrobenzene
Using Polymer-Bound Catalyst (Run 578-72)

A portion of the catalyst prepared above (0.5 g), 20.0 g 4-bromo-nitrobenzene, 10.0 g 2-methyl-3-butyn-2-ol, 0.05 g cuprous iodide, and 200 ml triethylamine were refluxed under nitrogen with vigorous stirring for 26 hr.

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Analysis by gas chromatography indicated 33.8% conversion which corresponds to 5.4 moles converted/mole Pd-hr. A homogeneous run under these conditions gives about 714 mole/mole hr.

Use of Polymer-Bound Catalyst with Added Triphenylphosphine (Run 578-81)

The previous experiment was repeated with the addition of 0.25 g triphenylphosphine. Conversion was complete in 16 hr. Unfortunately, we do not know how much less than 16 hr was required. If just complete, this corresponds to 26 moles/mole hr.

Butynylation of BPDS Over Polymer-Bound Catalyst (Run 578-89)

A portion of polymer-bound catalyst (0.5 g), 14.0 g BPDS, 10.0 g 2-methyl-3-butyn-2-ol, 0.25 g triphenylphosphine, 0.05 g cuprous iodide and 200 ml triethylamine were refluxed under nitrogen with vigorous stirring. The reaction was monitored by TLC. After 72 hr all the BPDS had disappeared; however, a total of 138 hr was required to completely displace all the bromine atoms. The mixture was filtered and the solvent stripped. The residue was taken up in 200 mls toluene and washed with 1:1 HCl/H_2O (1 x 100 ml) and water (3 x 100 ml). The toluene layer was dried over magnesium sulfate, filtered and stripped under high vacuum. The product was analyzed by atomic adsorption as containing 24 ppm Pd.

Preparation of 4-Nitrobenzoin Acetate (Run 585-32)

Each of 5 22-l flasks equipped with mechanical stirrers and thermo-couples was charged with 2500 g benzoin and 9.3 l of acetic anhydride. After cooling to 15°C, sulfuric acid (400 ml/flask) was added dropwise (exotherm to about 30°C). The flasks were cooled to -20°C (dry ice-isopropanol), and 90% nitric acid was added (600 ml/flask) at a rate to maintain the temperature between -20 and -10°C. After the addition was complete, the mixture was allowed to come to room temperature and stand overnight. No crystals formed even when a seed crystal was added. The mixtures were poured into ice water,

ca. 8-10 gal/flask. The aqueous portion was decanted from the gummy solid which was then washed twice with equal volumes of water. The solid was recrystallized once from an equal volume of methanol and a second time from two volumes of methanol. Analysis by GC showed the material to be only about 90% pure at this point. The solids were then slurried with an equal volume of methanol and filtered hot. Air drying gave 5779 g of white solid, mp 124-6°C, 98+% purity by GC.

Preparation of 4-Nitrobenzil (Run 585-36)

Each of 2 22-l flasks equipped with a mechanical stirrer, a caustic scrubber, a thermocouple and a nitrogen source was charged with 2885 g of 4-nitrobenzoin acetate and 12 l of 70% nitric acid. A slow nitrogen sweep was employed to ensure that the caustic scrubber did not back up. The mixture was heated continuously (heating mantle). At ca. 40°C the solids dissolved. At 72°C vigorous oxidation occurred and the external heat was shut off. Exothermic reaction raised the temperature to 79-81°C where the temperature remained for about 60 minutes. The temperature dropped one degree and crystallization began. In one case we were able to pour the mixture into ice water immediately. In the other case, the temperature fell a second degree and the crystallization became so rapid that the entire contents became solid. Because of the still high acid concentration, additional water would have generated excessive heat. So the material was allowed to cool overnight and then scraped from the flask into ice water. The aqueous mixtures were filtered and washed with water. The crystals were crushed in a blender with water, filtered and washed until the filtrate exhibited a neutral pH. The filter cake from each run was slurried in 11 l of refluxing ethanol for 2 hr, filtered hot, and dried at 65°C under vacuum to a constant weight. The combined weight of the two batches was 4095 g (87.5% yield). A second crop of 365 g was obtained by filtering the ethanol after cooling to ambient temperature. Analysis by GC showed the first crop to be 99+% pure, while the second crop was only 95% pure.

Preparation of 1, 4-Bis(4-Benziloxy)Benzene (Run 585-49)

A 22-l flask equipped with a nitrogen inlet-outlet, mechanical stirrer, and thermocouple was charged with 4-nitrobenzil (1464 g, 5.72 mole), dimethylsulfoxide (12.3 l) and hydroquinone (312 g, 2.84 mole). Upon dissolution of the reactants, 975 g of anhydrous potassium carbonate (dried 30 minutes at 115°C) was added rapidly while maintaining a nitrogen positive pressure. The mixture went through the color sequence gold, green, brown, and purple. Stirring was continued overnight. The mixture was heated to 64°C for 5 hr and then allowed to cool slowly overnight with stirring. The brown mixture was carefully poured into a mixture of 19.5 l of water, 19.5 l of ice and 975 ml of sulfuric acid. The flask was washed with 9.75 l of water containing 325 ml sulfuric acid. The resultant solids were filtered, washed with 5 volumes of water, and pressed dry with a rubber dam. The filter cake was placed in a large kettle with 16 l of ethanol. The mixture was refluxed for an hour, cooled and filtered. Recrystallization from ethyl acetate (hot filtration) three times produced 876.4 g (59%), mp 157-9°C.

Preparation of 3-Ethynylphenol (Run 585-41)

Sulfuric acid, 570 ml, was added to 2880 ml of ice water and charged to a 22-l flask equipped with a mechanical stirrer, thermocouple, dropping funnel, and an ice-salt bath. The flask was cooled to 5°C and 702 g of aminophenyl acetylene was added dropwise maintaining the temperature below 10°C. Then a solution of 426 g of sodium nitrite dissolved in 1050 ml of water was added dropwise while keeping the temperature between 2 and 5°C. After the addition was complete, stirring was continued for 30 minutes. The resulting solution of diazonium salt was added in portions to each of three 4-l beakers containing 1200 ml of boiling water. Heat and stirring were supplied by magnetic stirrer-hotplates. The rate of addition was such that boiling continued throughout. Five minutes after the addition was complete, the beakers were removed from the heat and allowed to cool. The combined reaction mixture was extracted with ether (2 x 2 l). The extracts were washed with water until the washings were neutral, dried over magnesium sulfate,

filtered and stripped. Distillation through an 8" Vigreaux column gave 340.4 g, 48% yield, bp.70-2°C at 0.3 mm. A total of 1400 g of product was prepared in 4 runs.

Preparation of 4(3-Ethynyl Phenoxy)Benzil (Run 585-42)

To 582.5 g ethynylphenol in 2.8 l DMSO in a 12-l flask, under nitrogen, was added 1043 g of 25% sodium methoxide in methanol. After stripping 30 minutes at room temperature, the methanol was distilled under vacuum (skin temperature held at 30-35°C by heating mantle). The vacuum was broken with nitrogen and the solution transferred to a dropping funnel. This solution was added dropwise over ca. 1 hr to a solution of 1220 g 4-nitro-benzil in 5.1 l DMSO in a 22-l pot held at 90°C. When the addition was complete, the heat was shut off and the mixture allowed to cool while stirring overnight. The mixture was poured into 5 gal of water containing 3 pounds of sodium hydroxide. The aqueous layer was decanted from the gummy precipitate and extracted with methylene chloride (3 x 4 l). The extracts were washed with water to remove DMSO, dried over magnesium sulfate, filtered and stripped of solvent to give 42 g of viscous oil. The gummy precipitate was dissolved in methylene chloride, washed, dried, and stripped to give 900 g of brown oil which was combined with the 42 g obtained from the extracts. A second similar run was made except the extraction was eliminated. The material from the 2 runs was combined. Attempts to induce crystallization, even with seed crystals, failed. Purification was achieved by elution from 6 kg of silica gel by carbon tetrachloride. This removed the dark red-brown color giving, after stripping the solvent, a yellow oil which slowly crystallized, 1190 g (40%), mp-79-80°C.

Preparation of BATQ-H (Run 585-55)

To a 22-l pot equipped with a heating mantle, a mechanical stirrer, nitrogen inlet-outlet, a thermocouple, a dropping funnel, and a distillation head was charged 410 g 3.3'-diaminwith methylene chloride (3 x 4 l). The

temperature was brought to 90-100°C. A solution of 504 g 1,4-bis-(4-benzily-loxy)benzene in 4700 ml m-cresol was added over 1.5 hr. Stirring and temperature were maintained for 2 hr. A solution of 687 g 4-(3-ethynylphenoxy)benzil in 2000 ml of chloroform was then added rapidly. The chloroform distilled off in about one hour, and the temperature was maintained for an additional hour. The mixture was allowed to cool overnight and then poured into 12 gal of methanol containing 3000 g sodium hydroxide. The yellow precipitate was filtered and dissolved in 12 l of tetrahydrofuran. The product was reprecipitated from 12 gal of methanol containing 1500 g of sodium hydroxide. The solid was once again dissolved in tetrahydrofuran and filtered through a bed of celite to remove a suspended material (scraping the top of the celite layer periodically was necessary to maintain reasonable flow). The yellow precipitate was filtered and dried under in vacuo at 50°C and then under high vacuum at room temperature to a constant weight, 1064 g.
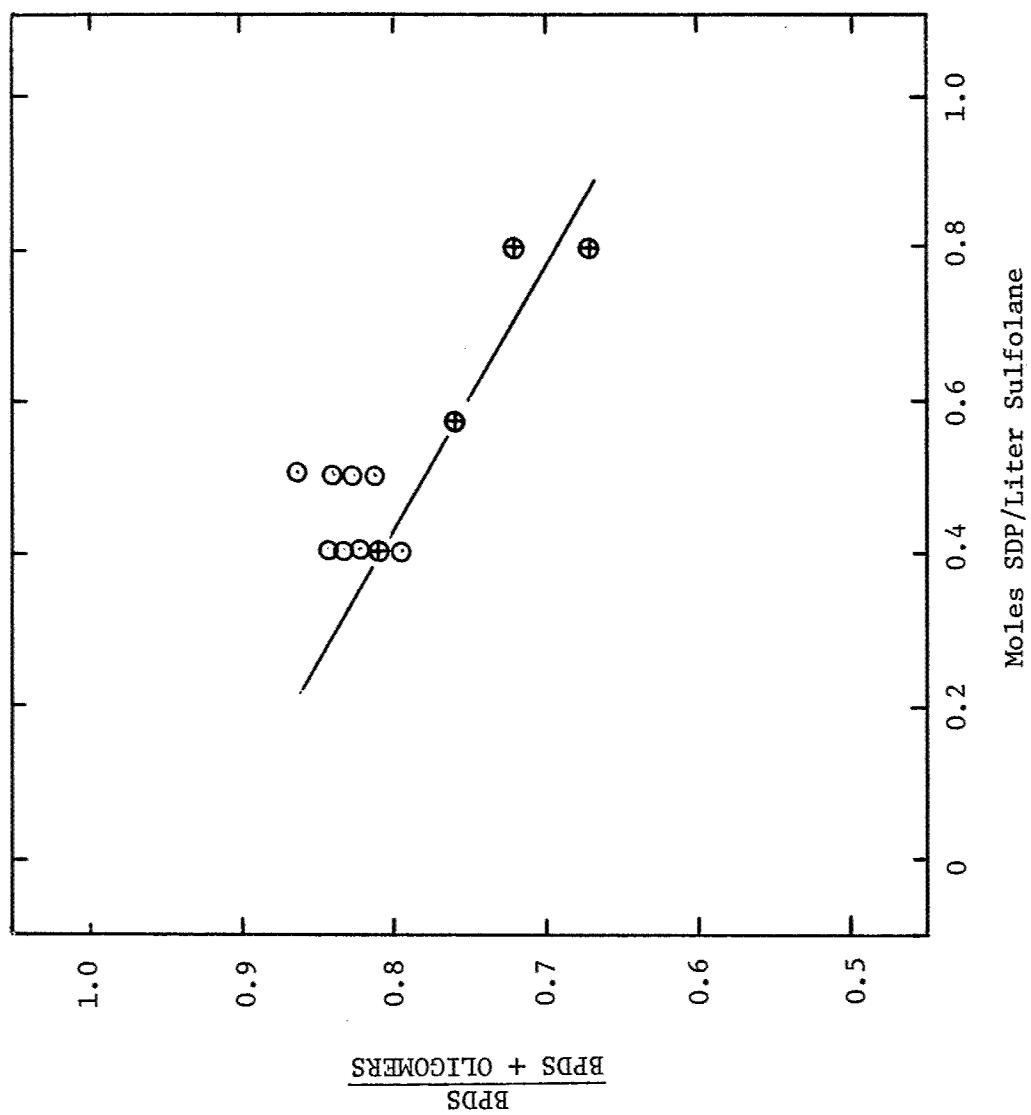
Figure 1

EFFECT OF CONCENTRATION

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METALS REMOVAL SCHEMES

Figure 2

Butynol
Reaction Mixture
Cu=1200 ppm; Pd=500 ppm

Sparge with Air
Strip
Dissolve in Tol.
Wash 10% Sulfuric
Wash Water

Wash 10% NH$_3$

Strip

Cu = 6 ppm
Pd = 86 ppm

Na$_4$ EDTA
Strip

Cu = 0.073%
Pd = 420 ppm

CH$_2$Cl$_2$ Soln.
Wash 10% NH$_3$

Cu = 50 ppm
Pd = 350 ppm

Cu = 21 ppm
Pd = 310 ppm

Wash 10% NH$_3$ (2)
Wash 10% Sulfuric
Wash Water
Wash 10% Sulfuric
Wash Water
Strip

Cu < 2 ppm
Pd = 160 ppm

Cleavage Reaction
Sigel
Strip

Cu < 2 ppm
Pd = 84 ppm

Strip
Dissolve in Tol.

Wash 10% Caustic (2)
Wash Water
Wash 10% Sulfuric
Wash Water
Strip

Cu < 2 ppm
Pd = 230 ppm

Strip
Dissolve in Tol.
Wash 10% Sulfuric
Wash Water

Sigel
Strip

Cu = 0.11%
Pd = 445 ppm

Al$_2$O$_3$
Strip

Strip

Cu = 0.095%
Pd = 395 ppm

Cu = 0.15%
Pd = 460 ppm

Reflux Tol.
Sparge with Air
Filter Strip
Strip

Cu = 0.15%
Pd = 440 ppm

Tol. Soln.
Wash Na$_2$ EDTA
Strip

Cu = 0.12%
Pd = 400 ppm

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Butynol Reaction Mixture
$Cu = 1200$ ppm; $Pd = 500$ ppm

Strip
Dissolve in Tol.
10% H_2SO_4 Wash
Water Wash
Conc. NH_4OH Wash (4X)
Water Wash

$Cu = 38$ ppm
$Pd = 130$ ppm

Strip
Dissolve in Tol.
10% HCl Wash
Water Wash

$Cu = 31$ ppm
$Pd = 500$ ppm

N_2H_4

$Pd = 390$

Conc. NH_4OH Wash
Water Wash

$Cu < 5$
$Pd = 57$

Conc. NH_4OH Wash
Water Wash

$Cu < 5$
$Pd = 47$

Conc. NH_4OH Wash 60°C
Water Wash

$Cu < 5$
$Pd = 16$

Strip
Dissolve in Tol.
10% HCl Wash
Water Wash (2X)
Conc. NH_4OH Wash
Water Wash

$Pd = 52$ ppm

Ethylenediamine Wash
Water Wash

$Pd = 30$ ppm

10% HCl Wash
Water Wash
Conc. NH_4OH Wash (2X)
Water Wash

$Pd = 59$ ppm

Ethylenediamine, 60°C
Water Wash

$Pd = 18$ ppm
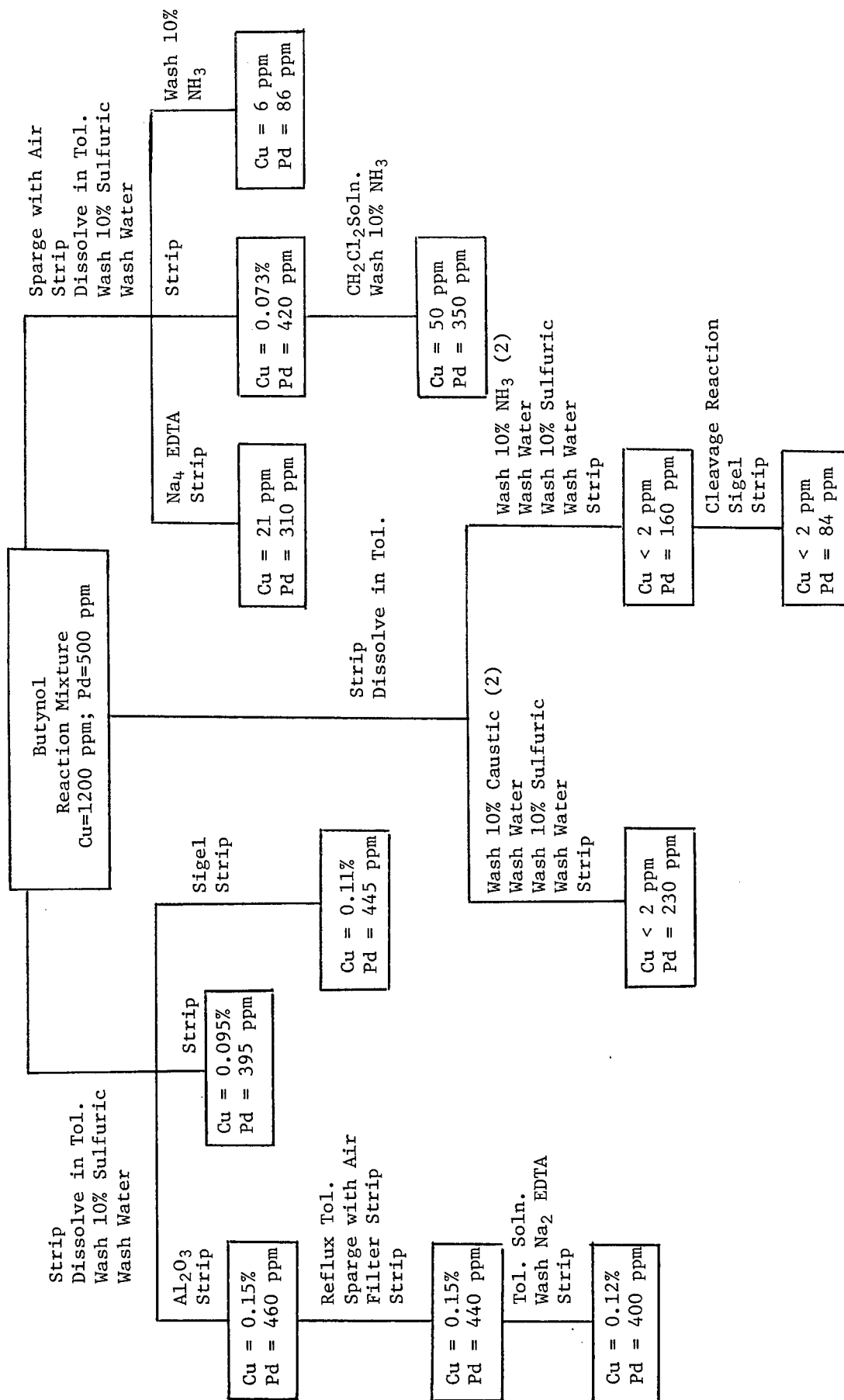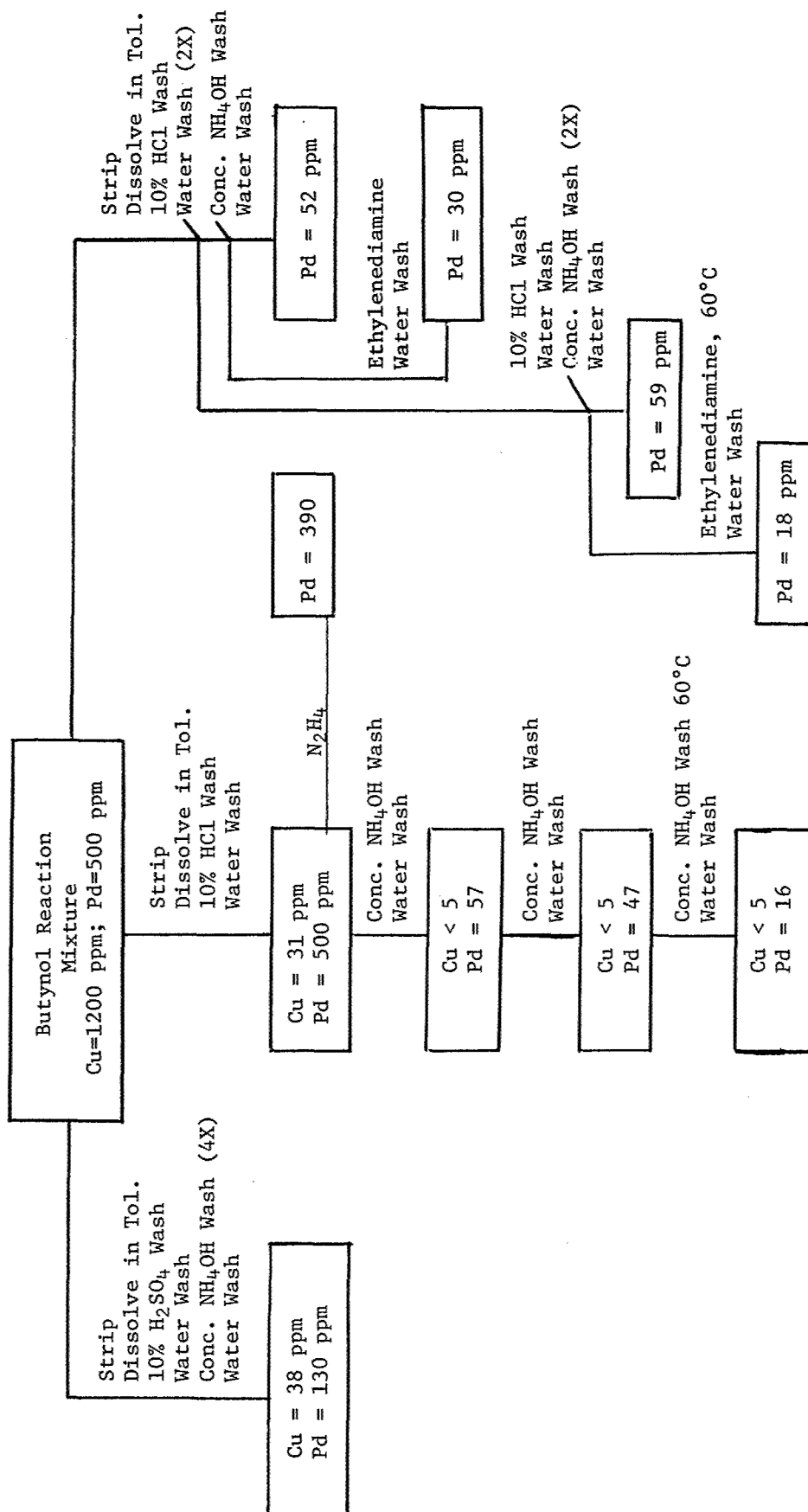
Figure 3

METALS REMOVAL SCHEMES

TABLE I

YIELD STRUCTURE FROM REACTION OF
SULFONYLDIPHENOL AND DIBROMOBENZENE

Run Number	Material	g	% Yield[a]	% Efficiency[b]
585-4[c]	SDP recovered	2.00	20.0	--
	BPDS	10.51	46.9	70.2
	Half-product	2.14	13.2	--
	Oligomer	2.73	15.4	23.0
	Higher Oligomers	0.64	3.9	5.8
585-12[d]	SDP recovered	139	13.9	--
	BPDS	977	43.6 (40.0)[e]	67.5
	Half-product	f	21.6	--
	Oligomer	295	16.7	25.9
	Higher Oligomers	69	4.3	6.6
585-16[d]	SDP recovered	143	14.3	--
	BPDS	907	40.5 (37.1)[e]	61.0
	Half-product	f	19.3	--
	Oligomer	324	18.3	27.6
	Higher Oligomer	122	7.6	11.4

[a] based on SDP.
[b] assumes total recycle of SDP and half-product.
[c] isolated products by column chromatography.
[d] analysis by gel-permeation chromatography.
[e] isolated.
[f] by difference.

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TABLE II

NMR SPECTRAL DATA FOR DIBROMO-INTERMEDIATES[a]

Compound	Chemical Shift (δ)	Multiplicity	Assignment[b]
6 (m,m-BPDS)	7.90	4H, d (J=8Hz)	H_B
	7.05	4H, d (J=8Hz)	H_A
	7.4-6.8	8H, m	H_C
8 (m,p-BPDS)	7.90	4H, d (J=8Hz)	H_B
	7.05	4H, d (J=8Hz)	H_A
	7.50	2H, d (J=9Hz)	H_D
	6.90	2H, d (J=9Hz)	H_E
	7.4-6.8	4H, m	H_C
11 (m,m,m-Oligomer)	7.90	8H, d (J=8Hz)	H_B
	7.5-6.7	20H, m	$H_A + H_C$

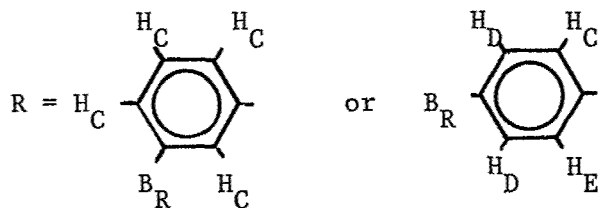---

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

[b]

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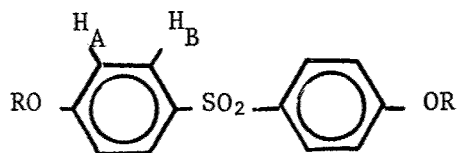
TABLE III

NMR SPECTRAL DATA FOR METHYLBUTYNOL INTERMEDIATE[a]

Compound	Chemical Shift (δ)	Multiplicity	Assignment[d]
$\underline{7}$ [b] (m,m-	7.85	4H, d (J=8 Hz)	H_B
	6.95	4H, d (J=8 Hz)	H_A
	7.4-6.8	8H, m	H_C
	2.45[c]	2H, s	hydroxyl
	1.60	12H, s	methyl
$\underline{16}$ (m,p-	7.90	4H, d (J=8 Hz)	H_B
	7.05	4H, d (J=8 Hz)	H_A
	7.45	2H, d (J=8 Hz)	H_D
	6.95	2H, d (J=8 Hz)	H_E
	7.3-6.9	4H, m	H_C
	2.40[c]	2H, s[c]	hydroxyl
	1.60	12H, s	methyl
$\underline{14}$ m,m,m	7.90	8.1H, d (J=8H_2)[e]	H_B
	7.4-6.8	21.3H, m	H_A + H_C
	2.45[c]	2H, s	hydroxyl
	1.60	12H, s	methyl

[a] sample in $CDCl_3$ in δ downfield from TMS

[b] in CCl_4

[c] peak disappears in D_2O

[d]
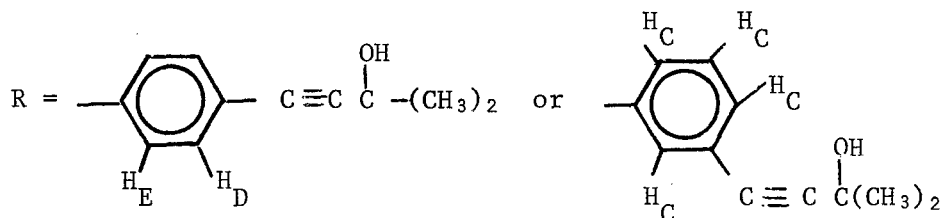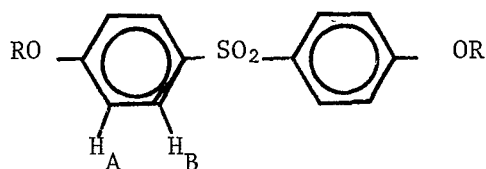
[e] Non-integral ratio of aromatic results from presence of ca. 20% $\underline{7}$

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TABLE IV

NMR SPECTRAL DATA FOR ACETYLENE TERMINATED PRODUCTS[c]

Compound	Chemical Shift (δ)	Multiplicity	Assignment[b]
<u>3</u> (m,m-ATS)	7.90	4H, d (J=8Hz)	H_B
	7.05	4H, d (J=8Hz)	H_A
	7.4-6.9	8H, m	H_C
	3.10	2H, s	H_G
<u>17</u> (m,p-ATS)	7.90	4H, d (J=8Hz)	H_B
	7.00	4H, d (J=8Hz)	H_A
	7.50	2H, d (J=9Hz)	H_D
	6.95	2H, d (J=9Hz)	H_E
	7.4-6.9	4H, m	H_C
	3.10	1H, s	H_G
	3.07	1H, s	H_F
<u>15</u> (m,m,m-OATS)	7.90	8.1H, d (J=8Hz)	H_B
	7.4-6.8	21.3H, m	$H_A + H_C$
	3.10	2H, s	H_G

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a   samples in $CDCl_3$ in δ downfield from TMS

b

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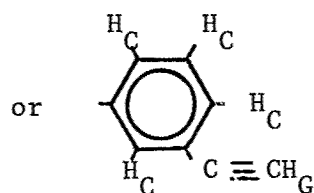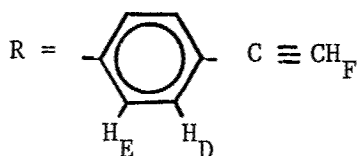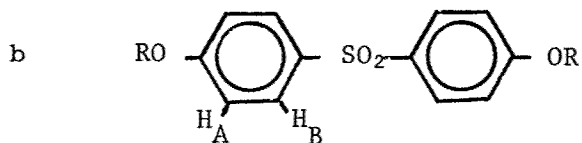
TABLE V

ANALYSIS OF PRODUCTS

Compound	Formula	mp°C		%C	%H	%Br	%S
6 m,m BPDS	$C_{24}H_{16}Br_2O_4S$	137-140	Calc.	51.45	2.88	28.53	14.28
			Found	52.34	3.18	29.68	---
7 m,m-adduct	$C_{34}H_{30}O_6S$	39-41	Calc.	72.07	5.34		
			Found	71.77	5.26		
16 m,p-adduct	$C_{34}H_{30}O_6S$	66-8	Calc.	72.07	5.34		
			Found	71.68	5.42		
3 m,m ATS	$C_{28}H_{18}O_4S$	---	Calc.	74.66	4.03	---	7.10
			Found	74.98	4.15		7.05
17 m,p ATS	$C_{28}H_{18}O_4S$	---	Calc.	74.66	4.03		
			Found	75.00	4.12		

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TABLE VI

EFFECT OF TEMPERATURE

Run Number	30	31	32	35	37	42	46	48	49	50
Stripping Temp., °C	140	160	160	170	170	190	170	170	190	170
Run Temp., °C	160	160	140	140	120	140	170	170	190	170
Run Time, hr	15.5	18.7	18.0	17.5	19.5	19.5	19.0	19.0	19.5	19.0
Product, g[a]	9.8	8.9	0	14.0	2.9	14.0	16.6	18.9	16.1	13.9
$\left(\dfrac{BPDS}{BPDS + HEAVIER}\right)$ by GPC	0.81	0.84	--	0.81	--	0.83	--	--	--	--
by HPLC	0.82	0.82	--	0.80	--	0.81	0.79	0.76	0.76	0.79

_____

[a] Theoretical yield 22.4 g.

TABLE VII

EFFECT OF TYPE AND MODE OF ADDITION OF BASE

Run Number	34	42	45	54	56	60
Base (g)	K_2CO_3(9.9)	KOH(5,12)[a]	b	KOH(5,12)[a] K_2CO_3(5.0)[c]	KOH(5,12)[a] KOH(2.00)[c]	KOH(5,12)[a] C_8H_9OK(3.4)[c,d]
Stripping Temp., °C	--	190	--	170	170	170
Run Temp., °C	140	140	160	170	170	170
Run Time, hr	7.5	19.5	5	18.0	18.0	18.0
Product, g[e]	0	14.0	11.6	20.4	15.1	13.7+
$\left(\dfrac{\text{BPDS}}{\text{BPDS + HEAVIER}}\right)$[g]	--	0.81	0.81	0.69	0.67	--

a 89% Assay.
b Dry dipotassium salt of SDP added through screw feeder over 5 min.
c Added after 3 h reaction time.
d Potassium 2, 6-dimethylphenoxide.
e Theoretical yield 22.4 g.
f Product orange in color.
g Analysis by HPLC.

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TABLE VIII

EFFECT OF ADDITIONAL SOLVENT COMPONENTS

Run Number	32	33	35	36	51
Additive, (ml)	NONE	Pydridine (10)	NONE	Pyridine (10)	PEG[a](20)
Stripping Temp., °C	160	160	170	170	170
Run Temp. °C	140	140	140	140	170
Run Time, hr	18.0	18.0	17.5	19.0	18.0
Product, g[b]	0	12.8	14.0	14.9	traces
$\left(\dfrac{\text{BPDS}}{\text{BPDS} + \text{HEAVIER}}\right)$[c]	--	0.79	0.80	0.79	--

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[a] Polyethylene glycol.

[b] Theoretical yield 22.4 g.

[c] Analysis by HPLC.

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TABLE IX

EFFECT OF COPPER SOURCE

Run Number	42	43	44	76
Catalyst (g)	Cuprous Chloride (0.2)	Copper Stearate (0.7)	Cupric Ethyl Acetoacetate (0.63)	Cuprous Bromide (0.3) Copper Powder (0.1)
Stripping Temp., °C	190	190	190	170
Run Temp., °C	140	140	140	170
Run Time, hr	19.5	18.5	18.5	19.0
Product, g[a]	14.0	8.0[b]	6.5	13.3
$\left(\dfrac{BPDS}{BPDS + HEAVIER}\right)^{c}$	0.81	0.90[b]	0.81	0.80

a Theoretical yield 22.4 g.

b Crude product contained sulfolane which was removed by washing with methanol-water, 90-10. This may have altered the ratio.

c Analysis by HPLC.

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