DOE/PC/90036--T7

SRI International

Final Report • July 1993

Synthesis of Model Compounds for Coal Liquefaction Research

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F/90/93
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SRI Project 1285
Period Covering June 21, 1990 through July 30, 1993

Prepared for:

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Pittsburgh, PA 15236

Contract No. DE-AC22-90PC90036

We have no objection from a patent standpoint to the publication or dissemination of this material.

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SUMMARY

This final report summarizes our research on Contract No. DE-AC22-90PC90036, "Synthesis of Model Compounds for Coal Liquefaction Research." The objectives of this project were to develop feasible synthetic routes to produce (1) 4(4'-hydroxy-5',6',7',8'-tetrahydro-1'-naphthylmethyl)-6-methyldibenzothiophene, and (2) a 1-hydroxynaphthalene-dibenzothiophene polymer. These compounds are thought to be representative of sulfur containing molecules in coal. The program was divided into two technical tasks. Unfortunately, the attempted syntheses of these compounds was unsuccessful due to their unusual reactivities. A summary of attempted synthetic routes and possible future routes are described in the following sections, and Appendix A lists the compounds that were synthesized during this program.

Task 2. Synthesis of 4(4--hydroxy-5',6',7',8'-tetrahydro-1'-naphthylmethyl)-6-methyldibenzothiophene

We have encountered numerous difficulties in the preparation of this compound. The failure to easily produce the model was due to the lack of selectivity of electrophiles generated from electron-rich benzylic alcohols in acidic media toward other electron-rich aromatics. Thus the reactions gave either polymers, low yields of mixtures, or both. From exploratory research we believe that eventually the basic skeleton can be created by using ketone linkages.

Task 3. Synthesis of 1-Hydroxynaphthalene-Dibenzothiophene Polymer Linked by Methylene Bonds

In Task 3, the polymer synthesis, the polymerization of naphthols was found to be facile. However, we found that the polymerization of naphthol or naphthol oligomers and dibenzothiophenes was not competitive because of differences in reactivities between the naphthol and dibenzothiophenes. Therefore we have been attempting to synthesize a dibenzothiophene with a naphthalene unit on either end to be used as the sulfur containing unit, however, although we have only been partially successful at this synthesis, with the final step leading to decomposition products.

INTRODUCTION

To effectively liquefy coal and convert it into usable coal liquids, we need to study the fundamental reaction chemistry for the individual molecular linkages in the coal matrix. For instance, we need to find which linkages are important during coal liquefaction and which substituents on these groups either aid or retard bond breaking. Furthermore, in competitive reactions, we need to know how these functional groups affect each other in hydrogenolysis and hydrogenation chemistry. One method to understand this chemistry is to study molecules designed to represent coal molecules. Thus, the DOE wants synthetic methods for and samples of such coal models with various functional groups thought to be present in coal.

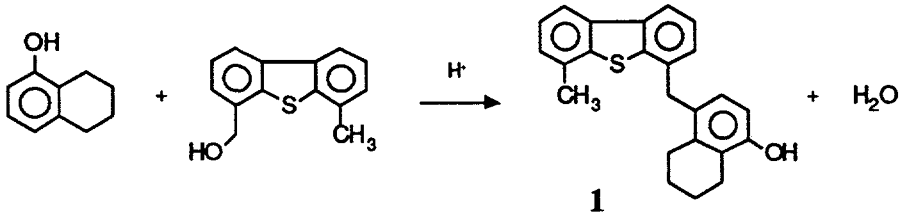
An important functional group in coal is that of sulfur. Given et al. have observed correlations between total sulfur and coal conversion.[1,2] Hydrogen sulfide, and organic sulfur groups that easily cleave to form hydrogen sulfide, are well known to enhance coal liquefaction.[3-9] Thus understanding the role of sulfur, whether organic or inorganic, and its fate is important to understanding coal liquefaction and pyrolysis mechanisms. The organic sulfur in coal is generally one-half to one-third of the total sulfur content, and the organic sulfur in bituminous coals is estimated to be composed mainly of thiophenes (40-70%), with the remainder as sulfides.[10] Sulfides are readily decomposed to liberate H_2S, which aids in coal liquefaction. However, thiophenes are much more stable and readily formed.[10] For instance, iron pyrite reacts with certain hydrocarbons such as ethylene to form thiophenes. Thiophenes are also formed from reactions of organic molecules and H_2S or sulfur. The thiophene ring is reported to be stable up to 800°C, but the alkyl groups may cleave at lower temperatures, such as 500°C. Decomposition of dibenzothiophene is catalyzed by alumina or aluminosilicates. Once thiophenic structures are formed, it is very difficult to decompose or to hydrogenate them, and therefore a knowledge of the reactivities of thiophenes thought to be present in coal or coal liquids is essential to be able to remove the sulfur to produce clean fuels.

The purpose of this research is to develop syntheses for specific coal models and deliver samples of these compounds to the DOE to be presented to various researchers throughout the United States. These particular compounds include sulfur heterocyclic monomers and polymers containing linkages of oxygen, methylene, and ethylene as well as phenolics. These models also contain hydrogen donor functionalities. Thus, these compounds will allow researchers to compare hydrogenolysis reactions of methylene, ethylene linkages, and hydrodesulfurization, hydrodeoxygenation, hydrogen transfer, and hydrogenation reactions.

The goal of this work is to develop syntheses for and supply of one-pound samples of the above sulfur containing compounds thought to be present in coal for coal liquefaction studies. These model compounds are to be packaged in small quantities for long-term storage and delivered to the DOE PETC, which will make them available to researchers throughout the United States for studies of the fundamental reaction chemistry of the individual molecular links in the coal matrix. From these models, researchers can systematically determine the role of each type of bond and functional group for coal liquefaction and pyrolysis.

TASK 2. SYNTHESIS OF 4(4'-HYDROXY-5',6',7',8'-TETRAHYDRO-1'-NAPHTHYLMETHYL)-6-METHYLDIBENZOTHIOPHENE

The objective of this task was to develop a facile synthesis for the coal model 4(4'-hydroxy-5',6',7',8'-tetrahydro-1'-naphthylmethyl)-6-methyldibenzothiophene (**1**). We investigated several potential routes to the synthesis of the target molecule, however, none proved to be feasible routes. The only route that gave the desired product, as described in QR 3, gave only a 2% yield, with mainly polymerization products being formed. This route involved an acid catalyzed condensation as shown in Scheme 1. Because of the strong tendency of acid catalyzed polymerizations an acidic Amberlyst resin was used, but even with this moderated catalyst, only a trace amount of product was formed.



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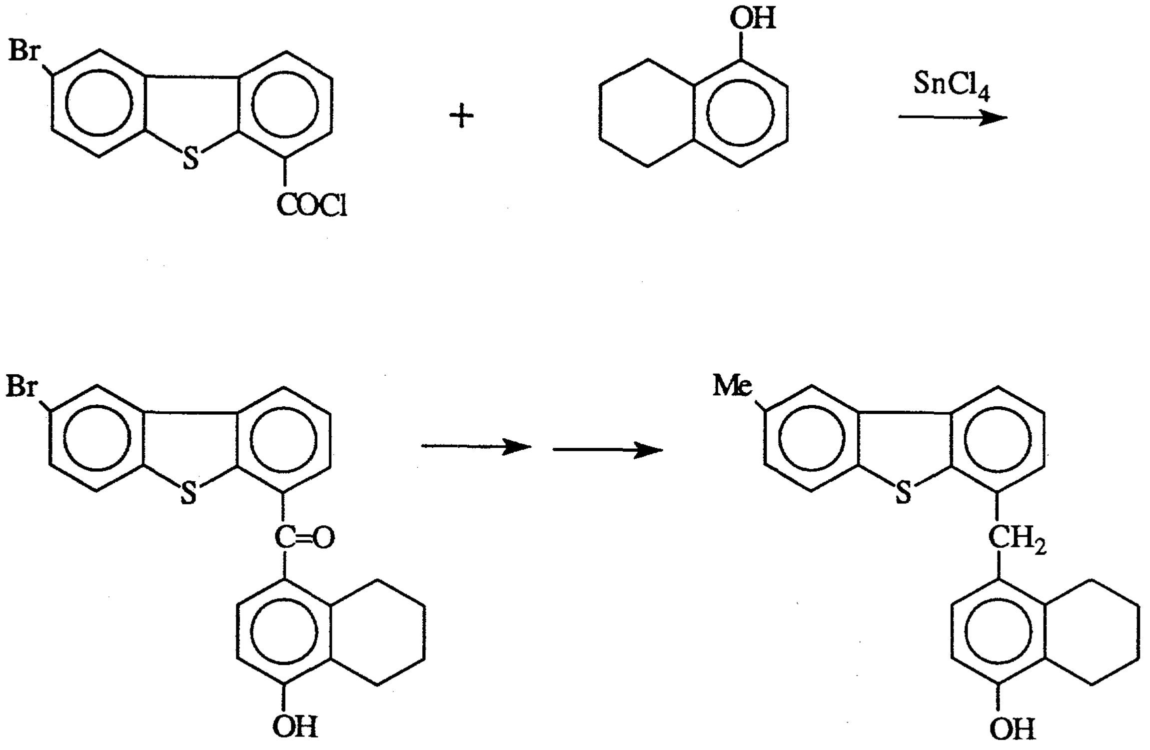
(1)

Scheme 1

Although the desired compounds were not produced during this project, a considerable amount of information was gathered from this task and the following task that will hopefully aid in producing these coal models. Our approaches to the unsymmetrical, disubstituted dibenzothiophene derivative **1** involved sequential metallation/alkylation steps to create an unsymmetrical dialkylated dibenzothiophene that can be coupled with the phenol. The synthesis of target compound **1** has been complicated by two factors: 1) the difficulty of unsymmetrically functionalizing dibenzothiophene without the first functional group undergoing side-reactions during attachment of the second group, and 2) the tendency of intermediates of acid condensation methods to cause self-polymerization. The failure of the Task 1 model was due to the lack of selectivity of electrophiles generated from electron-rich benzylic alcohols in acidic media toward other electron-rich aromatics. Thus the reactions gave either polymers, low yields of mixtures, or both. The attempted synthetic routes are described in Quarterly Reports 1 through 3. We believe the following route (Scheme 2), which avoids are some of these problems, will produce the desired coal models. The route involves using an acylation step to couple the molecule rather than coupling to a benzylic position. A similar acylation step was found to be successful in Task 2. The key problem to be overcome in these reactions is the reduction of the carbonyl intermediate without concurrent polymerization or degradation of the intermediate during the reduction step.



Scheme 2

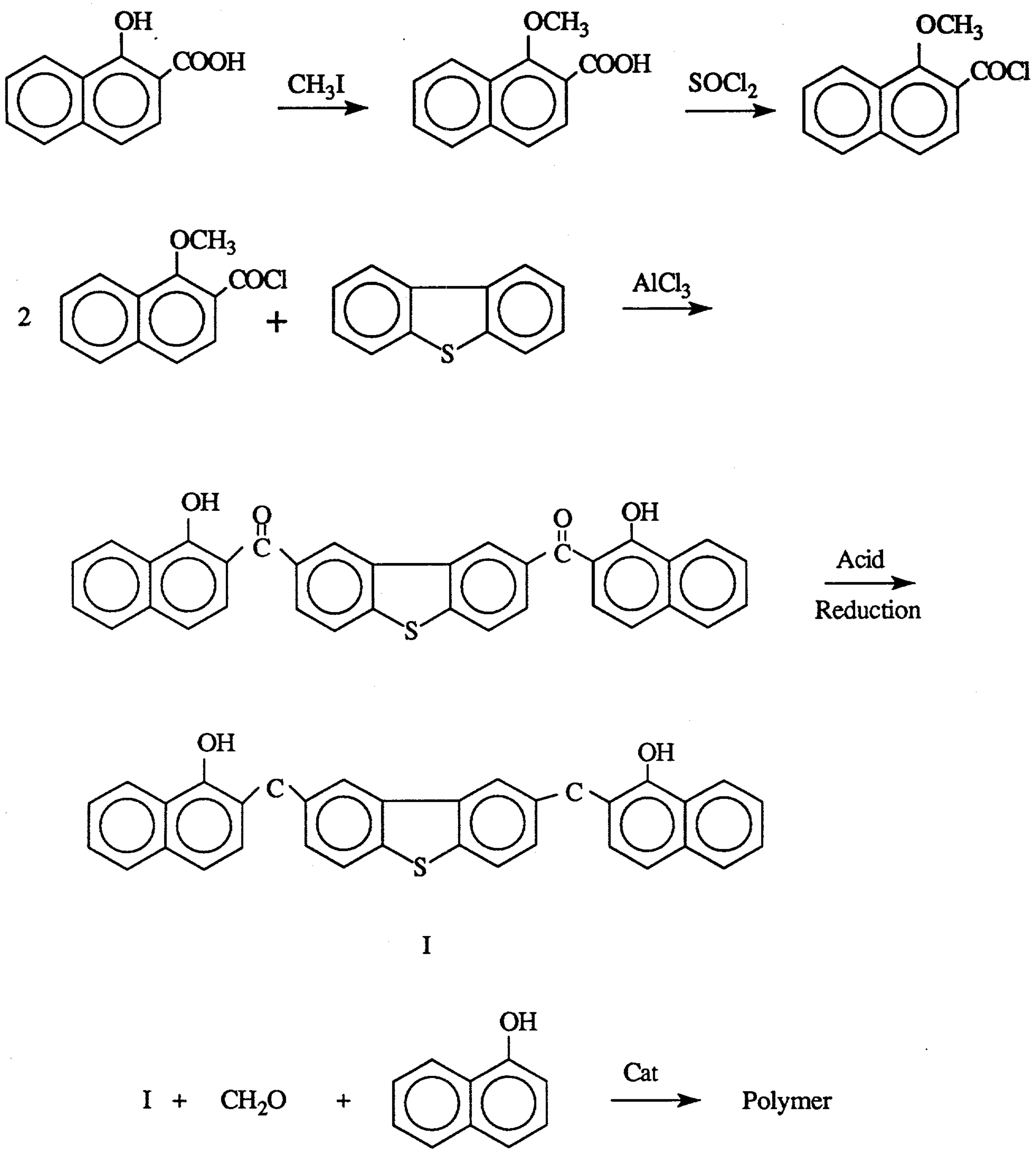
TASK 3. SYNTHESIS OF A 1-HYDROXYNAPHTHALENE POLYMER

The objective of this task is to prepare a copolymer of the 1-hydroxynaphthalene and dibenzothiophene moieties that is linked by methylene groups, contains 2 - 3 weight % sulfur, and has molecular weight in the range 10,000 - 30,000 amu.

Both acid and base catalyzed polymerization of 1-hydroxynaphthalene with formaldehyde to form oligomers was found to be facile with average molecular weights in the range of 1000 to 2000. However, the polymerization of these 1-hydroxynapthalene or these naphthalene oligomers with dibenzothiophene was not competitive because of differences in reactivities between the naphthalenes and dibenzothiophenes, and we could not control the sulfur content in the polymers. Therefore we attempted to synthesize a dibenzothiophene with a naphthalene unit on either end to be used as the sulfur containing unit as shown in Scheme 3. We have been successful with most of this route, with the exception of the last step, the reduction of the ketone. Once the dibenzothiophene has a naphthol unit on either side, its reactivity patter should be similar to that of 1-hydroxynapthalene. Once this unit is synthesized, it can be polymerized with naphthol to produced the sulfur containing polynaphthol polymer. However, as in task 1, the critical step is the ketone reduction. Initial attempts to reduce the ketone by means such as acidic borohydride reduction[11] and by hydrazine reduction have resulted in decomposition of the product.[12] Thus in future work protection of the phenolic groups may be needed to protect the molecule from polymerization and/or decomposition routes. However, the funds provided for this project do not warrant such additional efforts at this time. The following section describes our efforts on this synthesis for this project.

Preparation of disubstituted dibenzothiophene

1-hydroxy napthoic acid (0.159 mol), K_2CO_3 (0.163 mol) and methyl iodide (0.239 mol) were refluxed with 250 mL of anhydrous acetone for 6 hours to give a white slurry. The base was carefully neutralized with 10% HCl and the resultant mixture was extracted with dichloromethane to produce a crude product. The product was then taken up in 100 mL of tetrahydrofuran and 100 mL of 5 N NaOH (aq) to convert any ester to the carboxylic acid. The mixture was acidified with 10% HCl and extracted with dichloromethane to obtain the pure acid (I). The acid was then treated with excess thionyl chloride under argon. The mixture was refluxed for 1 hour, then cooled, evaporated under vacuum to remove all volatiles and crystallized from a dichloromethane/hexane mixture to produce the acid chloride (II) in approximately 60% yield. The acid chloride (II) (5 g) was then mixed with dibenzothiophene (1.91 g) in dichloromethane under argon and the reaction flask cooled to approximately 5°C in an ice bath. Aluminum chloride (5.5 g) was then slowly added to the stirring mixture after which time the reaction was refluxed for 3 hours until no more HCl was given off. The reaction was allowed to cool, and water and HCl were added. The mixture was extracted with dichloromethane, and chromatographed with a 1:1 mixture of hexane and dichloromethane to give predominately the monosubstituted product (III) (34% yield) and some disubstituted product (IV) (<5% yield). Additional disubstituted product (IV) could then be synthesized by taking the monosubstituted product and reacting it with the acid chloride and aluminum chloride in a similar manner, and with a similar yield. Three different methods were used to try to reduce the ketone functionality in (IV), two of the approaches used an acidic reduction medium. For instance, we attempted the reduction in a mixture of trifluroacetic acid using the method of Gribble et al., with an acidic borohydride reduction, and a mixture of trifluroacetic acid with a triethylsilane reductant. Both methods are known to reduce 2-hydroxybenzophenone.[11] The other approach used the method of Whitlock with a hydrazine reduction.[12] The triethylsilane approach gave no reaction and the other two approaches led to product decomposition. In the future, a methylation step of the phenol may help stabilize the intermediate from decomposition during reaction.


OH
COOH
CH_3I
OCH_3
COOH
$SOCl_2$
OCH_3
COCl
OCH_3
2
COCl
+
S
$AlCl_3$
OH
O
C
S
O
C
OH
Acid
Reduction
OH
C
S
C
OH
I
I + CH_2O +
OH
Cat
Polymer

Scheme 3

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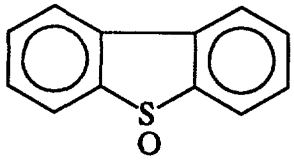
Appendix A

Compounds synthesized during project



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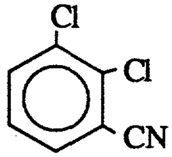

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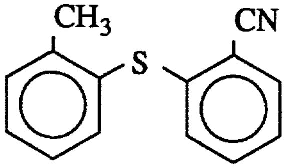

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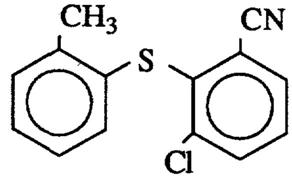

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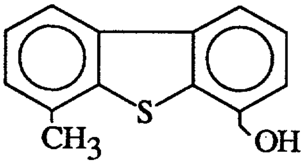

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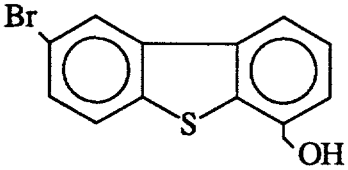

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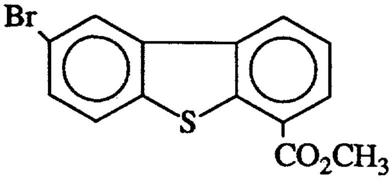

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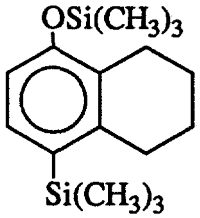

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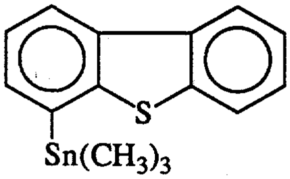

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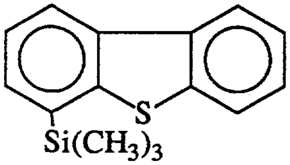

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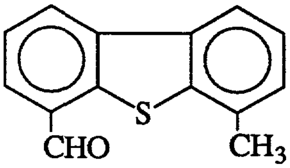

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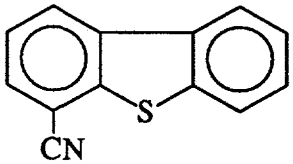

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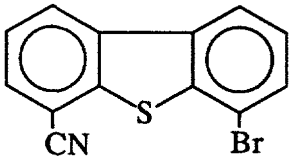

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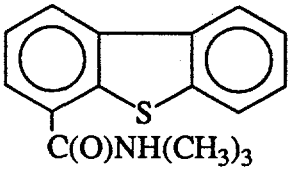

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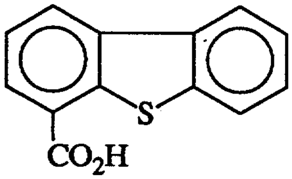

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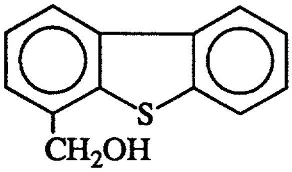

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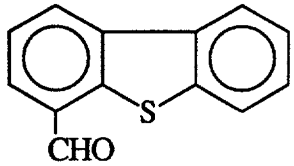

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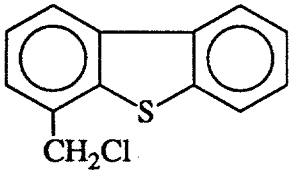

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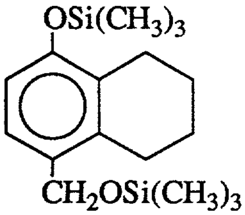

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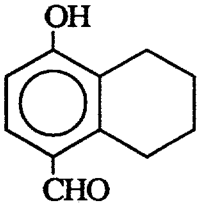

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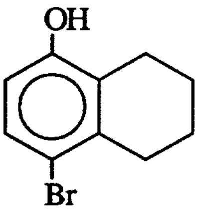

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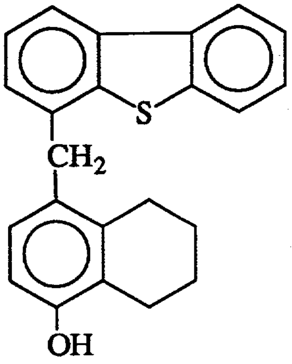

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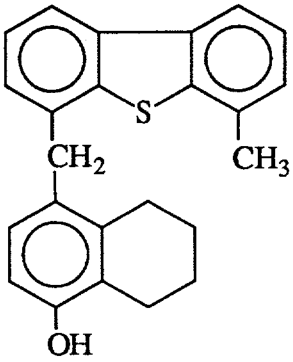

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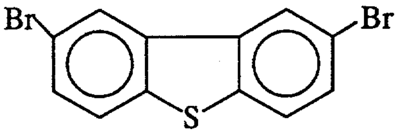

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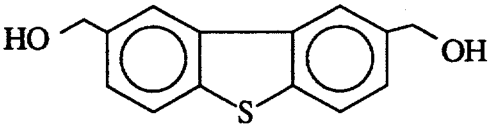

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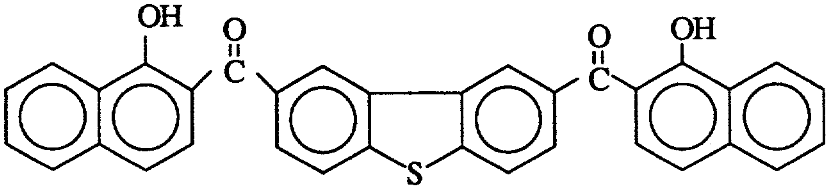

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