

# Aspects of the Chemistry of Donor Solvent Coal Dissolution Reactions. The Reduction of Benzophenone and the Disproportionation of Benzhydrol in Hydrocarbon Solvents at High Temperature

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The reduction of benzophenone by hydrogen donor molecules such as tetralin and dihydroanthracene to give diphenylmethane was investigated in the temperature range 300–400 °C. Several lines of evidence indicate that the reaction occurs in three distinct stages. The first stage is a radical process which gives benzhydrol. In the second stage, this intermediate undergoes an S<sub>N</sub> reaction to produce water and bis(diphenylmethyl) ether. The ether disproportionates in a readily initiated, free radical chain reaction to give diphenylmethane and benzophenone.

## Introduction

Ketones such as benzophenone and fluorenone and quinones such as benzoquinone and dichlorodicyanobenzoquinone have been employed as hydrogen acceptors in studies of the hydrogen donor reactivity of coals and macerals in several laboratories.<sup>1-4</sup> In addition, Brower has proposed that the carbonyl compounds native to coal play a special role in the thermal dissolution reactions of these complex molecules.<sup>5</sup> While it is well-known that benzhydrol, which is presumably the initial product of the reaction between benzophenone and the hydrogen donor molecules in the coals or in the solvents, readily undergoes disproportionation to benzophenone and diphenylmethane at elevated temperature,<sup>1,6-8</sup> the pathways important for the overall conversions of benzophenone to diphenylmethane in hydrocarbon-rich media of the kind that are widely used for the thermal decomposition of coal molecules have not been established. Stein noted that ionic intermediates were probably involved in the disproportionation of benzhydrol at 300 °C.<sup>9</sup> Indeed, a variety of different mechanisms including pericyclic processes, radical displacement reactions, and hydride transfers as well as free radical chain reactions need to be considered. Consequently, we studied the reduction of benzophenone by hydroaromatic compounds and the disproportionation of benzhydrol in hydrocarbon environments to define the course of these thermal reactions with more confidence.

## Results and Discussion

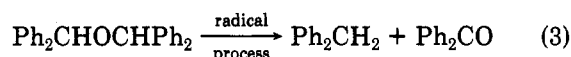
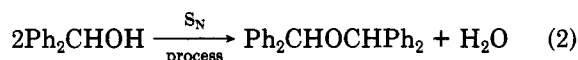
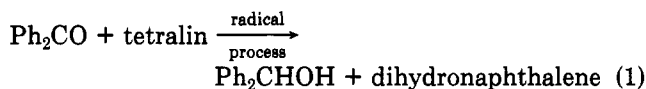
The evidence obtained in this study strongly suggests that benzhydrol and bis(diphenylmethyl) ether are discrete intermediates in the reduction of benzophenone to diphenylmethane by hydroaromatic compounds. The prin-

Table I. The Reduction of Fluorenone to Fluorene by Representative Hydrogen Donors at 400 °C

hydrogen donor	convn to fluorene, %
1,2,3,4-tetrahydroquinoline	28
5,12-dihydrotetracene	14
9,10-dihydroanthracene	14
1,2,3,4,5,6,7,8-octahydroanthracene	6
9,10-dihydrophenanthrene	5
tetralin	3
decalin	0.4

\* Fluorenone (0.025 mmol) and the hydrogen donor (0.025 mmol) were reacted in benzene (50 μL) under argon at 400 °C for 60 min.

cipal reactions are outlined in eq 1–3 for the convenience of this discussion.



Pure hydroaromatic compounds such as tetralin and 1,2,3,4-tetrahydroquinoline reduce benzophenone and fluorenone quite slowly at 400 °C.<sup>1,4,10</sup> Representative results for the reduction of fluorenone to fluorene by various hydroaromatic compounds are shown in Table I. The reduction reactions are greatly accelerated by the addition of small quantities of a representative bituminous coal to the reaction mixture as illustrated for the reactions of tetralin and 9,10-dihydroanthracene with Illinois No. 6 coal in Figure 1. These results and the related information obtained by Collins and his associates in a previous study<sup>1</sup> suggest that free radicals formed in the thermal decomposition reactions of the macromolecular coal molecules initiate the hydrogen-transfer reactions required for the reduction of the ketones. This interpretation was tested by the addition of benzyl phenyl sulfide to reactions of fluorenone and tetralin. The thioether, which is known to accelerate hydrogen atom exchange reactions between tetralin and diphenylmethane and to promote the decomposition of 1,3-diphenylpropane by radical processes,<sup>11</sup> also

(1) (a) Collins, C. J.; Benjamin, B. M.; Raaen, V. F.; Maupin, P. H.; Roark, W. H. In "Organic Chemistry of Coal"; Larsen, J. W., Ed.; American Chemical Society: Washington, D.C., 1978. (b) Raaen, V. F.; Roark, W. H. *Fuel* 1978, 57, 650.

(2) Whitehurst, D. D.; Mitchell, T. O.; Farcasiu, M. "Coal Liquefaction"; Academic Press: New York, 1980.

(3) Peover, M. E. *J. Chem. Soc.* 1960, 5020.

(4) (a) Choi, C.; Stock, L. M. In "Chemistry and Characterization of Coal Macerals"; Winans, R. E., Crelling, J. C., Eds.; American Chemical Society: Washington, D.C., 1984. (b) Choi, C.; Stock, L. M., unpublished work.

(5) (a) Brower, K. R. *Fuel* 1977, 56, 245. (b) Brown, K. R. *J. Org. Chem.* 1982, 47, 1889.

(6) Nef, J. U. *Liebigs Ann. Chem.* 1897, 298, 202.

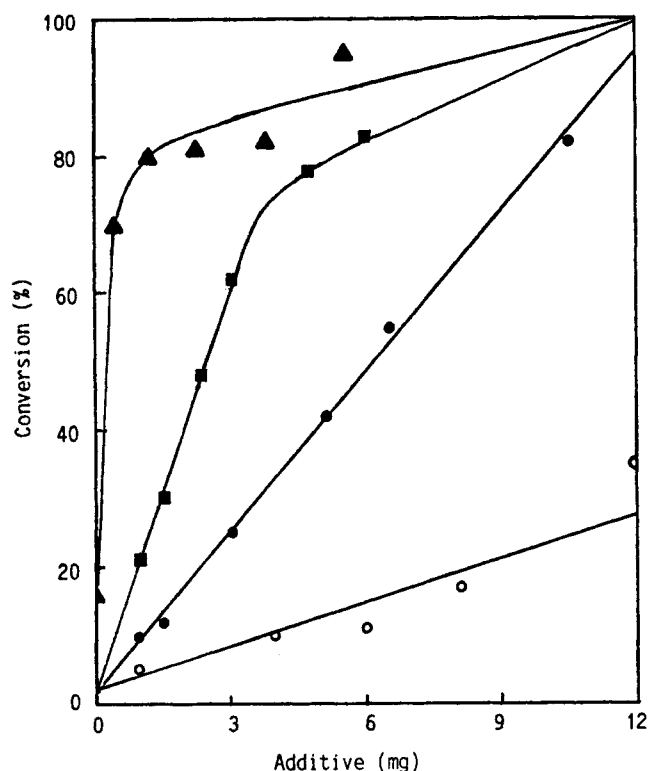
(7) Hurd, C. D. "The Pyrolysis of Carbon Compounds"; The Chemical Catalog Co., Inc.: New York, 1929; p 160.

(8) Jones, D.; Baltisberger, R. J.; Klabunde, K. J.; Woolsey, N. F.; Stenberg, V. I. *J. Org. Chem.* 1978, 43, 175.

(9) Stein, S. E. In "New Approaches in Coal Chemistry"; Blaustein, B. D., Bockrath, B. C., Friedman, S., Eds.; American Chemical Society: Washington, D.C., 1981.

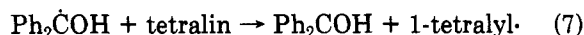
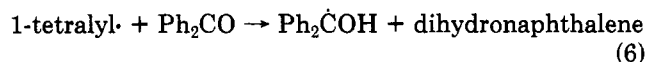
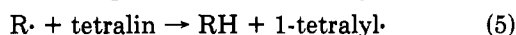
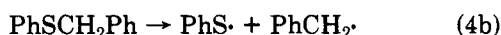
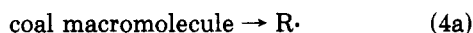
(10) (a) Yao, T.; Kamiya, Y. *Bull. Chem. Soc. Jpn.* 1979, 52, 492. (b) Kamiya, Y.; Yao, T.; Oikawa, S. In "Coal Liquefaction Fundamentals"; Whitehurst, D. D., Ed.; American Chemical Society: Washington, D.C., 1980.

(11) (a) King, H. H.; Stock, L. M. *Fuel* 1981, 60, 257. (b) King, H. H.; Stock, L. M. *Ibid.* 1984, in press.



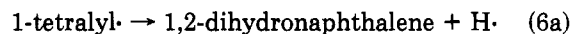
**Figure 1.** The extent of conversion of fluorenone to fluorene in the presence of a hydrogen donor, tetralin, or dihydroanthracene, and varying quantities of an additive, Illinois no. 6 coal or benzyl phenyl sulfide at 400 °C and 60 min. Fluorenone (0.03 mmol) and Illinois no. 6 coal (●); fluorenone (0.03 mmol), tetralin (0.04 mmol), and Illinois no. 6 coal (■); fluorenone (0.03 mmol), dihydroanthracene (0.03 mmol), and Illinois No. 6 coal (▲); fluorenone (0.03 mmol), tetralin (0.04 mmol), and benzyl phenyl sulfide (○).

considerably enhances the rate of the reduction of fluorenone to fluorene by tetralin. Preliminary experiments showed that the addition of 10 mol percent benzyl phenyl sulfide to an equimolar solution of fluorenone and tetralin led to a 7-fold increase in the conversion of fluorenone to fluorene at 400 °C in 15 min. These observations and the results presented in Figure 1 are compatible with the idea that the radicals produced during the thermal decomposition of the complex coal molecules and the thioether initiate a chain reaction as outlined for benzophenone in eq 4-7.



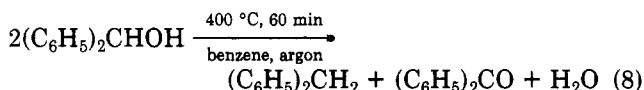
There is ample precedent for the importance of free radicals in the thermal decompositions of bituminous coals in the coal chemistry literature.<sup>1,11-14</sup> Although reaction 6 is not well preceded in the chemical literature,<sup>27</sup> the reaction is exothermic by about 13 kcal/mol as calculated by the Benson approach.<sup>15</sup> Hence, the reaction may be

important when the concentration of benzophenone is high. The alternative formulation involves the production of a hydrogen atom from 1-tetralyl radical (eq 6a and 6b).



The available results do not distinguish between the two alternative formulations. Reaction 7 in which a strong CH bond is formed is well preceded. This formulation of the reaction implies that benzhydrol is an intermediate in the reduction of benzophenone to diphenylmethane by hydroaromatic compounds and is in accord with information in the literature which indicates that benzophenone is reduced to benzhydrol during reactions of the ketone in media that are rich in hydrogen donor molecules. For example, Huyser and Neckers found that the *tert*-butyl peroxide induced reduction of benzophenone in 2-butanol at 130 °C gave benzhydrol as the predominant product.<sup>16</sup> In the present study, benzophenone was reduced by tetralin or 9,10-dihydroanthracene<sup>17</sup> in the presence of excess water at 400 °C. As discussed subsequently, water is necessary to suppress the conversion of benzhydrol to bis(diphenylmethyl) ether. Under these conditions, the reduction of benzophenone yields benzhydrol (3%) and diphenylmethane (7%). In the absence of water, only diphenylmethane is produced. Under similar experimental conditions, Jones and his co-workers reduced benzophenone in the presence of water and were able to detect benzhydrol among the products.<sup>8</sup> Benzhydrol disproportionates rapidly in the absence of water under these conditions to give diphenylmethane and benzophenone. These observations clearly establish that the alcohol is produced during the conversion of benzophenone to diphenylmethane.

It has been known for a long time that benzhydrol disproportionates to benzophenone and diphenylmethane when it is heated above its normal boiling point.<sup>6</sup> More recently, Jones and his co-workers reported that benzhydrol disproportionates at 425 °C to an equimolar mixture of benzophenone and diphenylmethane<sup>8</sup> and Collins and his associates in related work demonstrated that water was the other major product formed in the reduction of benzhydrol in tetralin.<sup>1</sup> These general features of the reaction, which are illustrated in eq 8, were confirmed in



preliminary experiments, but further study of the reaction products revealed that the decomposition of benzhydrol in benzene under an argon atmosphere at 400 °C led, in 60 min, to a mixture of 40% diphenylmethane and 40% benzophenone with 2% bis(diphenylmethyl) ether, a smaller quantity of 1,1,2,2-tetraphenylethane, and traces of tetraphenylethylene and triphenylmethane. Biphenyl is also obtained in small quantities. When the reaction is carried out in benzene-*d*<sub>6</sub>, only biphenyl-*d*<sub>10</sub> is formed, hence this substance is produced exclusively from benzene. The small quantities of the radical coupling products—biphenyl, triphenylmethane, and 1,1,2,2-tetraphenyl-

(16) Huyser, E. S.; Neckers, D. C. *J. Am. Chem. Soc.* **1963**, *85*, 3641.

(12) Cronauer, D. C.; McNeil, R. I.; Young, D. C.; Ruberto, R. G. *Fuel* **1982**, *61*, 610.

(13) Wilson, M. A.; Collin, P. J.; Barron, P. F.; Vassallo, A. H. *Fuel Process. Technol.* **1982**, *5*, 281.

(14) Skowronski, R. P.; Ratto, J. J.; Goldberg, I. B.; Heredy, L. A. *Fuel* **1984**, in press.

(15) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

(17) When 9,10-dihydroanthracene is used instead of tetralin, the degree of conversion of benzophenone to diphenylmethane is greater but the concentration of benzhydrol does not increase in a corresponding amount. Consequently, we suggest that the equilibrium normally favoring the formation of benzhydrol in the presence of excess water is displaced by the highly reactive dihydroanthracene which facilitates the disproportionation of bis(diphenylmethyl) ether into benzophenone and diphenylmethane.

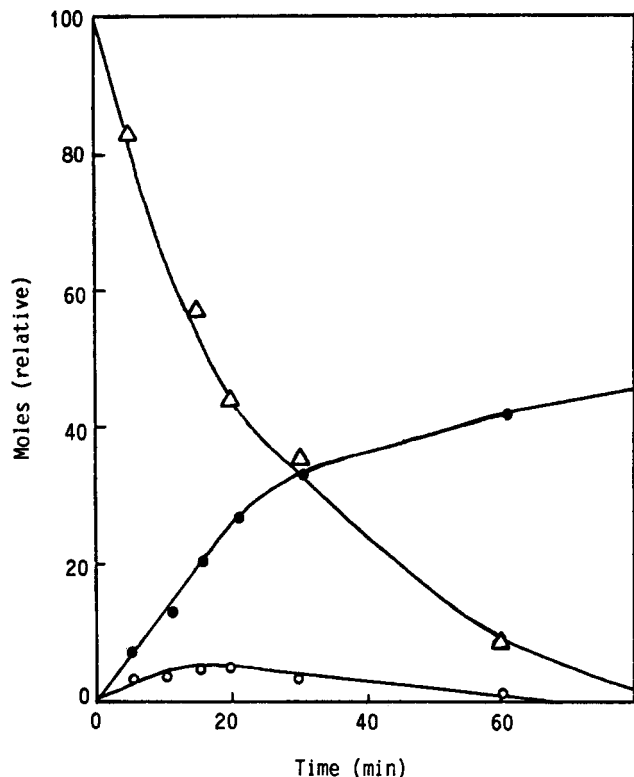


Figure 2. The relative quantities of diphenylmethane (●), benzophenone (●), and bis(diphenylmethyl) ether (○) formed from benzhydrol (Δ) at 400 °C.

Table II. Relative Quantities of Diphenylmethane and Benzophenone Formed during the Decomposition of Bis(diphenylmethyl) Ether at 400 °C

reactn time, min	compn of reactn, mol %		
	Ph <sub>2</sub> CH <sub>2</sub>	Ph <sub>2</sub> CO	(Ph <sub>2</sub> CH) <sub>2</sub> O
5	5	5	82
10	12	12	79
15	17	20	54
20	23	27	46
30	34	32	43
40	38	33	10
60	48	42	2

<sup>a</sup> Bis(diphenylmethyl) ether ( $6.3 \times 10^{-3}$  mmol) and naphthalene ( $3.2 \times 10^{-3}$  mmol) in benzene (50  $\mu$ L) were reacted under argon atmosphere.

ethane—are in accord with the involvement of radicals in the reaction. However, it is difficult to formulate a sensible mechanism for the formation of the products exclusively on the basis of free radical reactions.<sup>18</sup> A study of the rate of formation of the principal products revealed that the concentration of bis(diphenylmethyl) ether at first increased and then decreased as the reaction proceeded, Figure 2. This finding implies that the ether is an intermediate in the reaction. Accordingly, the ether was studied under the same conditions. The decomposition of this pure compound yields the same substances that are formed in the disproportionation reaction. Benzophenone and diphenylmethane are the principal products and the minor constituents—1,1,2,2-tetraphenylethane, tetraphenylethylene, and triphenylmethane—are obtained in even smaller amounts than in the disproportionation of

(18) A mechanism involving a radical displacement reaction on the oxygen of benzhydrol by a benzhydryl radical leads to the same products, diphenylmethane, benzophenone, and water, but this type of reaction mechanism is unprecedented.

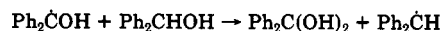


Table III. Degree of Conversion of Benzhydrol, Benzhydrol-*l-d*, and Benzhydrol-*O-d* to Diphenylmethane<sup>a</sup>

substrate $\mu$ mol	additive, $\mu$ mol	conditions		
		temp, °C	time, min	convn, %
Ph <sub>2</sub> CHOH	none	300	30	20
Ph <sub>2</sub> CHOH 5.2	none	350	30	28
Ph <sub>2</sub> CHOH, 5.2	none	400	15	18
Ph <sub>2</sub> CHOH, 5.2	none	400	30	34
Ph <sub>2</sub> CDOH, 5.2	none	300	30	21
Ph <sub>2</sub> CHOD, 5.1	none	300	30	21
Ph <sub>2</sub> CDOH, 5.2	none	400	15	19
Ph <sub>2</sub> CDOH, 5.2	none	400	30	32
Ph <sub>2</sub> CHOH, 5.2	benzyl phenyl sulfide, 0.5	400	15	17
Ph <sub>2</sub> CHOH, 5.2	water, 1400	300	60	0.4
Ph <sub>2</sub> CHOH, 50	water, 2800	400	60	5
Ph <sub>2</sub> CHOH, 50	water, 2800 sodium hydroxide, 50	400	60	1

<sup>a</sup> The reactions were carried out in glass capillaries with benzene (50  $\mu$ L) under an argon atmosphere.

Table IV. The Deuterium Content of the Diphenylmethane Produced in the Reduction Reactions of Benzhydrol and Bis(diphenylmethyl) Ether<sup>a</sup>

substrate, mmol	additive, mmol	conditions		<sup>2</sup> H content of Ph <sub>2</sub> CH <sub>2</sub> , % <sup>b</sup>	
		temp, °C	time, min	ar	Me
Ph <sub>2</sub> CDOH, 0.24	none	300	210	7	76
Ph <sub>2</sub> CHOH, 0.24	tetralin- <i>d</i> <sub>12</sub> , 0.24	300	210	0	13
(Ph <sub>2</sub> CH) <sub>2</sub> O, 0.23	tetralin- <i>d</i> <sub>12</sub> , 0.24	350	120	0	37

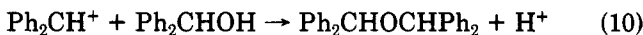
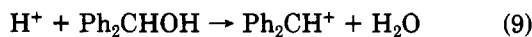
<sup>a</sup> The reactions were carried out as described in Table III. <sup>b</sup> The estimated error is  $\pm 5\%$ .

benzhydrol. Moreover, the principal products are formed at comparable rates under the same conditions, Table II. Thus, the rates and product distributions are entirely compatible with the idea that the ether is an intermediate in the reaction.

The reactions of benzhydrol, benzhydrol-*l-d*, and benzhydrol-*O-d* were examined over a range of temperatures and in the presence of radical initiators and nucleophiles to gain more information on the course of the reaction. Results which are representative of data obtained in replicate experiments (reproducibility,  $\pm 2\%$ ) are summarized in Table III. The deuterium content of the diphenylmethane formed in reactions with labeled molecules is presented in Table IV.

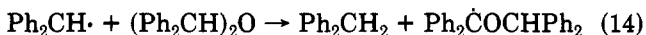
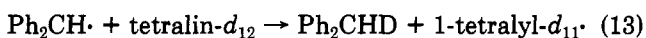
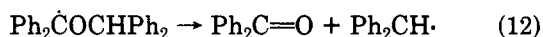
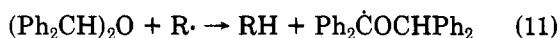
The manner in which benzhydrol is converted into the ether was investigated by the addition of water, phenol, and other substances to the reaction. The fact that the rate of decomposition of benzhydrol is not influenced appreciably by the addition of benzyl phenyl sulfide to the reaction mixture suggests that the conversion is not limited by a radical initiated process. The addition of excess water and excess phenol to the reaction system changes the course of the reaction entirely. The decomposition of benzhydrol in the presence of excess phenol in benzene at 400 °C for 30 min provided the disproportionation products, 28% diphenylmethane, 15% benzophenone and substitution products, 5% 2- and 20% 4-(diphenylmethyl)phenol, and 29% 9-phenylxanthene. The addition of water decreases the rate of the disproportionation reaction and the addition of aqueous base depresses the rate even more, Table III. These observations are most com-

patible with the view that the ether is formed in a reversible, rate-limiting, acid-catalyzed ionic substitution reaction, which is formulated in the simplest possible way in eq 9 and 10. High concentrations of phenol and water



compete with benzhydrol for the ionic intermediates and, therefore, inhibit the disproportionation reaction.

The rates of disproportionation of benzhydrol-*1-d* and benzhydrol-*O-d* to not differ from the rate for the unlabeled alcohol. Consequently, the reaction proceeds without a primary kinetic isotope effect. Thus, the carbon-hydrogen bond is not broken in the rate-limiting step of the reactions. This observation is also compatible with the formation of the ether in a rate-limiting step. However, the rate of the decomposition of the ether is greatly accelerated by the addition of benzyl phenyl sulfide to the reaction system. For example, bis(diphenylmethyl) ether with 10 mol percent benzyl phenyl sulfide decomposes completely to diphenylmethane and benzophenone within 5 min at 400 °C whereas in the absence of benzyl phenyl sulfide, the complete decomposition of bis(diphenylmethyl) ether takes over 60 min, Table II. The decomposition of the ether in the presence of tetralin-*d*<sub>12</sub> leads to the incorporation of deuterium into the reaction products, Table IV. All of these results are compatible with the formulation of the decomposition of the ether as a free radical chain reaction in which reactions 13 and 14 occur com-



petitively. This formulation of the reaction is in accord with the mechanism advanced for the decomposition of benzylic ethers under similar conditions.<sup>11,19,20</sup>

### Conclusion

A representative diaryl ketone such as benzophenone is reduced by hydroaromatic compounds in three steps, eq 1-3, to produce diphenylmethane. Radical reactions and ionic S<sub>N</sub> processes are both important. The fact that bituminous coals and reagents such as benzyl phenyl sulfide initiate the reaction between the ketone and the hydroaromatic compound and other information in the literature provide strong support for the view that the dissociation reactions of the coal molecules initiate the reduction of benzophenone to benzhydrol. When the initiation reagents are present in excess the conversion of the alcohol to the ether in an S<sub>N</sub> process can become the slow step in the sequence. Moreover, nucleophilic agents such as water and phenol change the course of the reaction by the interception of ionic intermediates to yield, in the case of phenol, the products of electrophilic aromatic substitution reactions. There is no doubt that the reactions of the diaryl ketones with bituminous and subbituminous coals are exceedingly complex processes in which the intermediate radicals and ions are adducted to coal molecules in the course of the reaction. However, the reactivity pattern observed in this work indicates that the quantity

of diphenylmethane produced in reactions of a large excess of benzophenone with a coal or a maceral at high temperatures provides a reasonable measure of the capability of the material to initiate the reduction reaction and to serve as a hydrogen donor.

The results obtained in this study also suggest that the diaryl ketones, which are presumably present in only low abundance in bituminous coals, would be reduced and adducted to reactive aromatic molecules under the conditions of coal liquefaction. The formation of 9-phenylxanthene in the reaction with phenol reflects the facility with which these adducts undergo dehydrogenation to form cyclic ethers. Elementary considerations suggest that the polycyclic aromatic hydrocarbons and phenols in the coals are among the most reactive structural elements in these substances. The adduction-cyclization-dehydrogenation reactions with the phenols lead, of course, to cross-linked cyclic ethers which would presumably be detrimental to the achievement of the goals of a liquefaction reaction.

### Experimental Section

The chemicals and solvents used in this work were obtained from commercial sources and purified as necessary prior to use. Bis(diphenylmethyl) ether,<sup>21</sup> bis(9-fluorenyl) ether,<sup>22</sup> 1,1,2,2-tetraphenylethane,<sup>23</sup> diphenylmethyl phenyl ether,<sup>24</sup> 2-(diphenylmethyl)phenol,<sup>24</sup> and 4-(diphenylmethyl)phenol<sup>25</sup> were prepared according to literature procedures. Benzhydrol-*O-d* was prepared by deuterium exchange using sodium ethoxide and deuterium oxide. Benzhydrol-*1-d* was prepared by reduction of benzophenone using lithium aluminum deuteride. Diphenylmethane-*1,1-d*<sub>2</sub> was prepared by reduction of benzophenone with tetralin-*d*<sub>12</sub>. The physical and spectroscopic properties of these materials are in good accord with previously reported values.

The proton NMR spectra were recorded on the Bruker 270-MHz or the Chicago 500-MHz spectrometers with chloroform-*d* as the solvent. Infrared spectra were obtained with a Perkin Elmer 283 instrument with potassium bromide pellets. Product distributions were determined by using a Perkin Elmer 3920B gas chromatograph interfaced with a Sigma 10 data station with a 20% OV-101 on Chromosorb W column (0.125 in. × 20 ft). Mass spectra were recorded on a Finnigan 1015 spectrometer or performed by the University of Illinois at Urbana-Champaign. All the reactions were carried out in a Techno SEL-2 fluidized sandbath.

**Reduction Reactions.** In a typical experiment, fluorenone (4.5 mg, 0.025 mmol), dihydroanthracene (4.5 mg, 0.025 mmol), and benzene (50 μL) were sealed in a glass capillary under an argon atmosphere. The capillary was heated at 400 °C for 60 min. After cooling, the contents of the vessel were extracted into methylene chloride and analyzed by gas chromatography with appropriate internal standards.

**Reaction of Benzophenone with Tetralin.** Benzophenone (70 mg, 0.38 mmol), tetralin (100 μL, 0.78 mmol), and water (50 μL, 2.8 mmol) were sealed in a glass capillary. The capillary was reacted at 400 °C for 4 h. The contents of the capillary were extracted into ether, the solution was dried over magnesium sulfate prior to the removal of the volatile solvents in vacuo. Examination of the remaining products by NMR spectroscopy revealed the benzylic proton frequencies of both benzhydrol (δ 5.83) and diphenylmethane (δ 3.97), with relative peak areas of 1:4. Gas chromatography revealed that 10% of the benzophenone had been converted to products. The reaction in the absence of water

(21) Ward, A. M. *J. Chem. Soc.* 1927, 2285.

(22) Burton, H.; Cheeseman, G. W. H. *J. Chem. Soc.* 1953, 986.

(23) Gilman, H.; Kirby, J. E. *J. Am. Chem. Soc.* 1926, 48, 1733.

(24) Schorigin, P. *Chem. Ber.* 1926, 59, 2502.

(25) Busch, M.; Knoll, R. *Chem. Ber.* 1927, 60, 2247.

(26) Burr, J. G.; Scarborough, J. M.; Shudde, R. H. *J. Phys. Chem.* 1960, 64, 1359.

(27) Note added in proof: D. F. McMillen in a private communication has recently presented persuasive evidence for hydrogen transfer reactions of this kind.

(19) Schlosberg, R. H.; Ashe, T. R.; Pancirov, R. J.; Donaldson, M. *Fuel* 1981, 60, 155.

(20) (a) Gilbert, K. E.; Gajewski, J. J. *J. Org. Chem.* 1982, 47, 4899.  
(b) Gilbert, K. E. *Ibid.* 1984, 49, 6.

showed no trace of benzhydrol after the reaction.

**Thermal Decomposition of Benzhydrol.** A solution of benzhydrol (75.6 mg, 0.413 mmol) and naphthalene (28.3 mg, 0.221 mmol) was prepared in benzene (2 mL). A glass capillary (10 cm, 9 mm OD, 2.5 mm ID) was filled with 25  $\mu$ L of this solution, degassed and sealed under argon, and heated for 20 min in the sandbath at 400 °C. Upon cooling to room temperature, the capillary was cooled under liquid nitrogen and opened and the contents were extracted into chloroform. Gas chromatography revealed that 60% of the benzhydrol had been converted to products: diphenylmethane (42%), benzophenone (44%), triphenylmethane (<1%), 1,1,2,2-tetraphenylethane (1%), tetraphenylethylene (<1%), and bis(diphenylmethyl) ether. The properties of all products were recorded by GC-MS and NMR spectroscopy and were identical to authentic samples.

Experiments with naphthalene in the presence of these materials showed that naphthalene was unreactive under these conditions.

Benzene- $d_6$  was substituted for benzene as the co-solvent in a replicate experiment and the biphenyl produced in the reaction was examined by GC-MS techniques. The MS data were in close agreement with previous reports of the spectrum of biphenyl- $d_{10}$ .<sup>26</sup> Signals corresponding to biphenyl or biphenyl- $d_6$  were absent.

**Thermal Decomposition of Bis(diphenylmethyl) Ether.** A solution of bis(diphenylmethyl) ether (87.8 mg, 0.251 mmol) and naphthalene (16.4 mg, 0.128 mmol) was prepared in benzene (1 mL). A glass capillary was filled with 25  $\mu$ L of this solution, sealed under argon, and reacted for 20 min at 400 °C. Gas chromatography revealed that 46% of the ether had been converted to products: diphenylmethane (46%), benzophenone (54%), triphenylmethane (<1%), and tetraphenylethane (<1%).

**Reaction of Benzhydrol with Phenol.** Benzhydrol (0.712 g, 3.91 mmol), phenol (1.81 g, 19.2 mmol), and benzene (200  $\mu$ L) were placed in a stainless steel reactor and heated at 400 °C for 30 min. The reaction mixture was washed several times with 0.5 N sodium hydroxide and water and extracted into diethyl ether. The ether was dried over magnesium sulfate and the volatile solvents were removed under vacuum. The reaction products were chromatographed on a silica gel column and eluted with mixtures ranging from 1% to 50% diethyl ether in hexane. Fifteen fractions were collected and examined by gas chromatography, mass spectrometry, and nuclear magnetic resonance techniques. Diphenylmethane (28%), dibenzofuran (0.6%), fluorene (trace),

benzophenone (15%), triphenylmethane (0.5%), diphenylmethyl phenyl ether (0.5%), 2-(diphenylmethyl)phenol (5%), 4-(diphenylmethyl)phenol (20%), 9-phenylxanthene (29%), and tetraphenylethylene (0.3%) were shown to be present by comparison with the properties of authentic materials.

**Reaction of Benzhydrol in Nonacidic Aqueous Solution.** (A) **In Neutral Solution.** Benzhydrol (10 mg, 0.05 mmol) dissolved in benzene (25  $\mu$ L) and distilled water (50  $\mu$ L) were sealed in a glass capillary. The capillary was heated at 400 °C for 60 min. The products were dissolved in ether and dried over magnesium sulfate and the volatile solvents were removed under vacuum. Analysis by NMR spectroscopy established that 5% of benzhydrol was converted to diphenylmethane.

(B) **In Basic Solution.** Benzhydrol (10 mg, 0.05 mmol) dissolved in benzene (25  $\mu$ L) and aqueous sodium hydroxide (1 N, 50  $\mu$ L) were reacted in a glass capillary at 400 °C for 60 min. The contents of the capillary were acidified with dilute hydrochloric acid and extracted into ether. The solution was dried over magnesium sulfate and the ether was removed under vacuum. Only 1% of benzhydrol was converted to diphenylmethane.

**Exchange Reactions.** In a typical experiment, bis(diphenylmethyl) ether (81 mg, 0.23 mmol), tetralin- $d_{12}$  (22  $\mu$ L, 0.23 mmol), and benzene (50  $\mu$ L) were sealed in a glass capillary under an argon atmosphere. The capillary was heated at 350 °C for 120 min. After cooling, the contents of the vessel were extracted into methylene chloride and separated by preparative GC. The deuterium contents of the recovered tetralin and diphenylmethane were examined by NMR spectroscopy and gas chromatography with mesitylene as an internal standard.

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**Registry No.** Ph<sub>2</sub>CO, 119-61-9; Ph<sub>2</sub>CHOH, 91-01-0; (Ph<sub>2</sub>CH)<sub>2</sub>O, 574-42-5; Ph<sub>2</sub>CHOD, 90718-39-1; Ph<sub>2</sub>CDOH, 17498-07-6; PhSCH<sub>2</sub>Ph, 831-91-4; Ph<sub>2</sub>CH<sub>2</sub>, 101-81-5; tetralin, 119-64-2; dihydroanthracene, 613-31-0; 1,1,2,2-tetraphenylethane, 632-50-8; diphenylmethyl phenyl ether, 4733-41-9; 2-(diphenylmethyl)phenol, 4970-23-4; 4-(diphenylmethyl)phenol, 791-92-4; diphenylmethane-1,1- $d_2$ , 3947-98-6; fluorenone, 486-25-9; naphthalene, 91-20-3; phenol, 108-95-2; 1,2,3,4-tetrahydroquinoline, 635-46-1; 5,12-dihydrotetracene, 959-02-4; 1,2,3,4,5,6,7,8-octahydroanthracene, 1079-71-6; 9,10-dihydrophenanthrene, 776-35-2; Decalin, 91-17-8; 9-phenylxanthene, 3246-80-8.

## Selective Cleavage of Carbon-Nitrogen Bonds with Platinum

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The selective hydrogenolysis of carbon-nitrogen bonds relative to carbon-carbon bonds with a heterogeneous platinum catalyst is studied on a wide variety of nitrogen-containing organic molecules. Nitriles, secondary and primary amines, nitro compounds, heterocycles, and aromatic amides are cleanly converted to the parent hydrocarbon and ammonia in the gas phase with a platinum on silica catalyst and hydrogen. Aliphatic amides pass the catalyst unchanged. Unusual is the high platinum content of the catalyst (40%) which proved to be essential for the catalytic activity reported.

### Introduction

The cleavage of carbon-nitrogen bonds is a desirable but rarely addressed problem in organic synthesis. Hydrodenitrogenation (HDN) has received increasing attention during the past decade, as the high nitrogen content of synthetic oils derived from shale oil, oil sands, and coal makes hydrodenitrogenation imperative if the liquids are

to be refined to replace products presently obtained from petroleum. The major research activity in hydrodenitrogenation has been the investigation of HDN properties of hydrodesulfurization catalysts which are composed of various combinations of Ni, Mo, W, and Co on different supports.<sup>2</sup> Numerous investigations have consistently shown that these catalysts are not selective

(1) Exxon Fellow.

(2) Shah, Y. T.; Cronauer, D. C. *Catal. Rev.-Sci. Eng.* 1979, 20, 209.