representative conditions for column temperature, flow rate, injector, and detector temperature were 155 °C, 14 mL/min of N_2, 255 °C, and 260 °C, respectively. Retention times for *cis*- and *trans*-stilbene are 3.4 and 11.7 min, respectively. In this representative analysis, retention times of *m*-(trifluoromethyl)acetophenone and fluorenone are 6.4 and 21.8 min, respectively. The internal standard was *trans*-stilbene for both the product (fluorenone and acetophenones) and isomerization (*cis*-stilbene formation) studies. A blank was also measured in which dioxetane was omitted in order to determine the net amount of *cis*-stilbene produced in the presence of dioxetane. Four to five analyses were made for *cis*-stilbene and an average value was used to calculate $\%\alpha_{T_1}$(fluorenone).

Light Emission Measurements. These methods were previously described,[8] except a thermostated aluminum block cell compartment was employed here.

Luminescence Spectrum. The CL spectrum of **2** (Ar = C_6H_5 and *m*-BrC_6H_4) was measured in benzene solution (1.67 × 10^{-4} M) at 66 °C with a Perkin-Elmer MPF-3 spectrofluorimeter with the emission slit set at 10 nm. With **2** (Ar = *m*-BrC_6H_4), the measurement was repeated after purging the solution with N_2 for 30 min. The fluorescence spectrum of fluorenone (1.25 × 10^{-4} M, MCB, recrystallized from cyclohexane) was measured at 66 °C, with emission slit set at 6 nm and excitation wavelength at 320 mn.

Acknowledgment. We thank the U.S. Army Research Office for support of this work and Professor Dewit Coffey for assistance in the use of the Gear numerical integration program.

Thermolysis of Bibenzyl: Roles of Sulfur and Hydrogen Sulfide

Virgil I. Stenberg* and Robert D. Hei

Department of Chemistry, University of North Dakota, Grand Forks, North Dakota 58202

Received June 8, 1984

The presence of sulfur in the thermolysis of bibenzyl considerably reduces the severity of the conditions required to cleave the aliphatic carbon–carbon bond. Bibenzyl rapidly reacts with sulfur at 425 °C to give nine fully characterized products: benzene, toluene, ethylbenzene, diphenylmethane, 1,1-diphenylethane, *trans*-stilbene, phenanthrene, 2-phenylbenzothiophene, and 2,3,4,5-tetraphenylthiophene. Toluene is the principal product, and its yields are dependent on reaction time, temperature, and sulfur loading. With the addition of H_2S to the sulfur–bibenzyl reaction mixture, the required elemental sulfur loading for maximum toluene yields is greatly decreased, and the mass recovery decreases with amounts of sulfur loaded. The two minor products, 2-phenylbenzothiophene and 2,3,4,5-tetraphenylthiophene, give evidence of sulfur incorporation under these sulfur concentration conditions. The addition of hydrogen to the reaction mixtures improves mass recovery and decreases conversion.

The presence of sulfur in the form of hydrogen sulfide (H_2S) or elemental sulfur (S^0) has been found to promote the conversion of diphenylmethane,[1] diphenyl ether,[2] and *N,N*-dimethylaniline,[3] as well as the liquefaction of various coals and lignites.[4,5] Since the cause and effect relationship between sulfur and coal liquefaction is hindered because of limited knowledge about coal structures, it is necessary to study select model compounds to understand the reactivity of elemental sulfur and hydrogen sulfide with organic compounds.

For this study on the cleavage of the ethylene linkage, which has been shown to exist in coals,[6] bibenzyl was selected because it has three important bonds for rupture: (1) methylene hydrogens, (2) two aromatic–aliphatic carbon–carbon bonds, and (3) one aliphatic–aliphatic carbon–carbon bond. The β-bond in bibenzyl is thermally labile and, in the absence of an external source of hydrogen, bibenzyl has been shown to yield toluene and *trans*-stilbene as the major products.[7] In the presence of hydrogen-donor solvents or molecular hydrogen, the major products are toluene, benzene and ethylbenzene.[8,9] In this study, hydrogen sulfide alone is shown to have little effect on the reaction, the conversion, and product distribution, while sulfur under argon, hydrogen sulfide, or hydrogen is found to extensively promote the conversion of bibenzyl to toluene.

Experimental Section

Bibenzyl (Aldrich, Milwaukee, WI), sulfur (J. T. Baker, Phillipsburg, NJ), hydrogen (H. E. Everson Co., Grand Fords, ND), and hydrogen sulfide (Matheson, Joliet, IL) were used as supplied. All reactions were carried out in a 12-mL 316 stainless steel microautoclave.[10] Heat-up time was 2 min and cool-down time was 0.5 min. The times listed refer to times at designated temperatures. After cooling in dry ice–acetone (−78 °C), the gases were vented, the reactor was dismantled, and a known amount of internal standard was added, and the mixture was taken up in ether. This ether solution was used to quantitatively analyze the products. Product analyses were done with a Varian Aerograph Model 2100 gas chromatograph equipped with a 0.64 cm

---

(1) Moreau, R. C. *Bull. Soc. Chim. Fr.* **1955**, 628.

(2) Stenberg, V. I.; Sweeny, P. G., submitted for publication in *Ind. Eng. chem. Fundam.*

(3) Stenberg, V. I.; Srinivas, V. R.; Sweeny, P. G.; Baltisberger, R. J.; Woolsey, N. F. *Fuel* **1983**, *62*, 913.

(4) (a) Baldwin, R. M.; Vinciguerra, S. *Fuel* **1983**, *62*, 498. (b) Ratcliffe, C. T.; Abdel-Baset, M. B. *Prepr. Pap.—Am. Chem. Soc., Div. Fuel Chem.* **1979**, *25*, 1. (c) Bearden, R., Jr.; Aldridge, C. L. U.S. Patents 4 149 959 (1979) and 4 094 765 (1978). (d) Okutani, T.; Yokoyama, S.; Maekawa, Y.; Furuichi, R.; Ishii, T. *Ind. Eng. Chem. Process Des. Dev.* **1983**, *22*, 306.

(5) Sondreal, E. A.; Willson, W. G.; Stenberg, V. I. *Fuel* **1982**, *61*, 925.

(6) (a) Heredy, L. A.; Kostyo, A. E.; Neuworth, M. B. *Fuel* **1965**, *44*, 125. (b) Benjamin, B. M.; Douglas, E. C.; Canonico, D. M. *Fuel* **1984**, *63*, 888.

(7) (a) Benjamin, B. M. *Fuel* **1978**, *57*, 378. (b) Miller, R. E.; Stein, S. E. *J. Phys. Chem.* **1981**, *85*, 580.

(8) Cronauer, D. C.; Jewell, D. M.; Shah, Y. T.; Kueser, K. A. *Ind. Eng. Chem. Fundam.* **1978**, *17*, 291.

(9) Vernon, L. W. *Fuel* **1980**, *59*, 102.

(10) Van Buren, R. L.; Stenberg, V. I. *Chem. Ind.* (*London*) **1980**, 569.

0022-3263/85/1950-1810$01.50/0

Table I. Reaction Conditions

reacn system	temp, °C	time,[a] min	bibenzyl, mmol	Ar,[b] psi	H_2, psi	H_2S, psi	S^0, mol × 10^{-3}
pyrolysis (argon)	450	30	2.8	800			
H_2S	450	30	2.8			50	
H_2	450	30	2.8		1000		
H_2S–H_2	450	30	2.8		1000	50	
sulfur	450	30	2.8				2.8
sulfur–argon (sulfur concn study)	425	15	2.8				0–5.6
sulfur–H_2S (sulfur concn study)	425	15	2.8			245	0–2.8
sulfur–argon (reacn temp study)	270–450	15	2.8				2.8
sulfur–H_2S (reacn temp study)	270–425	15	2.8			245	0.56
sulfur–H_2	425	15	2.8		1000		2.8

[a] Reaction time excludes 2-min heat-up. [b] All reactions include 1 atm argon.

Table II. Effect of H_2S, H_2, H_2S–H_2, and S_8 on the Thermolysis of Bibenzyl[a]

	reacn system				
	Ar[b]	H_2S[c]	H_2[d]	H_2–H_2S[e]	S_8[f]
product, mol %					
benzene	1.6	0.1	46.3	21.2	1.2
toluene	50.7	51.3	55.4	49.1	77.8
ethylbenzene	0.9	1.1	24.0	14.7	0.5
diphenylmethane	0.5	1.2	0.1	0.1	0.5
1,1-diphenylethane	1.7	11.0	2.0	12.7	1.0
bibenzyl	45.1	40.9	33.2	41.8	4.8
trans-stilbene	16.6	12.9	0.4	0.2	0.7
phenanthrene	1.4	0.8	0.7	0.5	0.1
2-phenylbenzothiophene					9.0
2,3,4,5-tetraphenylthiophene					2.6
% conversion	54.9	59.1	66.8	58.2	95.2
% cleavage	26.6	26.2	62.8	42.4	40.0
% mass recovery	90.8	93.0	94.4	97.6	63.3

[a] Reaction conditions: 2.75 mmol of bibenzyl, 30 min,[g] 450 °C, argon (1 atm). [b] 800 psi. [c] 50 psi. [d] 1000 psi. [e] H_2 (1000 psi), H_2S (50 psi). [f] 0.088 g of S_8 (2.75 mmol of S^0). [g] The reaction time excludes a 2-min heat-up.

× 183 cm OV-17 on 80/100 Supelcoport column. The temperature of the column was programmed to increase at a rate of 10 °C/min from 30 to 300 °C, and the products were identified by GC/MS (Hewlett-Packard 5875B and Hewlett-Packard 5970A). GC/MS analyses were carried out for three samples obtained from different reaction conditions, and the mass spectra of all compounds were compared to those found in the literature.[11] The mass spectra of the two identified organosulfur compounds are as follows: 2-phenylbenzothiophene, m/e (relative %) 212 (5.5), 211 (17.3), 210 (100.0), 208 (13.9), 178 (13.2), 165 (20.5), 105 (7.0), 104 (4.2); 2,3,4,5-tetraphenylthiophene, m/e (relative %) 390 (9.3), 389 (29.4), 388 (100.0), 310 (7.8), 309 (8.2), 308 (8.4), 281 (7.0), 278 (6.2), 267 (6.8), 265 (8.7), 209 (5.3), 208 (7.9), 190 (5.8), 178 (7.3), 165 (15.1), 155 (16.6), 154 (6.3), 121 (8.3). Retention times for most products were compared with those of commercially available authentic samples. All reactions were duplicated. An elemental analysis was obtained for the polymer formed in the bibenzyl–sulfur–hydrogen sulfide (1.0 mol:0.2 mol:3.0 mol) reaction done at 425 °C in 15 min. The polymer was separated from other products and washed with CS_2, THF, $(C_2H_5)_2O$, and C_2H_5OH and dried at room temperature for 24 h.

Reactor Cleaning Procedure. After the reactions, the tubes were rinsed with water, treated with concentrated HNO_3 for 1 h, rinsed with water and acetone, and scrubbed with steel wool. This procedure was repeated, after which the reactors were washed with aqueous $NaHCO_3$, rinsed with acetone and distilled water, and dried at 110 °C. The valves were washed several times with acetone and diethyl ether.

Reaction Conditions. See Table I.

Time Study of the S^0–*trans*-Stilbene System. The reaction temperature was 425 °C, and the system included 0.12 g of *trans*-stilbene (0.67 mmol), 0.22 g of S^0 (0.67 mmol), and argon (1 atm).

Two-Stage Reaction with H_2. The first stage consisted of exposing 0.5 g of bibenzyl (2.8 mmol) to a reaction temperature of 425 °C, 0.088 g of S^0 (2.8 × 10^{-3} mol), and argon (1 atm) for 0.25 h. For the second stage, the reactor was cooled and vented, and then the cooled reactor was pressurized with 1000 psi of H_2 and heated for 45 min at 425 °C.

Two-Stage Reaction with H_2 and Catalyst. The first stage consisted of exposing 0.5 g of bibenzyl (2.8 mmol) to a reaction temperature of 425 °C, 0.088 g of S^0 (2.8 × 10^{-3} mol), and argon (1 atm) for 0.25 h. For the second stage, 0.05 g of Harshaw Co–Mo-0402T1/8 catalyst was added after cooling and venting, and then the reactor was pressurized with 1000 psi of H_2 and heated for 45 min at 425 °C.

Calculations. The calculations were done by a method of internal standards. The internal standard, tetralin, was chosen on the basis that it is separated from product peaks on the GLC chromatogram. Response factors were determined from standard solutions. Mole percents were calculated by dividing the moles of each product by the starting moles of bibenzyl and multiplying the result by 100. The maximum yields of benzene, ethylbenzene, and toluene are 200%. The conversion percent equals 100 minus the mole percent of recovered bibenzyl. The high molecular weight product percent equals 100 minus the mass recovery (total grams of all identifiable products).

Gas Analyses. Methane, ethane, ethylene, and propane were quantitatively determined on an F and M Scientific 700 GLC with a Porapak Q column. The hydrogen sulfide concentration was determined by using the American Society for Testing and Materials procedure 0-2383.

Results

At 450 °C under an argon atmosphere, toluene and *trans*-stilbene are the principal products formed in 30 min. Vernon[9] has reported the pyrolysis of bibenzyl in a stainless steel bomb at 450 °C produced mostly toluene, *trans*-stilbene, and smaller amounts of phenanthrene. The data of Table II illustrate the effect of H_2S, H_2, H_2S–H_2, and S^0 on the thermolysis of bibenzyl. The presence of H_2S causes only a slight increase in conversion but has no effect on the toluene, benzene, and ethylbenzene yields. However, a rearrangement[12] forming 1,1-diphenylethane

---

[11] "EPA/NIH Mass Spectral Data Base". *Natl. Bur. Stand. Circ. (U.S.)* 1978, NSRDS-NBS 63.

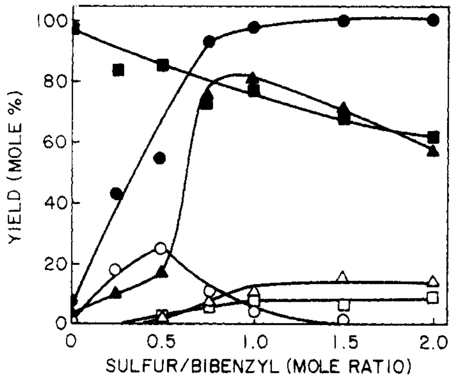


Figure 1. Bibenzyl–sulfur–argon (1.0 atm) reaction products and conversion as a function of sulfur concentration at 425 °C and 15-min reaction time: (●) conversion; (▲) toluene; (■) mass recovery; (○) *trans*-stilbene; (△) 2-phenylbenzothiophene; (□) 2,3,4,5-tetraphenylthiophene.

(1,1-DPE) is promoted. In a hydrogen atmosphere, the conversion and yields of benzene and ethylbenzene are increased, and, within experimental error, the toluene yield is unaffected. Vernon[9] and more recently Burr and Javeri[13] have interpreted these results in terms of a radical chain mechanism in which the chain carrier is the hydrogen atom. The rate of formation of toluene is first order with respect to bibenzyl concentration and independent of hydrogen pressure, and the rate of formation of benzene and ethylbenzene is first order with respect to both bibenzyl and molecular hydrogen concentrations. The results presented here are consistent with these earlier studies. A combination of hydrogen and hydrogen sulfide decreases the conversion, benzene, and ethylbenzene yields as compared to the data when hydrogen is used. The toluene yield is relatively unaffected. When sulfur under argon is used, virtually complete conversion can be achieved to yield nine products, but the mass recovery is lower. The major identifiable product is toluene. A gas analysis of a sulfur–bibenzyl reaction showed that hydrogen sulfide (7 wt %) is formed along with small amounts of low molecular weight carbon-containing compounds. A large portion of the product mixture is high molecular weight (HMW) material. The elemental analysis for the polymer (HMW material) obtained by using H_2S and S^0 was as follows: C, 75.80; H, 4.27; S, 19.43. Sulfur incorporation is found in two identifiable products: 2-phenylbenzothiophene (2-PBT) and 2,3,4,5-tetraphenylthiophene (4-PT).

The data of Figure 1 illustrate that virtually complete conversion of bibenzyl can be achieved in 15 min at 425 °C with increasing amounts of sulfur in the reaction mixture. Relatively low conversion, 7% occurs when no sulfur is present. *trans*-Stilbene is the predominant characterized product at low sulfur concentrations, but it decreases at higher sulfur concentrations. The yield of toluene increases dramatically between a sulfur:bibenzyl ratio of 0.5 and 1.0. At higher sulfur loadings, the yields of 2-PBT and 4-PT both increase and then level off. The mass recovery is inversely proportional to the amount of sulfur added.

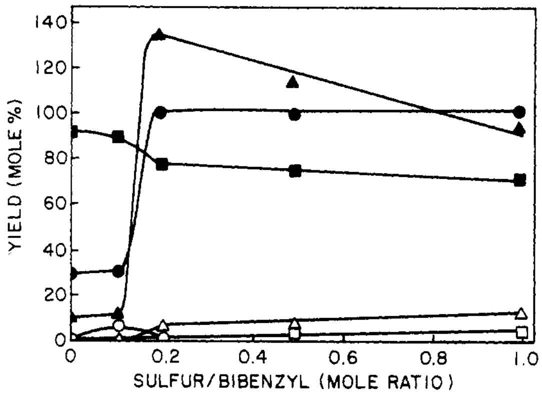


Figure 2. Bibenzyl–sulfur–hydrogen sulfide reaction products and conversion as a function of sulfur concentration with the bibenzyl:hydrogen sulfide mole ratio of 3.0, a reaction temperature of 425 °C, and a reaction time of 15 min: (●) conversion; (▲) toluene; (■) mass recovery; (○) *trans*-stilbene; (△) 2-phenylbenzothiophene; (□) 2,3,4,5-tetraphenylthiophene.

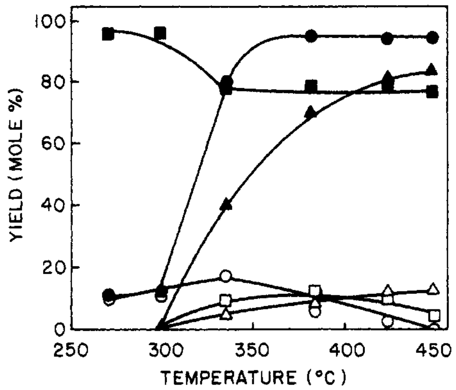


Figure 3. Bibenzyl–sulfur–argon (1.0 atm) reaction products and conversion as a function of temperature with the mole ratio 1.0 mol:1.0 mol and a reaction time of 15 min: (●) conversion; (▲) toluene; (■) mass recovery; (○) *trans*-stilbene; (△) 2-phenylbenzothiophene; (□) 2,3,4,5-tetraphenylthiophene.

Table III. Effect of S_8 on the Thermolysis of *trans*-Stilbene[a]

	reacn time,[b] min			
	0	2.0	4.0	5.0
product, mol %				
toluene	28.5	30.7	41.4	45.6
1,1-diphenylethane	1.5	1.5	2.0	3.0
bibenzyl	0.8	0.3		
trans-stilbene	30.7	14.6	9.2	4.1
2-phenylbenzothiophene	18.3	15.6	13.0	15.7
2,3,4,5-tetraphenylthiophene	13.3	13.1	10.2	11.5
% conversion	69.3	85.4	90.8	95.9
% mass recovery	97.5	74.2	69.6	69.8

[a] Reaction conditions: 0.67 mmol of *trans*-stilbene, 0.67 mmol of S^0, 425 °C, argon (1 atm). [b] The reaction time excludes a 2-min heat-up.

The data of Table III illustrate that *trans*-stilbene is unstable in the presence of sulfur (1.0 mol:1.0 mol) at 425 °C. Considerable conversion of *trans*-stilbene occurs during the 2-min heat-up period and then increases with reaction time. Toluene is the major cleavage product, and its yields increase with reaction time. 2-PBT and 4-PT are formed rapidly, and their yields remain essentially constant. With increasing time the amount of HMW material increases.

When sulfur is added to the hydrogen sulfide–bibenzyl reaction mixture, the extent of conversion and the yield of toluene increase; cf. Figure 2. A relatively small amount of sulfur is needed to promote conversion to the cleavage product toluene. Its maximum yield occurs when a molar sulfur:bibenzyl ratio of 0.2 is reached. When the reaction is done with higher ratios, the mass recovery decreases. The yields of 2-PBT and 4-PT slightly increase with increased sulfur loading.

---

(12) Poutsma, M. L. *Fuel* **1980**, *59*, 335.

(13) Burr, J. G.; Javeri, I. *Fuel* **1984**, *63*, 854.

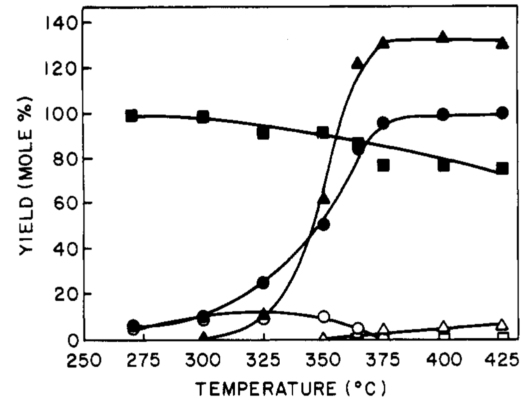


Figure 4. Bibenzyl–sulfur–hydrogen sulfide reaction products and conversion as a function of temperature with the bibenzyl:sulfur:hydrogen sulfide ratio of 1.0 mol:0.2 mol:3.0 mol and the reaction time of 15 min: (●) conversion; (▲) toluene; (■) mass recovery; (○) *trans*-stilbene; (△) 2-phenylbenzothiophene; (□) 2,3,4,5-tetraphenylthiophene.

Table IV. Effect of H_2 on the Bibenzyl–Sulfur System

	S^0 [a]	S^0–H_2 [b]	S^0 [c] or H_2 [f]	S^0 [d] or H_2–cat. [f]
1st step				
time, min	15	15	15	15
H_2, psig	0	1000	0	0
2nd step [e]				
time, min	0	0	45	45
H_2, psig	0	0	1000	1000
product, mol %				
benzene		1.1	2.5	22.8
toluene	77.1	79.3	84.1	83.6
ethylbenzene		0.6	0.6	5.4
diphenylmethane	0.3	0.2	0.4	2.2
1,1-diphenylethane	0.3	0.5	0.4	0.9
bibenzyl	8.0	29.5	10.0	16.7
trans-stilbene	4.4	0.4		
2-phenylbenzothiophene	9.4	5.4	5.4	
2,3,4,5-tetraphenylthiophene	7.1	2.9	4.4	
% conversion	92.0	70.5	90.0	83.3
% mass recovery	75.6	82.6	70.0	76.1

[a] Bibenzyl (0.5 g); S^0:bibenzyl mole ratio = 1.0; 425 °C. [b] Bibenzyl (0.5 g); S^0:bibenzyl mole ratio = 1.0; 425 °C; H_2 (1000 psi). [c] 1st step data. Two-step reaction. 1st step: 0.5 g bibenzyl; S^0:bibenzyl mole ratio = 1.0; 425 °C. 2nd step: H_2 (1000 psi); 425 °C. [d] 1st step data. Two-step reaction. 1st step: 0.5 g bibenzyl; S^0:bibenzyl mole ratio = 1.0; 425 °C. 2nd step: H_2 (1000 psi); 425 °C; 10 wt % of bibenzyl commerical Harshaw CO-MO catalyst. [e] A second step was not used for the reactions shown in the first two columns. [f] 2nd step data.

The data of Figure 3 illustrate a temperature study of the bibenzyl–sulfur reaction done under argon. In the 15-min reaction time, the conversion increases with increasing temperature up to 385 °C and then levels off at higher temperatures. *trans*-Stilbene is the principal product at lower temperatures but decreases in concentration at the higher temperatures. 2-PBT and 4-PT appear at higher temperatures. 2-PBT increases linearly over all temperatures while the 4-PT yield maximizes at 385 °C and then decreases at higher temperatures. The low-boiling product toluene is not formed at 270 °C but becomes the predominant product at higher temperatures. Mass recovery decreases significantly between 270 and 335 °C and then levels off at higher temperatures.

With hydrogen sulfide and sulfur concentrations constant, increasing reaction temperatures increase conversion and reduce mass recovery; cf. Figure 4. The toluene yield roughly parallels the conversion, while the *trans*-stilbene yield parallels mass recovery. The yield of 2-PBT increases with increasing reaction temperature.

The addition of hydrogen to a reaction mixture with a sulfur:bibenzyl molar ratio of unity causes mass recovery to increase at the expense of conversion; cf. Table IV. Only minor changes in the product distribution occur, but most notable is the lowering of the 2-PBT and 4-PT yields.

When bibenzyl is first exposed to sulfur at 425 °C for 15 min and the reaction contents are then reacted with hydrogen for 45 min without workup except for venting of gases formed in the first step, only slight changes in the reaction system occur; cf. Table IV. When a commercial desulfurizing catalyst (cobalt–molybdenum oxide) is included in the second step, the yields of 2-PBT and 4-PT are found to vanish. The main benefactors of this desulfurization appear to be the yields of benzene, ethylbenzene, and bibenzyl. Overall mass recovery is unaffected.

Discussion

The principal objective of this study is to use sulfur and hydrogen sulfide for achieving aromatic–aliphatic or aliphatic–aliphatic bond rupture of bibenzyl under as mild conditions as possible.

Hydrogen-donor solvents have been used to react with the thermolysis fragments of bibenzyl, i.e., presumably benzyl radicals, to yield toluene.[8,14] Under these conditions, solvent incorporation and isomerization have been demonstrated. Molecular hydrogen has been shown to cleave bibenzyl at the α-position, with the rate being dependent upon the concentration of hydrogen.[9,15]

Elemental sulfur causes rapid conversion of the moderately strong (57 kcal/mol)[9,16] carbon–carbon β-bond in bibenzyl under relatively mild conditions. Sulfur is known to rupture, forming a variety of $\cdot S_x\cdot$ diradical species during thermal reactions.[17] These sulfur species are expected to be reactive toward bibenzyl and promote conversion. Nearly quantitative conversion of bibenzyl was found as the ratio of sulfur to bibenzyl was increased. In the absence of hydrogen, the starting material, an excellent hydrogen donor, must act as the hydrogen source. Consequently, the formation of *trans*-stilbene occurs together with intractable, high molecular weight products. The latter are presumed to be due to organic polysulfides. The occurrence of 2-phenylbenzothiophene and 2,3,4,5-tetraphenylthiophene demonstrates the formation of aliphatic carbon–sulfur bonds.

Aromatic substitution reactions of halogenated aromatics by thermally produced sulfur species ($\cdot S_x\cdot$[18] and $HS\cdot$[19]) have been demonstrated. No evidence is found for a similar homolytic substitution reaction of bibenzyl to yield phenethyl ($C_6H_5CH_2CH_2\cdot$) and thiophenolic ($C_6H_5S_x\cdot$) radicals. Formation of 2-phenylbenzothiophene demonstrates an aromatic substitution reaction by sulfur of a hydrogen atom. Formation of a probable intermediate 1

---

[14] (a) Sato, Y.; Yamakawa, T.; Onishi, R.; Kameyama, H.; Amano, A. *Sekiyu Gakkaishi* **1978**, *21* (2), 110. (b) Benjamin, B. M.; Raaen, V. F.; Maupin, P. H.; Brown, L. L.; Collins, C. J. *Fuel* **1978**, *57*, 269.

[15] Govek, M. Ph.D. Dissertation, University of North Dakota, Grand Forks, ND, 1980.

[16] Coleman, D. J.; Pilcher, G. *Trans. Faraday Soc.* **1966**, *62*, 821.

[17] (a) Pryor, W. A. "Mechanisms of Sulfur Reactions"; McGraw-Hill: New York, 1962; p 8. (b) Meyer, B. *Chem. Rev.* **1976**, *76*, 367. (c) Oae, S., Ed. "Organic Chemistry of Sulfur"; Plenum Press: New York, 1977; pp 43–44. (d) Gee, G. *Trans. Faraday Soc.* **1952**, *48*, 515.

[18] (a) Hortling, B.; Borchers, K.; Lindberg, J. J. *Phosphorus Sulfur* **1981**, *11*, 111. (b) Oae, S.; Tsuchida, Y. *Tetrahedron Lett.* **1972**, *13*, 1283.

[19] Voronkov, M. G.; Deryagina, E. N. *Phosphorus Sulfur* **1979**, *7*, 123.

leading to the high selectivity to toluene (β-cleavage) and the dehydrogenation reaction to yield *trans*-stilbene are rationalized by the pathway in Scheme I. It is assumed that the normal disproportionation reaction to yield *trans*-stilbene is also occurring. Bibenzyl appears to undergo a facile benzyl hydrogen atom abstraction in the presence of sulfur. This finding is consistent with Tagaki et al.'s[20] results in which a sulfur radical was found to initiate the sulfur reactions of other bibenzylic compounds by abstraction of the benzylic hydrogens. The dehydrogenation reaction to yield *trans*-stilbene is reversible as evidenced by the formation of small quantities of bibenzyl, and even larger yields of toluene, when *trans*-stilbene is pyrolyzed in the presence of sulfur (Table III). A major loss of *trans*-stilbene is through formation of 2-PBT, 4-PT, and HMW material.

Scheme I

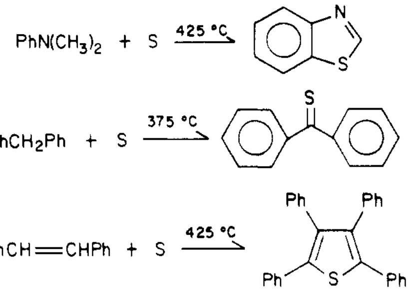
$$S_8 \underset{}{\overset{\text{heat}}{\rightleftharpoons}} \cdot S_x\cdot \qquad (1)$$

$$PhCH_2CH_2Ph + \cdot S_x\cdot \rightleftharpoons Ph\dot{C}HCH_2Ph + HS_x\cdot \qquad (2)$$

$$Ph\dot{C}HCH_2Ph + \cdot S_x\cdot \rightleftharpoons \underset{1}{PhCH(\dot{S}_x)CH_2Ph} \qquad (3)$$

$$Ph\dot{C}HCH_2Ph + \cdot S_x\cdot \rightleftharpoons PhCH{=}CHPh + HS_x\cdot \qquad (4)$$

By analogy, intermediate 1 is proposed on the basis of the formation of benzothiazole from *N,N*-dimethylaniline, thiobenzophenone from diphenylmethane, and 2,3,4,5-tetraphenylthiophene from *trans*-stilbene; cf. reactions 5–7.[3,21,22] These products suggest the precursor intermediates 2, 3, and 4, and the cited products are presumed to be trapped forms of the corresponding intermediates.



(5)

(6)

(7)

$$\underset{2}{PhNRCHS\cdot} \qquad \underset{3}{PhCH(S\cdot)Ph} \qquad \underset{4}{PhCH(S\cdot)CHPh}$$

For the bibenzyl reaction, a 1,2-rearrangement of 1, analogous to 1,2-shifts in various oxygen[20,23,24] and sulfur[20] systems with a subsequent hydrogen atom abstraction, would give rise to bibenzyl sulfide. This could pyrolyze in the presence of sulfur to produce toluene as the major cleavage product. A similar 1,2-rearrangement to yield phenyl β-phenethyl sulfide, which could pyrolyze to yield thiophenol and ethylbenzene, is inconsistent with the results. One factor hindering this second rearrangement might be the high α-bond (Ph—CH$_2$CH$_2$Ph, 97 kcal/mol)[25] dissociation energy vs. the lower β-bond (PhCH$_2$—CH$_2$Ph, 57 kcal/mol)[9,16] dissociation energy. An alternate mechanism where intermediate 1 undergoes a direct β-scission to a benzyl radical and thiobenzaldehyde, followed by reduction, is also possible. The current work cannot differentiate between the two mechanisms.

To increase yields by improving the hydrogen-donor conditions, hydrogen sulfide, a second source of hydrogen atoms, was introduced into the reaction solution. Hydrogen sulfide is expected to react with elemental sulfur in accordance with eq 8.[26] It is known that hydrogen sulfide decreases the chain length (S$_x$) and increases the reactivity of sulfur at elevated temperatures.[27]

$$\cdot S_x\cdot + H_2S \rightleftharpoons HS_x\cdot + HS\cdot \qquad (8)$$

Comparing Figures 1 and 2, sulfur in the presence of argon is a reactant and gives a maximum toluene yield at a sulfur:bibenzyl ratio of 1.0, while in the presence of high pressures of hydrogen sulfide, smaller loadings of elemental sulfur are required for complete conversion of bibenzyl and higher yields of toluene. The toluene yield enhancement is most probably the result of appropriate radical quenching by the increased amount of available hydrogens in the medium. The increase in conversion with lower loadings of sulfur is consistent with the operation of eq 8, which increases the number of sulfur radicals in the system.

The reaction of sulfur with bibenzyl (1.0 mol:1.0 mol) at 425 °C is rapid, and this is emphasized by the observation that near-complete conversion was obtained during the 2-min heat-up time. *trans*-Stilbene was formed early in the reaction, but its yields decreased with time. 2-PBT and 4-PT appear to be the main benefactors of these secondary reactions. Toluene was the principal product at high-conversion levels.

The presence of sulfur in these reaction mixtures reduced the severity of the reaction conditions necessary to get quantitative thermal conversion of bibenzyl. Temperature studies of the bibenzyl–sulfur (1.0 mol:1.0 mol; Figure 3) and bibenzyl–sulfur–hydrogen sulfide (1.0 mol:0.2 mol:3.0 mol; Figure 4) systems show that temperatures of ca. 300 °C are required to cause substantial conversion in the 15-min reaction time. Dehydrogenation, by cleavage of methylene carbon–hydrogen bonds, is the principal reaction at lower temperatures, while cleavage of the aliphatic carbon–carbon bond, to form toluene, predominates at higher temperatures. This observation infers that there is a higher activation energy for cleavage of the aliphatic carbon–carbon bond vs. the methylene carbon–hydrogen bond. The extent of reaction greatly increases at temperatures at which carbon–carbon bond cleavage to toluene occurs.

Hydrogen sulfide augments the ability of sulfur to quantitatively convert bibenzyl into products. A mixture of sulfur and hydrogen sulfide converts a higher percentage of bibenzyl into low molecular weight identifiable products than does elemental sulfur alone. To account for this, hydrogen sulfide can increase the (1) sulfur radical concentration by the action of eq 8[26] and/or (2) hydrogen-donor capacity of the medium to donate hydrogen atoms[5] to radicals before they form HMW products. Using a constant ratio of sulfur to bibenzyl (0.2 mol:1.0 mol), a hydrogen sulfide concentration study revealed that increasing the hydrogen sulfide concentration increased conversion. The conversion increase was not linear with hydrogen sulfide concentration but jumped from 39% at a bibenzyl:hydrogen sulfide ratio of 1.0 to 100% at a ratio of 2.0. Low concentrations of hydrogen sulfide did little to influence the sulfur–bibenzyl reaction whereas higher

---

(20) Tagaki, W.; Kiso, S.; Oae, S. *Bull. Chem. Soc. Jpn.* **1965**, *38*, 414.
(21) Moreau, R. C. *Bull. Soc. Chim. Fr.* **1955**, 918.
(22) Horton, A. W. *J. Org. Chem.* **1949**, *14*, 761.
(23) Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1969**, *47*, 3797.
(24) Wieland, H. *Ber.* **1911**, *44*, 2553.
(25) Reference 15, p 17.
(26) Wiewiorowski, T. K. *Endeavour* **1970**, *29*, 9.
(27) (a) Wiewiorowski, T. K.; Touro, F. J. *J. Phys. Chem.* **1966**, *70*, 234. (b) Mayer, R. In ref 17c, pp 64–65.

concentrations had an important effect. This could be attributed to the known reaction of hydrogen sulfide with the metals in the reactor walls. When a glass reactor was used, the effect of hydrogen sulfide on the sulfur–bibenzyl reaction was nearly linear.

The ultimate success of using sulfur and H_2S to cleave bibenzyl will depend upon controlling the formation of high molecular weight products. These materials have sulfur incorporated into their structures. The two-step reactions in Table IV show that desulfurization of 2-PBT and 4-PT is readily accomplished but recovery of higher molecular weight products is more difficult. Inclusion of hydrogen in a high-sulfur reaction, Table IV, demonstrates that improving the mass recovery is possible while maintaining high reactivity in the bibenzyl–sulfur system to yield toluene.

In conclusion, elemental sulfur is shown to be very reactive with bibenzyl at conditions that would be considered as relatively low coal liquefaction temperatures and short reaction times.

Acknowledgment. We are grateful for the financial support via a Mining and Mineral Resources Research Fellowship (R.D.H.), a Fellowship from the University of North Dakota Energy Center (R.D.H.), and a contract from the Department of Energy. We thank David Miller for providing GLC/MS data and Art Ruud for the gas analyses.

Stereochemistry of P–N Bond Cleavage. First Crystal and Structural Assignment in Cyclic Phosphoramidofluoridates[†]

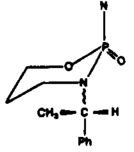
Konrad Misiura,[‡] James V. Silverton,*[§] and Wojciech J. Stec*[‡]

Polish Academy of Sciences, Centre of Molecular and Macromolecular Studies, Department of Bioorganic Chemistry, 90362 Lodz, Poland, and Laboratory of Chemistry, National Heart, Lung, and Blood Institute, National Institutes of Health, Bethesda, Maryland 20205

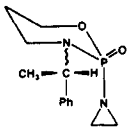
Received September 26, 1984

Diastereomers of 2-(*N*-ethyleneimino)-2-oxo-3-(α-methylbenzyl)-1,3,2-oxazaphosphorinane have been found to react with poly(hydrogen fluoride–pyridine). Displacement of the ethyleneimino ligand by the fluoride ion is fully stereospecific and occurs with inversion of configuration at the P atom. This is proved by X-ray crystallographic examination of the product resulting from 2(*S*)-(ethyleneimino)-2-oxo-3-[(*S*)-α-methylbenzyl]-1,3,2-oxazaphosphorinane. In this product the phosphorinane N atom is nearly planar and, thus, is equatorially substituted.

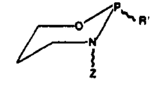
Diastereomers of 2-(*N*-ethyleneimino)-2-oxo-3-(α-methylbenzyl)-1,3,2-oxazaphosphorinane (1) have proven to be valuable intermediates in the synthesis of enantiomeric forms of alkylating anticancer drugs such as cyclophosphamide and its congeners (2).[1] The abolute configuration at the P atom in diastereomers of 1 was unambigously assigned by X-ray crystallographic determination of the absolute configuration in both enantiomers of cyclophosphamide (**2a**),[2] which was derived from 1 by stereochemically well-defined pathways: opening of the aziridinyl ring by means of HCl, chloroacetylation at the exocyclic nitrogen atom, and sequential reduction of the carbonyl function with diborane followed by hydrogenolytic cleavage of the α-methylbenzyl/carbon–endocyclic nitrogen bond. All of the steps occur without cleavage of any bond directly attached to the stereogenic phosphorus atom.



(S,S$_p$)-1a



(S,R$_p$)-1b



2a Z = H, R = O, R′ = $N(CH_2CH_2Cl)_2$
2b Z = CH_2CH_2Cl, R = O, R′ = $NHCH_2CH_2Cl$
2c Z = CH_2CH_2Cl, R = O, R′ = $N(CH_2CH_2Cl)_2$
2d Z = Ch_2CH_2Cl, R = O, R′ = $NHCH_2Ch_2X$

Since alkylating and chemotherapeutic properties of cyclophosphamide congeners may differ from the parent compound **2a** if the β-halo alkyl function attached to the nitrogen atom is varied, we investigated the stereospecific synthesis of compounds **2d**, X = Br, I, SO_3CF_3, F. We present here the stereochemical results of the reaction of 1 with poly(hydrogen fluoride–pyridine) (3).

Discussion

In contrast to the reaction of 1 with hydrogen bromide, which leads to opening of the aziridinyl ring and formation of the corresponding (β-bromoethyl)amido derivative **2d**, X = Br,[3] treatment of (*S*,*S*$_p$)-1 with 3 under strictly anhydrous conditions leads to the cleavage of the phosphorus–exoxyclic nitrogen bond and formation of 2-fluoro-2-oxo-3-(α-methylbenzyl)-1,3,2-oxazaphosphorinane (4). This observation is not unprecedented: Skrowaczewska and Mastalerz in 1955 reported splitting of the P–N bond by hydrogen halides[4] and Greenghalgh and Blanchfield in 1966 demonstrated that the reaction of dialkyl phosphoramidates with hydrogen fluoride gives dialkyl phosphorofluoridates.[5] However, compounds such as isophosph-

---

[†] This work is dedicated to Prof. Jan Michalski on the occasion of his 65th birthday.

[‡] Polish Academy of Sciences.

[§] National Heart, Lung, and Blood Institute.

(1) Pankiewicz, K; Kinas, R.; Stec, W. J.; Foster, A. B.; Jarman, M.; Van Maanen, J. M. S. *J. Am. Chem. Soc.* **1979**, *101*, 7712–7718.

(2) Stec, W. J. "Organophosphorus Chemistry-Specialist Periodical Reports"; Hutchinson, D. W., Miller, J. A., Eds; The Royal Society of Chemistry: London, 1982; Vol. 13, pp 145–174 and reference cited therein.

(3) Misiura, K.; Stec, W. J., unpublished results.

(4) Skrowaczewska, Z.; Mastalerz, P. *Rocz. Chem.* **1955**, *29*, 415–430.