as an eluent. The resultant material was added to 80 mL of concentrated H_2SO_4 stirred at 0 °C. The reaction mixture was stirred 1.75 h at 0 °C until a homogenous solution was obtained. Ice was added, and the aqueous phase was extracted with ether. The organic phase was dried and the solvent removed under reduced pressure to give an oil which was subjected to MPLC on silica with 1:99 ether/hexane as an eluent to afford a clear, colorless oil. The oil was treated with 2,4-dinitrophenylhydrazone solution to give 2.71 (18%) of the 2,4-dinitrophenylhydrazone of cyclohexyl ethyl ketone as an orange solid, mp 147–148 °C (lit.[32] mp 149–151 °C).

Acknowledgment. We are grateful to the National Institutes of Health, Institute of General Medicine, for support of this work and to Dr. M. Baillargeon for advice and assistance.

Registry No. **2** (R = Me), 63846-76-4; **2** (R = Et), 77256-39-4; **2** (R = *n*-heptyl), 77256-40-7; **2** (R = Ph), 77256-41-8; **2** (R = CH_2OMe), 77256-42-9; **2** (R = CH_2NMe_2), 77256-43-0; **2** (R = *n*-pentadecyl), 77256-44-1; **2** (R = $CH=CH_2$), 77256-45-2; **3** (R = Me), 77256-46-3; **3** (R = H), 77256-47-4; **3** (R = *n*-butyl), 77256-48-5; **6** (Ar = 2,4,6-triisopropylphenyl; R = Me; E = D), 77256-49-6; **6** (Ar = 2,4,6-triisopropylphenyl; R = Me; E = $CH_2CH=CH_2$), 68027-60-1; **6** [Ar = 2,4,6-triisopropylphenyl; R = Me; E = $(CH_2)_3CH_3$], 77256-50-9; **6** [Ar = 2,4,6-triisopropylphenyl; R = Me; E = Sn $[(CH_2)_3CH_3]_3$], 68058-27-5; **6** [Ar = 2,4,6-triisopropylphenyl; R = Me; E = $Si(CH_3)_3$], 68027-61-2; **6** [Ar = 2,4,6-triisopropylphenyl; R = CH_3; E = $HOC(CH_3)_2$], 68027-59-8; **6** [Ar = 2,4,6-triisopropylphenyl; R = CH_3; E = $HOC(CD_3)_2$], 68027-62-3; **6** [Ar = 2,4,6-triisopropylphenyl; R = Me; E = $HOC(CH_2)_5$], 77256-51-0; **6** [Ar = 2,4,6-triisopropylphenyl; R = Me; E = $HOCHCH_3$], 77256-52-1; **6** [Ar = 2,4,6-triisopropylphenyl; R = Me; E = $CH_2N(CH_3)_2$], 77256-53-2; **6** [Ar = 2,4,6-triisopropylphenyl; R = Me; E = $HOCCH=CH(CH_2)_3$], 77256-54-3; **6** [Ar = 2,4,6-triisopropylphenyl; R = Et; E = D], 77256-55-4; **6** [Ar = 2,4,6-triisopropylphenyl; R = Et; E = $HOC(CH_3)_2$], 77256-56-5; **6** (Ar = 2,4,6-triisopropylphenyl; R = Et; E = $CH_2CH=CH_2$), 77256-57-6; **6** [Ar = 2,4,6-triisopropylphenyl; R = $(CH_2)_6CH_3$; E = D], 77256-58-7; **6** [Ar = 2,4,6-triisopropylphenyl; R = $(CH_2)_6CH_3$; E = $CH_2CH=CH_2$], 77256-59-8; **6** [Ar = 2,4,6-triisopropylphenyl; R = $(CH_2)_6CH_3$; E = $Si(CH_3)_3$], 77256-60-1; **6** [Ar = 2,4,6-triisopropylphenyl; R = $(CH_2)_6CH_3$; E = $HOC(CH_3)_2$], 77256-61-2; **6** (Ar = 2,4,6-triisopropylphenyl; R = Ph; E = CH_3), 77256-62-3; **6** [Ar = 2,4,6-triisopropylphenyl; R = $CH_2N(CH_3)_2$; E = D], 77256-63-4; **6** [Ar = 2,4,6-triisopropylphenyl; R = $CH_2N(CH_3)_2$; E = $(CH_2)_3CH_3$], 77256-64-5; **6** [Ar = 2,4,6-triisopropylphenyl; R = $(CH_2)_{14}CH_3$; E = D], 77256-65-6; **6** [Ar = 2,6-bis(dimethylamino)-3,5-diisopropylphenyl; R = Me; E = D], 77256-66-7; **6** [Ar = 2,6-bis(dimethylamino)-3,5-diisopropylphenyl; R = CH_3; E = $CH_2CH=CH_2$], 77256-67-8; **6** [Ar = 2,6-bis(dimethylamino)-3,5-diisopropylphenyl; R = CH_3; E = $Si(CH_3)_3$], 77256-68-9; **6** [Ar = 2,6-bis(dimethylamino)-3,5-diisopropylphenyl; R = CH_3; E = Sn $[(CH_2)_3CH_3]_3$], 77256-69-0; **6** [Ar = 2,6-bis(dimethylamino)-3,5-diisopropylphenyl; R = CH_3; E = $HOC(CD_3)_2$], 77256-70-3; **6** [Ar = 2,6-bis(dimethylamino)-3,5-diisopropylphenyl; R = C_4H_9; E = D], 77256-71-4; **7** (E = H), 77256-72-5; **8** (E = CH_3), 77256-73-6; **9**, 77256-74-7; **10**, 77256-75-8; **11** [Ar = 2,4,6-(*i*-Pr)$_3$Ph; R = CH_3], 77256-51-0; **12** [Ar = 2,4,6-(*i*-Pr)$_3$Ph; R = Et], 77256-76-9; 2,4,6-triisopropylbenzoic acid, 49623-71-4; 2,4,6-triisopropylbromobenzene, 21524-34-5; isopropyl 2,4,6-triisopropylbenzoate, 77256-77-0; 1,3-diisopropyl-4,6-dinitrobenzene, 77256-78-1; 4,6-diamino-1,3-diisopropylbenzene, 3102-71-4; 2,6-diamino-3,5-diisopropylbromobenzene, 77256-79-2; 2,6-bis(dimethylamino)-3,5-diisopropylbromobenzene, 77256-80-5; 2,6-bis(dimethylamino)-3,5-diisopropylbenzoic acid, 77256-81-6; isopropyl 2,6-bis(dimethylamino)-3,5-diisopropylbenzoate, 77256-82-7; 2-(2-phenylpropyl) 2,4,6-triisopropylbenzoate, 77256-83-8; 2-heptanol, 543-49-7; 2′-hexyl 3,5-dinitrobenzoate, 10574-13-7; 2′-nonyl 3,5-dinitrobenzoate, 77256-84-9; 2-methyl-2,3-butanediol, 5396-58-7; cyclohexyl methyl ketone 2,4-dinitrophenylohydrazone, 1160-74-3; cyclohexyl ethyl ketone 2,4-dinitrophenylhydrazone, 1163-56-0; *m*-diisopropylbenzene, 99-62-7.

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Preparation, Characterization, and Flash Vacuum Pyrolysis of Dibenz[*c*,*e*][1,2]oxathiin 6-Oxide (Biphenylene Sultine)

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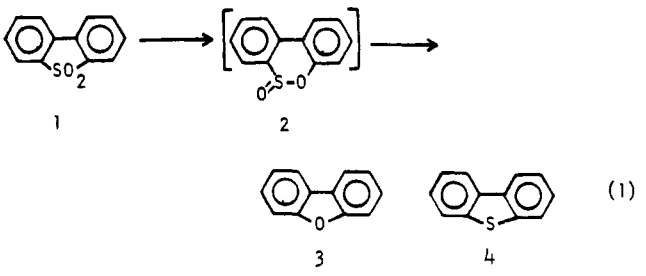
Received March 11, 1981

Dibenz[*c*,*e*][1,2]oxathiin 6-oxide (**2**), previously proposed as an intermediate in the pyrolysis of dibenzothiophene 5,5-dioxide (**1**), has been prepared by the treatment of **1** with KOH in the presence of crown ether followed by an acid workup. The likely intermediacy of the dipotassium salt of 2-(2-hydroxyphenyl)benzenesulfinic acid is demonstrated. Flash pyrolysis of **2** gives dibenzofuran and dibenzothiophene in essentially the same ratio as when they are formed in the pyrolysis of **1**, suggesting that both products arise from the intermediacy of **2**.

Pyrolysis of dibenzothiophene 5,5-dioxide (**1**) at 690 °C over Vycor chips with contact times of 15 s is reported to afford a 95% yield of a 6:1 mixture of dibenzofuran (**3**) and dibenzothiophene (**4**)[1] (eq 1). Fields and Meyerson proposed that **1** rearranges to sultine **2** which extrudes SO to give **3**.[1] A mechanism to account for the formation of **4** was not suggested. The proposal of the intermediacy of sultine **2** has not been verified because, until now, it has not been prepared. Fully unsaturated 1,2-oxathiins are known only with sulfur in the +6 oxidation state (sul-



1 2 3 4 (1)

†Operated for the U.S. Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Assistant Secretary for Fossil Energy, Office of Coal Mining, WPAS-AA-75-05-05.

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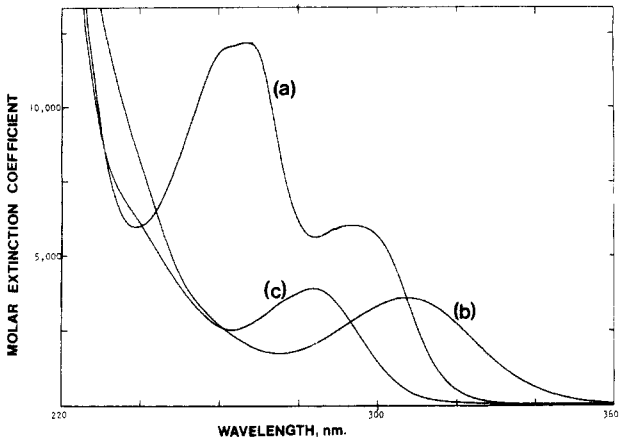
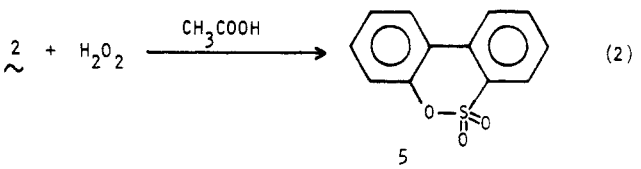


Figure 1. Dependence of the ultraviolet spectrum of biphenylene sultine (2) on pH: (a) biphenylene sultine (2), (b) dipotassium salt of 2-(2-hydroxyphenyl)benzenesulfinic acid (7), (c) 2-(2-hydroxyphenyl)benzenesulfinic acid (8). See Experimental Section for details.

tones).[2-4] Because dibenzothiophene derivatives are believed to constitute a large fraction of the organic sulfur structures in coal,[6] we have been studying the chemical[7] and pyrolytic[8] reactions of dibenzothiophene and its oxidized derivatives.

Results and Discussions

Treatment of dibenzothiophene 5,5-dioxide (1), in refluxing mesitylene (163 °C) with KOH pellets in the presence of 18-crown-6, followed by an acid workup, gave, besides 2-phenylphenol and potassium 2-phenylbenzenesulfonate, a new compound in 30% yield which proved to be isomeric with 1 on the basis of elemental and mass spectral analysis. None of this product was observed in the absence of crown ether even at long reaction times. The absence of SO_2 absorbtion in the infrared and the presence of putative S=O bands near 1150 cm^{-1} and the observation of 12 different carbons in the carbon NMR strongly suggested the sultine structure, 2. Chemical proof of the structure took advantage of two common reactions of sulfinate esters. First, oxidation to the known sultone, dibenz[c,e][1,2]oxathiin 6,6-dioxide (5)[9] (eq 2) was carried



(2)

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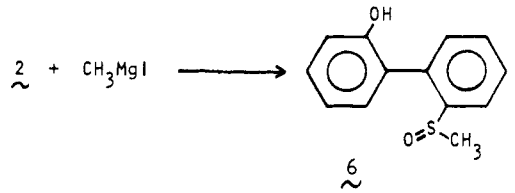
out with hydrogen peroxide in acetic acid. Sulfinate esters also react rapidly with organometallic reagents, particularly Grignard reagents, to give sulfoxides.[10] Treatment of 2 with methyl magnesium iodide, followed by acid workup, gave a new material whose spectral properties [IR 3150 (OH), 1000 and 1010 cm^{-1} (S=O); ^1H NMR δ 2.58 (s, 3 H), 6.9–8.1 (m, 8 H)] and elemental analysis were consistent with the predicted structure 6 (eq 3).



(3)

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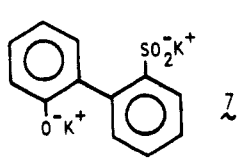
The sultine 2 is the cyclic ester of 2-(2-hydroxyphenyl)benzenesulfinic acid. It is insoluble in water yet is isolated by acidification of the basic aqueous layer from the workup procedure. This suggests that 7 is the actual



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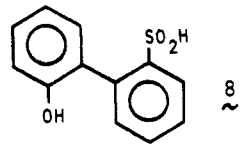

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product of the reaction and that its conjugate acid, 8, cyclizes to 2 during workup. The intermediacy of 7 is further supported by the observation that 2 reacts rapidly with dilute KOH in 90% CH_3CN–H_2O to give a species whose ultraviolet spectrum (curve b, Figure 1) is markedly different from that of 2 itself (curve a, Figure 1). Reacidification of the dilute basic solution with HCl until it is weakly acidic causes another change in the spectrum (curve c, Figure 1). The third curve is the ultraviolet spectrum of 2-(2-hydroxyphenyl)benzenesulfinic acid or its potassium salt,[11] the long wavelength band in sulfinic acids and their salts being virtually identical.[12] In this case they may be obscured by the relatively stronger phenol band. The difference in the long-wavelength position in curves 2 and 3 ($\Delta\lambda$ = 23 nm) is consistent with the shifts in other phenols, particularly biphenylols.[13] Upon acidification of a solution of 7 with more concentrated acid (2.4 M HCl), the absorbtion spectrum of 2 reappears, confirming that 7 can be converted to 2 by aqueous acid. In view of the rapidity of nucleophilic reactions at sulfinyl centers,[14] these observations are not surprising. In fact, Kice[15] has studied a similar system, dibenz[c,e][1,2]dithiin 5,5,6-trioxide, and found rapid interconversion of the closed system and the open biphenyl-2,2'-disulfinic acid or its salt. Previous reports of the reaction of 1 with KOH make no mention of either the salt or the sultine.[16,17] In view of the good material balances in those reports and our own findings that in the absence of the crown ether the reaction is much slower and only a small amount (ca. 1%) of the sultine can be detected by GC, the isolation of 2 in 30% yield in the presence of

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(4) During the prepartion of this manuscript, another group published the preparation of a different oxathiin *S*-oxide by essentially the same route.[5]
(5) Udre, V. E.; Lukevits, E. Y.; Kemme, A. A.; Bleidelis, Y. Y. *Khim. Geterotskl. Soedin.* **1980**, 320.
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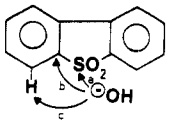
Table I. Flash Vacuum Pyrolysis of Dibenzothiophene 5,5-Dioxide (1) and Dibenz[c,e][1,2]oxathiin 6-Oxide (2)

compd	temp, °C	residence time, s	% yield or recovery 1	2	3	4	ref
1	690	15	0		81	14	1
1	900	10^{-3}	70		20	3	8
2	700	10^{-3}	0	75	15	2	this work
2	900	10^{-3}	tr[a]	6	63	8	this work

[a] Detected by TLC (silica gel G).

18-crown-6 signals a remarkable mechanistic change. Mechanistically, one can envision three potential reactions of 1 with KOH: (a) attack at sulfur, (b) attack at carbon,



and (c) attack at hydrogen. Path a would lead to the usually observed product, potassium 2-phenylbenzenesulfonate, while paths b and c are likely to give the dipotassium salt 7, a precursor to the sultine. Aryne formation by 1,2-elimination has been ruled out as the pathway for the production of benzenesulfinate in the reaction of diphenyl sulfone with sodium piperidide[18] and for the production of phenol in the reaction of diphenyl sulfone with KOH,[19] and there is no reason to suspect aryne formation here. Thus, the production of significant quantities of the sultine 2 in the presence of 18-crown-6 can be explained by increased attack of hydroxide at aromatic carbon at the expense of attack at sulfonyl sulfur. This loss of selectivity is probably best rationalized on the basis that the addition of crown ether leads to "naked" hydroxide[20,21] and that "naked" hydroxide is much more reactive than solvated potassium–hydroxide ion pairs.

Flash vacuum pyrolysis (FVP)[22] of sultine 2 at 700 and 900 °C with collection of the pyrolyzate on a cold-finger condenser cooled with liquid nitrogen to −196 °C gave 3 and 4 in approximately the same ratio (6:1) as that reported for the pyrolysis of 1 (Table I). These results strongly suggest that the sultine 2 is formed in the pyrolysis of 1 and is the most likely source of dibenzofuran 3. Furthermore, our results suggest that dibenzothiophene (4) obtained in the pyrolysis of 1 *also* results from the sultine intermediate rather than directly from 1.

Sequential loss of oxygen atoms from sultine 2 to form dibenzothiophene (4) is apparently not occuring. Such a transformation would, at some point, give dibenzothiophene 5-oxide. The FVP of dibenzothiophene 5-oxide at 900 °C affords a 55% yield of 1-hydroxydibenzothiophene,[8] a product not detected in the FVP of 2. Much more likely is the extrusion of molecular oxygen from the sultine, possibly via a thioperoxide intermediate (S–O–O). Indeed, the 70 eV mass spectra of both 1 and 2 display M − 32 ions. Mass spectra (EI) can often be used as a crude guide for predicting pyrolysis products.[1]

Experimental Section

Dibenzothiophene 5,5-dioxide (1, Aldrich), 18-crown-6 (Aldrich), KOH, and solvents were of commercial origin and were used without further purification. Melting points are uncorrected. Combustion analyses were by Galbraith Laboratories. Infrared spectra were recorded on a Beckman 4320 spectrophotometer, ^{1}H NMR spectra on a Varian EM-360 spectrometer, ^{13}C NMR spectra on a JEOL FX-90Q spectrometer, and ultraviolet spectra on a Varian Model 210 spectrophotometer.

Reaction of 1 with KOH in the Presence of 18-Crown-6 in Mesitylene. To a 100-mL, three-necked flask containing pellets of potassium hydroxide (85%, 3.84 g, 0.058 mol) and equipped with a Dean–Stark water trap connected to a condenser were added 18-crown-6 (4.5 g, 0.017 mol), 70 mL of mesitylene (predried by distillation from $LiAlH_4$), and 10 mL of xylene. The reaction mixture was heated to boiling, and after about 10 mL of distillate was collected in the Dean–Stark trap (two layers, ca. 1 mL of H_2O), the mixture was cooled, the trap drained, and 1 (2.50 g, 0.0115 mol) added. The mixture was heated (1 is soluble at 163 °C), held at reflux for 20 h, cooled to room temperature, and filtered. The collected solid, consisting of excess KOH and organic salts, was washed thoroughly with hexanes and then dissolved in water. The resultant aqueous solution was acidified with 6 N H_2SO_4, stirred for 10 min, and extracted with ether. The combined ether extracts were dried over $MgSO_4$, and the ether was removed under vacuum, leaving a light yellow oil. Three-fourths of this oil was dissolved in acetone and introduced onto an acid-washed alumina column. Elution with hexanes and chloroform gave, after evaporation of the solvents, 0.573 g of a white solid (mp 93–95 °C) which had spectral properties as follows: mass spectrum, m/e 216 (M^+); IR ($CDCl_3$) 3065 (w), 1610 (m), 1590 (m), 1475 (s), 1450 (m), 1430 (m), 1290 (m), 1240 (m), 1185 (s), 1140 (s), 1125 (s), 1110 (s); ^{1}H NMR ($CDCl_3$) δ 7.35–8.30 (complex); ^{13}C NMR ($CDCl_3$) quaternary carbons δ 145.0, 137.3, 126.7, 120.6, hydrogen-bearing carbons δ 133.0, 130.8, 128.4, 125.8, 125.5, 124.6, 124.5, 121.5; UV (MeOH) λ_{max} 293 nm (ϵ 6300), 268 (12 500), λ_{min} 285 nm (ϵ 5900), 241 (7000), shoulder at 262 nm. On this basis, the compound was assigned the structure dibenz[c,e][1,2]oxathiin 5-oxide (2). The yield was 0.764 g (30.5%). Anal. Calcd for $C_{12}H_8O_2S$: C, 66.65; H, 3.73; S, 14.83. Found: C, 66.73; H, 3.83; S, 15.01.

The residue washed from the column with pure chloroform was identified as 2-phenylphenol by comparison to an authentic sample (Aldrich); 0.128 g (6.5%).

Evaporation of the aqueous layer remaining after sulfuric acid acidification until a precipitate became clearly visible followed by cooling and filtration led to isolation of a solid identified as potassium 2-phenylbenzenesulfonate on the basis of its spectra [IR (KBr) 3050 (w), 1465 (w), 1445 (w), 1430 (w), 1200 (s, br), 1140 (m), 1090 (m), 1050 (m), 1020 (m), 1000 (m), 750 (m), 735 (m), 695 (m); UV (H_2O) λ_{max} 271 nm (ϵ_{271} 1.87 × 10^3); ^{1}H NMR δ 7.9–8.1 (m, 1 H), 7.25–7.65 (m, 8 H)] and elemental analysis. A yield of 1.79 g (57%) was deduced from quantitative analysis of the ultraviolet spectrum. Anal. Calcd for $C_{12}H_9KO_3S$: C, 52.92; H, 3.33; K, 14.36; S, 11.77. Found: C, 52.80; H, 3.47; K, 14.15; S, 11.67.

Reaction of 1 with KOH in the Presence of 18-Crown-6 in Mesitylene (4 h). A reaction was run and worked up exactly as described in the preceeding experiment, except that the reaction

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(21) The presence of crown ether also accelerates the conversion of 2-biphenylsulfonic acid into 2-biphenylol. Under these conditions and in the absence of crown ether only a trace of 2-biphenylol is formed, but in its presence the yield is 6.5%.

(22) For leading references on the FVP technique, see: Davis, F. A.; Yocklovich, S. G.; Baker, G. S. *Tetrahedron Lett.* **1978**, 97; Brown, R. F. C. "Pyrolytic Methods in Organic Chemistry"; Academic Press: New York, 1980.

time was 4 h. The products were potassium 2-phenylbenzenesulfonate (62%), biphenylene sultine (2, 26%), and 2-phenylphenol (4%).

Reaction of 1 with KOH in the Absence of 18-Crown-6 in Mesitylene (20 h). The reaction was run exactly as it was in the presence of the crown ether. For efficient removal of unreacted 1 from the precipitated acid salts and KOH, after filtration of the precipitate, the mixture was washed with 50 mL of $CHCl_3$. Unreacted 1 (0.494 g, 20%) was isolated from the combined $CHCl_3$ and mesitylene layers. The amount of 2-phenylbenzenesulfonate was determined by UV spectroscopy (72%). The ether layer from the acid hydrolysis contained only a trace of sultine 2 and 2-phenylphenol as determined by GC.

Ultraviolet Spectra of 2, 7, and 8. A stock solution of 2 (1.20×10^{-3} M) was prepared by dissolving 0.0130 g (0.060 mmol) of 2 in 90% CH_3CN–10% H_2O in a 50-mL volumetric flask. The stock solution was diluted 1/10, and the spectrum of 2 (curve a, Figure 1) was determined. To 1 mL of stock solution and 5 mL of 90% CH_3CN–10% H_2O in a 10-mL volumetric flask was added 0.2 mL of 2.5 M KOH. The mixture was diluted to 10 mL and the spectrum of 7 recorded (curve b, Figure 1). To 1 mL of stock solution and 5 mL of 90% CH_3CN–10% H_2O was added 0.2 mL of 2.5 M KOH. After several minutes (long enough for 7 to be formed from the 2 in the stock solution), 0.1 mL of concentrated HCl was added, the mixture diluted to 10 mL, and the spectrum of 8 recorded (curve c, Figure 1). If 2 mL of concentrated HCl, rather than 0.1 mL, was used, the spectrum of the solution changed over a period of a few hours, the final spectrum becoming identical with that of 2 (curve a, Figure 1).

Reaction of 2 with Methylmagnesium Iodide. Methylmagnesium iodide (1.0 mmol) in ether was added dropwise to a solution of 2 (0.210 g, 1.0 mmol) in 5 mL of ether. The solution was stirred for 30 min, the milky white suspension was poured into 20 mL of cold 5% aqueous NH_4Cl, and the solid was collected, washed successively with water, acetone, and ether, and dried ($MgSO_4$). The solid (0.158 g, 0.68 mmol, 68%; 203–205.5 °C dec) was identified as 2-[2-(methylsulfinyl)phenyl]phenol based on spectral properties and elemental analysis: IR (KBr) 3150 (br, OH), 1590 (m), 1475 (m), 1450 (s), 1375 (m), 1010 (s), 1000 (s), 965 (m), 840 (m), 780 (m), 765 (s); ^1H NMR (CH_3CN–D_2O, 1/1) δ 2.58 (s, 3 H), 6.9–8.1 (m, 8 H). Anal. Calcd for $C_{13}H_{12}O_2S$: C, 67.21; H, 5.20; S, 13.80. Found: C, 66.90; H, 5.22; S, 13.61.

Oxidation of 2 to Dibenz[*c*,*e*][1,2]oxathiin 6,6-Dioxide. To a stirred solution of 30% H_2O_2 (0.264 g, 2.3 mmol) in 3 mL of acetic acid was added 2 (0.069 g, 0.32 mmol). The solution was refluxed for 23 h, cooled, and poured onto ice. The solid was dissolved in $CHCl_3$, and the $CHCl_3$ solution was washed successively with water, saturated $NaHCO_3$, and water and dried ($CaCl_2$). Evaporation of the $CHCl_3$ gave solid dibenz[*c*,*e*][1,2]oxathiin 6,6-dioxide: mp 105–106.5 °C (lit.[9] mp 108.5–109.5 °C); 0.069 g (0.30 mmol, 93%); IR ($CDCl_3$) 3065 (w), 1475 (m), 1430 (m), 1375 (s), 1205 (s), 1175 (s), 1140 (m), 1070 (m).

Flash Vacuum Pyrolysis of 2. Flash vacuum pyrolyses were carried out by vaporizing at 80 °C 100–150-mg samples of 2 into a 1.5 × 20 cm pyrolysis chamber at 10–20 μmHg. The pyrolysate was collected on a cold finger cooled to −196 °C with liquid N_2. The temperature of the pyrolysis was monitored at the center of the pyrolysis chamber by using a Barber-Coleman thermocouple, the accuracy of which is estimated to be ±10 °C. This FVP apparatus will be described in a forthcoming publication. The yields of reaction products (Table I) were determined by GLC using a 6 ft × 1/8 in. OV-17 on Anakorm Q 90/100-mesh column by comparison of peak areas with standard solutions of the reaction products via the internal standard method.

Registry No. 1, 1016-05-3; 2, 77123-91-2; 3, 132-64-9; 4, 132-65-0; 5, 4371-25-9; 6, 77123-92-3; 7, 77123-93-4; 8, 77136-31-3; 2-phenylphenol, 90-43-7; potassium 2-phenylbenzenesulfonate, 65426-43-9.

Notes

Friedel–Crafts Chemistry. 6. Substituent Effects on the Ipso Nitration and the Novel Nitration of Some Diphenylmethanes[1a]

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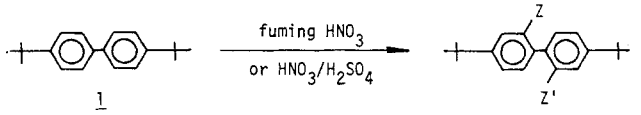
Received March 20, 1980

The nitration of 4,4′-di-*tert*-butylbiphenyl (1) with fuming nitric acid and with mixed nitric–sulfuric acids has afforded 2-nitro- (2) and 2,2′-dinitro-4,4′-*tert*-butylbiphenyl



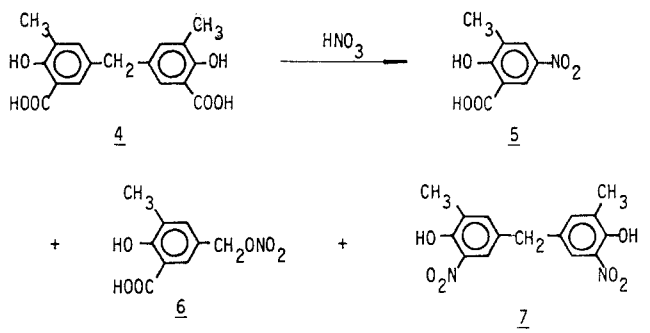
1

2: Z = NO_2, Z′ = H

3: Z = Z′ = NO_2

(3).[2,3] These compounds are useful intermediates for the preparation of carbazoles. Products resulting from replacement of the *tert*-butyl group were not observed, although such an "ipso" attack, with replacement of a group other than hydrogen on an aromatic ring carbon, is well-known.[4] For example, nitration of the diphenylmethane 4 produces the ipso nitration product 5 in addition to 6 and 7[5] (Scheme I). There has been little systematic investigation of the nitration of diphenylmethanes, however. The present study was undertaken to determine the yields

Scheme I



4 5 6 7

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