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THE DECOMPOSITION OF DIBENZOTHIOPHENE DIOXIDE AND RELATED COMPOUNDS IN THE PRESENCE OF MOLTEN ALKALI

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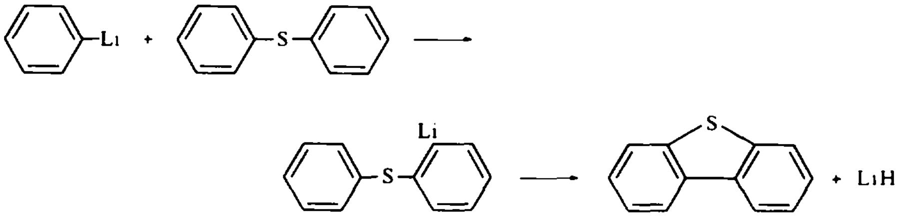
Abstract—A detailed study was carried out on the decomposition of dibenzothiophene dioxide in the presence of both sodium and potassium hydroxide at 200–300°. Our results show that the stability of the dibenzothiophene nucleus is markedly dependent on the oxidation state of the S-atom. The products formed in the decomposition reaction vary with temperature, contact time, and the initial ratio of base to dioxide. In the presence of excess base at 300°, dibenzothiophene dioxide was converted to dibenzofuran in high yield. The formation of the furan apparently proceeds by a multistep reaction sequence in which 2-phenylbenzene sulfonic acid and 2-phenylphenol are unstable intermediates. We also investigated the decomposition of dibenzothiophene monoxide, benzothiophene dioxide, n-octyl sulfoxide and sulfone, and diphenyl sulfoxide and sulfone under these conditions. The aliphatic S-derivatives decomposed by a typical beta-elimination reaction. The products formed from the other oxidized S-derivatives suggest that the decomposition process involves a complex series of addition, cleavage, and elimination reactions.

INTRODUCTION

NO DETAILED study has been carried out on the chemical decomposition of dibenzothiophene and related compounds. This is due to the fact that dibenzothiophene is an extremely stable sulfur derivative. The thermal decomposition of various sulfur compounds was studied in a semi quantitative manner by Rudenko and Gromova.[1] These authors passed the vapors of several sulfur derivatives through a hot tube filled with steel fragments and reported the minimum temperature at which the rate of decomposition became significant as evidenced by evolution of hydrogen sulfide. Thiols, disulfides, and dialkylsulfides readily decomposed in the temperature range of 150 to 400°. Diaryl sulfides, e.g. diphenyl sulfide, decomposed at 450° but thiophene was stable at 500°. At a temperature of 475°, a very slight evolution of hydrogen sulfide was observed with 2,5-dimethylthiophene. The unreactivity of the thiophenes at this temperature is not surprising since pyridine does not undergo any appreciable thermal decomposition below 850°.[2] Condensed thiophenes should be even more resistant to thermal decomposition, i.e. loss of sulfur, because of an increase in resonance energy.[3] The acid-catalyzed decomposition of dibenzothiophene also appears to be unattractive. Thiophene itself is more reactive toward acids than benzene. However, acids such as H_3PO_4, H_2SO_4, and Friedel–Crafts Catalysts promote the formation of S-containing polymers and stable pentamers and trimers.[3] Obviously, a condensed thiophene such as dibenzothiophene will be stable in the presence of acids and heat and, the tendency to lose the S-atom by C–S bond cleavage will be even less. Therefore, the other possible techniques that can be employed for sulfur removal from condensed thiophenes are: (1) oxidation of the S-atom followed by thermal treatment, (2) thermal treatment in the presence of basic reagents, and (3) thermal treatment of oxidized thiophene derivatives in the presence of basic reagents.

McOmie and Bullimore[4] have recently investigated the thermal decomposition of 2,3,4,5-tetraphenylthiophene dioxide. At 340°, 15% conversion of the dioxide occurred in 1 hr. The products were 1,2,3-triphenylnaphthalene and 1,2,3-triphenylazulene. At 500–550°, the principal product was a polymer along with 10% tetraphenylthiophene and 17% tetraphenylfuran. In the presence of nickel bromide and cuprous bromide at 350°, undetermined quantities 2,3,8-triphenylbenzofulvene and the above mentioned compounds were obtained. Since this dioxide is not a condensed thiophene dioxide, the thermal removal of oxidized sulfur from condensed thiophenes should be even more difficult. There is considerable evidence in the literature which suggests that compounds containing bivalent sulfur ($-\ddot{\underset{\cdot\cdot}{S}}-$) linkages are most resistant to attack by basic reagents. For example, aliphatic sulfides are not cleaved readily by alcoholic KOH at 200°. On the other hand, aliphatic sulfones may be cleaved under these conditions to produce olefins.[5] Studies in these laboratories[6] have shown that the ease of alkaline cleavage in potassium t-butoxide dimethyl sulfoxide is sulfone $>$ sulfoxide $\gg$ sulfide. In the aromatic series, the data are consistent with the conclusion that sulfur in a higher oxidation state activates the molecule. For example, diphenyl sulfoxide can be cleaved at low temperatures by phenyl lithium and butyl lithium.[7] We are not aware of any similar cleavage data for the corresponding sulfide. Rather, cyclization occurs to produce thiophene derivatives. In the thiophene series, dibenzothiophene-5-oxide reacts with butyl lithium in ether to produce a metallated derivative but dibenzothiophene is inert.[8] This is consistent with earlier work by Weisgerber and Seidler[9] which showed that benzothiophene was decomposed to potassium formate and potassium *o*-toluenethiolate in the presence of molten KOH (300°) but dibenzothiophene was inert. It was also shown that dibenzothiophene dioxide could be converted to the potassium salt of either 2-phenylbenzene sulfonic acid[10] or 2-phenylphenol.[11] Based on these limited results we chose to study route C, thermal decomposition of oxidized S-derivatives in the presence of alkali, in detail as a chemical technique for the conversion of dibenzothiophene and related compounds to sulfur free materials.



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RESULTS

The alkaline decomposition of a number of oxidized sulfur derivatives has been studied under a variety of conditions. The objectives of this study were (a) to uncover a selective method for sulfur removal and (b) to identify the principle products formed from the decomposition of each compound investigated. A general procedure was used in all decomposition reactions: a white oil–alkali metal hydroxide mixture was heated to the desired temperature, a preheated solution of the sulfur compound in white oil was injected into the hydrocarbon-base mixture, and the reaction was initiated by stirring. Each reaction mixture was heterogeneous in nature, i.e., it involved either solid and liquid or two distinct liquid phases. The nature of the heterogeneous mixture was dependent on the reaction temperature employed. Samples were withdrawn from the oil phase periodically and analyzed by gas chromatography by the techniques described in the experimental section. This allowed us to follow the disappearance of reactants and the appearance of the nonacidic decomposition products. The acidic products remained in the alkaline phase and they were identified by ultraviolet spectroscopy at the end of each reaction.

In view of previous work, the reactivity of dibenzothiophene (DBT)[12] in the presence of both sodium and potassium hydroxide was first determined as a function of the oxidation state of the sulfur atom. In each reaction, a ten to one mole ratio of alkali metal hydroxide to sulfur compound was used and the temperature was varied from 200 to 300°. All pertinent data are summarized in Table 1. DBT did not undergo any appreciable reaction at 200° in the presence of KOH after a contact time of 20 hr.

TABLE 1. DEPENDENCE OF DIBENZOTHIOPHENE REACTIVITY ON THE OXIDATION STATE OF THE SULFUR ATOM

10^{-2} Mole sulfur compound/100 ml white oil.
10^{-1} Mole alkali metal hydroxide.

Reactant	Base	Temp.	Time	% Conversion
Dibenzothiophene	KOH[b]	200°	20 hr	3
Dibenzothiophene monoxide	KOH[b]	200°	20 hr	30
Dibenzothiophene dioxide[c]	KOH[b]	200°	10 min	54
			1 hr 25 min	73
			1 hr 50 min	84
Dibenzothiophene dioxide	KOH[b]	250°	30 min	68
			1 hr	
Dibenzothiophene dioxide[c]	KOH[b]	300°	10 min	100
Dibenzothiophene dioxide[c]	NaOH[a]	300°	10 min	93

[a] No reaction observed with NaOH in same time periods.

[b] This material was assayed as 87% KOH and 13% H_2O.

[c] Essentially the same results were observed in duplicate runs.

About 30% conversion of DBT monoxide was observed under the same conditions DBT dioxide decomposed readily at 200° and as the temperature was increased, the ease of dioxide conversion also increased. At 300°, greater than 90% DBT dioxide conversion was obtained in 10 min in the presence of both KOH and NaOH. These results clearly show that the reactivity of DBT is dependent on the oxidation state of the sulfur atom. Thus, our base-catalyzed decomposition studies were limited to oxidized S-derivatives. The rate of DBT dioxide conversion was also determined as a function of the KOH/dioxide ratio at 200°. As shown in Fig. 1, a decrease in the KOH/dioxide ratio from 10 to 1 produced a marked decrease in the rate of conversion of the dioxide. This reactivity sequence is consistent with the initial formation of an anionic intermediate.

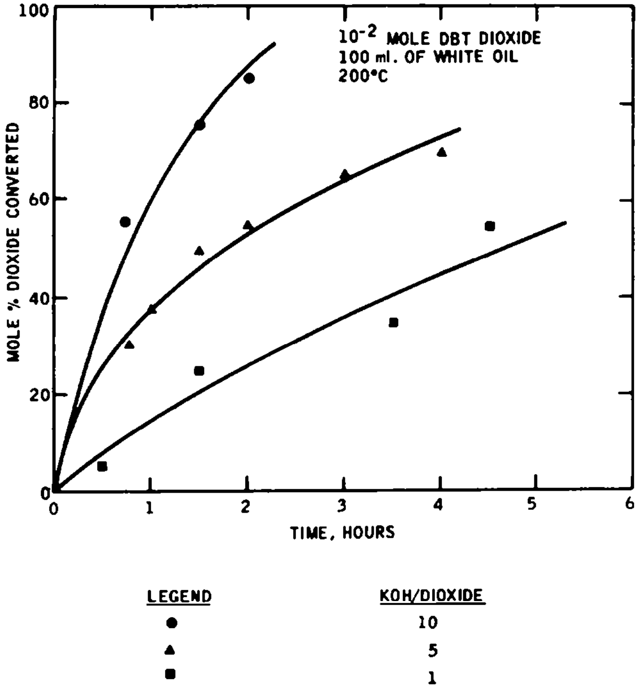


FIG. 1. Dependence of the rate of dibenzothiophene dioxide conversion on the mole ratio of potassium hydroxide to dioxide.

Large-scale decompositions of DBT dioxide were next investigated so that products could be isolated and identified. Excess alkali metal hydroxide was employed in each reaction. The results of these studies are summarized in Table 2. In the presence of KOH at 200°, the following products were identified after 3 hr of reaction: potassium 2-phenylbenzene sulfonate (45%), potassium 2-phenylphenolate (40%), and dibenzofuran (5%). This reaction was repeated at 250° for 1·7 hr and, no significant change was observed in the yield of the phenolate and sulfonate salts. In addition to dibenzofuran, we also observed a small amount of biphenyl (3% yield). At 300°, the KOH-catalyzed decomposition of DBT dioxide could not be carried out for extended reaction times because the system was extremely hazardous. This could be due to the fact that KOH contains 13% water of hydration. A 10-minute reaction at 300° in the presence of KOH produced a 70% yield of the sulfonate salt, a 30% yield of the phenolate salt, and low yields (1–2%) of biphenyl and dibenzofuran. An extended decomposition of the dioxide at 300° was carried out in the presence of NaOH without much difficulty. After 5·5 hr, the products consisted of dibenzofuran (∼90% yield) and biphenyl (about 5% yield). The NaOH-catalyzed reaction at 300° was repeated and terminated after 4 hr. The main product was sodium 2-phenylphenolate (58% yield). Thus, the products formed from the alkali-catalyzed decomposition of DBT dioxide are markedly dependent on temperature and contact time with the excess alkali metal hydroxide.

The formation of dibenzofuran in the above reactions, though unexpected, was of prime interest. Therefore, we attempted to gain some further insight into the mode of formation of this compound. We first determined how the yield of dibenzofuran

TABLE 2. DECOMPOSITION OF DIBENZOTHIOPHENE DIOXIDE UNDER VARIOUS REACTION CONDITIONS
0·1 Mole DBT dioxide/750 ml of white oil.

Base	Base/DBT dioxide	Temp.	Time	Product(s), mole % yield	
KOH[a]	5	200°	3 hr	Potassium-2-phenyl benzene sulfonate	45·0
				Dibenzofuran	5·0
				Potassium-2-phenyl phenolate	40·0
KOH[a]	5	250°	1·7 hr	Potassium-2-phenyl benzene sulfonate	47·6
				Potassium-2-phenyl phenolate	50·7
				Dibenzofuran	1·0
				Biphenyl	3·0
KOH[a]	5	300°	10 min[b]	Potassium-2-phenyl benzene sulfonate	70·0
				Potassium-2-phenyl phenolate	29·6
				Dibenzofuran	1·7
				Biphenyl	0·8
NaOH	5	300°	5·5 hr	Dibenzofuran	>90
				Biphenyl	~5
NaOH[c]	5	300°	4 hr	Sodium-2-phenyl benzene sulfonate	18·0
				Sodium-2-phenyl phenolate	58·0
				Biphenyl	2·0
				Dibenzofuran	19·5
None	—	300°	23 hr	No reaction	

[a] This material was assayed as 87% KOH and 13% H_2O.

[b] The reaction was terminated at this time since it became violent.

[c] The following sodium distribution was found in this reaction: 0·0004 g atom as $CO_3^=$, 0·0084 g atom as $S^=$, 0·0364 g atom as $SO_3^=$, 0·0028 g atom as $SO_4^=$, and 0·0046 g atom as $S_2O_3^=$.

varied with the ratio of NaOH to DBT dioxide. Four experiments were carried out at 300° for 5 hr and the base to dioxide ratio was varied from 1 to 5. The results are summarized in Table 3. As shown, high yields (50–90%) of dibenzofuran required an excess of NaOH (3 to 5 fold). At the lower base to dioxide ratios, the base is consumed by the inorganic by-products and this probably inhibits the formation of dibenzofuran. A series of rate studies were carried out in the presence of NaOH at 300°. The rate of formation of dibenzofuran from the dioxide, sulfonate salt, and phenolate salt was determined by gas chromatography. The data are summarized in Fig. 2. Dioxide cleavage and the formation of dibenzofuran from the phenolate salt were rapid reactions. The latter reaction proceeded readily even at 200°. The rate of dibenzofuran formation from the sulfonate salt was the slowest reaction and, it was similar to the rate of dibenzofuran formation observed with the dioxide. These

TABLE 3. DEPENDENCE OF DIBENZOFURAN YIELD ON THE MOLE RATIO OF SODIUM HYDROXIDE TO DIBENZOTHIOPHENE DIOXIDE AT 300°
0·1 mole DBT dioxide/750 ml white oil.
300°, 5 hr.

Mole NaOH per mole DBT dioxide	Dibenzofuran, % yield*
5	90
3	51
2	22
1	0

* Greater than 90% dioxide conversion was observed in each run.

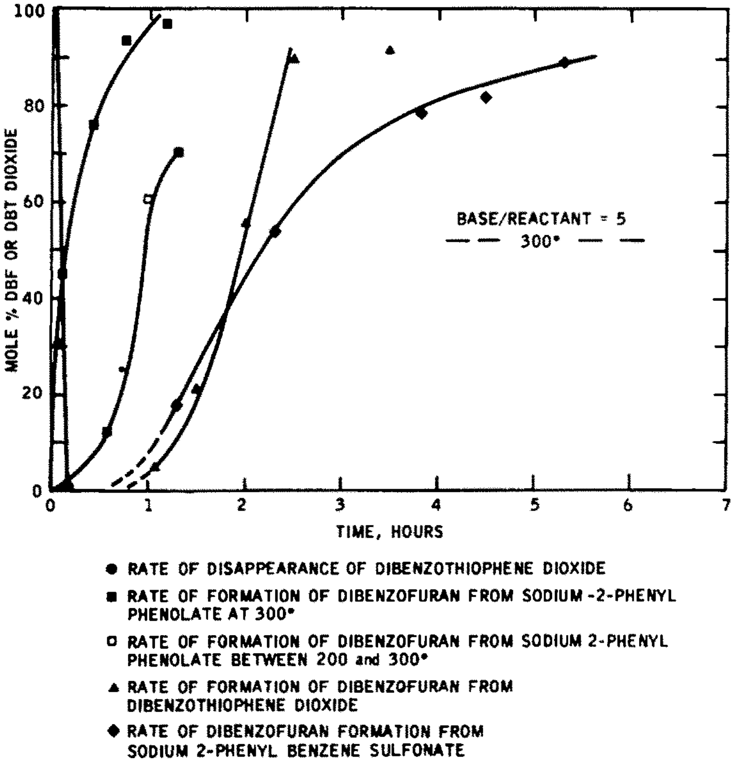


FIG. 2. Rate of formation of dibenzofuran and rate of disappearance of dibenzothiophene dioxide.

rate studies and the data summarized in Table 2 suggest that the formation of dibenzofuran from DBT dioxide proceeds by a multistep sequence in which the rate-determining step is conversion of the sulfonate salt to the phenolate salt. We also found that dibenzofuran did not undergo any decomposition at 300° in the presence of excess base.

TABLE 4. SUMMARY OF OTHER SULFOXIDE AND SULFONE DECOMPOSITION STUDIES IN THE PRESENCE OF SODIUM HYDROXIDE AT 300°

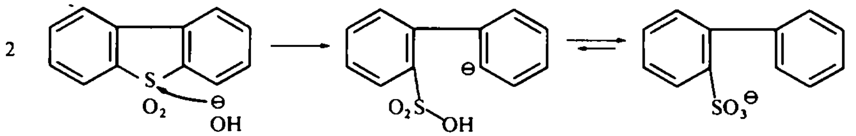
Reactant,[a] mole		NaOH reactant	Time	% Conversion	Product(s), mole % yield[b]	
Di-n-octyl sulfoxide	0·10	5	2·25 hr	—	1-octene	37·5[c]
Di-n-octyl sulfone	0·10	5	3·5 hr	—	1-octene	100[c]
Diphenyl sulfoxide	0·1	5	3·33 hr	47	Diphenyl sulfide	14·9
					Biphenyl	8·5
					Benzene	8·5
					Dibenzohtiophene	4·2
					Sodium phenolate	~53·0[d]
Diphenyl sulfone	0·1	5	3·25 hr	~100	Sodium phenolate	~70[d]
					Biphenyl	20·0
					Benzene	18·0
					Sodium sulfite	100
Dibenzothiophene monoxide	0·1	5	4 hr	~100	Dibenzothiopjene	20·1
					Sodium-2-phenyl benzene sulfonate	25·2
					Sodium-2-phenyl phenolate	41·9
					Dibenzofuran	11·2
					Biphenyl	1·3
Benzothiophene dioxide[f]	0·1	5	4 hr	100	Sodium-2-methyl benzene sulfonate	Mixture[e] 50 (maximum)
					Sodium-2-methyl phenolate	
					Sodium sulfite	27·4
					Sodium carbonate	31·6
					Benzene	6·4

[a] Each reactant was dissolved in 750 ml of white oil.
[b] Mole of product/mole of reactant converted × 100 unless indicated different.
[c] Mole of product/mole of reactant × 100.
[d] Some sodium benzene sulfonate was also present based on IR analyses.
[e] Other products could not be identified. Benzofuran was not detected by either GLC or MS.
[f] Complete conversion of the dioxide required about 10 min.

The decomposition of other oxidized sulfur derivatives was investigated at 300° in the presence of NaOH. The details of each reaction are summarized in Table 4. As expected, sulfones were more reactive than sulfoxides. Di-n-octyl sulfone underwent complete decomposition to 1-octene in 3·5 hr. The yield of 1-octene from the sulfoxide was only 37·5% after 2·2 hr of reaction. The major product formed from diphenyl sulfone was sodium phenolate (70% yield); the minor products were biphenyl and benzene. The decomposition of diphenyl sulfoxide was extremely complex; the major product was sodium phenolate and the minor products were diphenyl sulfide, biphenyl, dibenzothiophene, and benzene. DBT monoxide underwent complete decomposition in 4 hr. The products were the same as those formed from the dioxide with the exception of dibenzothiophene which was formed in 20% yield. Complete decomposition of benzothiophene dioxide was obtained in 10 min but the reaction was carried out for 4 hr. The main product(s) was a mixture of the sodium salts of *o*-cresol and *o*-toluene sulfonic acid. Sodium carbonate and sodium sulfite were also formed in substantial yields (27 to 32%) along with a small amount of benzene. The other products from this reaction could not be identified.

DISCUSSION

The data summarized in Table 2 and Fig. II are consistent with a multistep reaction sequence for the formation of dibenzofuran. The initial step in the process appears to be attack of hydroxide ion on the C—S bond to produce a carbanion that rapidly tautomerizes to the sulfonate ion. Simple alkaline fusion would lead to the phenolate ion and this appears to be the slowest step in the overall reaction. The phenolate ion apparently undergoes an intramolecular cyclization reaction to produce an unstable anion that loses sodium hydride to yield the furan which is as stable as DBT under these conditions. Reaction 3 is analogous to reaction 1 in which DBT is formed from diphenyl sulfide. The proposed sequence is consistent with (1) the dependence of



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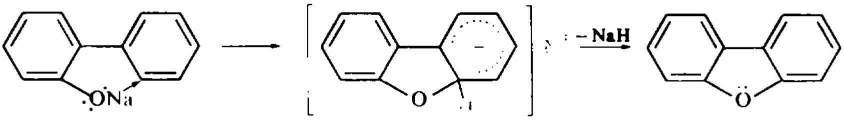
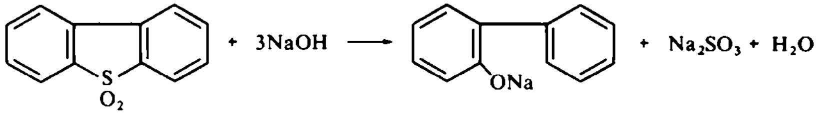


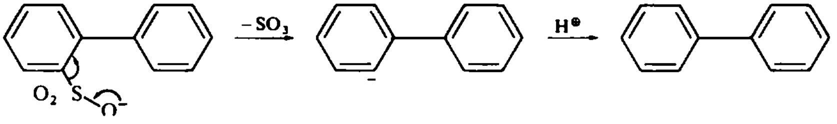
(3)

the yield of dibenzofuran on the initial base/dioxide ratio (Table 3) and (2) the detection of small quantities of dihydrodibenzofuran by mass spectroscopy. The nature and quantity of the inorganic products formed from the decomposition reaction (Table 2) suggest that the overall reaction for formation of the phenolate ion is



(4)

Once the sodium sulfite is formed, some decomposition and/or disproportionation to the other inorganic products must occur. Small quantities of biphenyl were produced in several of the reactions listed in Table 2. Since dibenzofuran is stable under the reaction conditions listed, the hydrocarbon could arise by thermal expulsion of the sulfur group from DBT dioxide and/or loss of SO_3 from the sulfonate salt followed by rapid protonation of the resulting anion.



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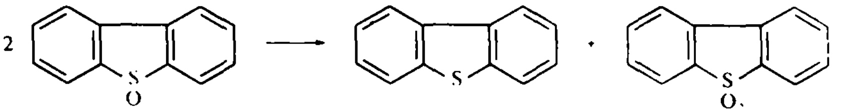
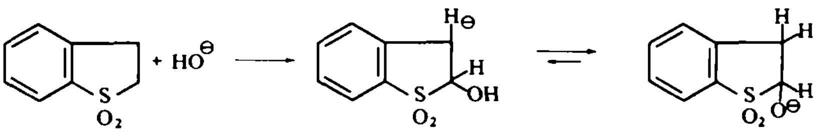
Our results with DBT dioxide should be compared with those of Melles[13] who studied the reaction of various thiophene dioxides with alkali at 100°. The dioxides of tetraphenylthiophene and 3,4-dimethylthiophene were not decomposed by alkali but the dioxides of 3,4- and 2,5-diphenylthiophene were decomposed to sodium sulfite and resinous materials. In the case of the last two dioxides, it would appear that hydroxide ion adds to the dioxides to produce intermediate benzylic carbanions which are unstable and decyclize to yield reactive unsaturates and sodium sulfite. In the case of the more stable thiophene dioxides, such reactions are unfavorable and severe reaction conditions are required to obtain any appreciable decomposition.

The products from DBT monoxide (Table 4) are similar to those observed with the dioxide. However, the formation of DBT suggests that some disproportion occurs to produce DBT and DBT dioxide.



(6)

The dioxide would then decompose in the usual manner. Another possibility is that the monoxide decomposes to DBT and oxygen which would be analogous to the decomposition of quinoline-N-oxide to quinoline and oxygen.[14] The decomposition of benzothiophene dioxide is not nearly as simple as the decomposition of the DBT derivatives. The small quantity of benzene could result from a thermal fragmentation reaction. The mixture of *o*-cresolate and *o*-toluene sulfonate salts and the high yield of sodium carbonate suggest that some loss of carbon precedes the formation of the products. A possible path by which this occurs is outlined below. It involves



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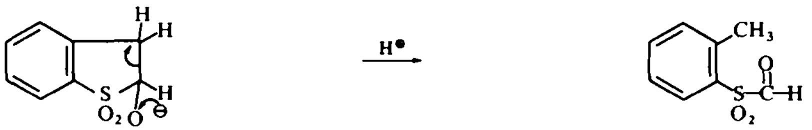

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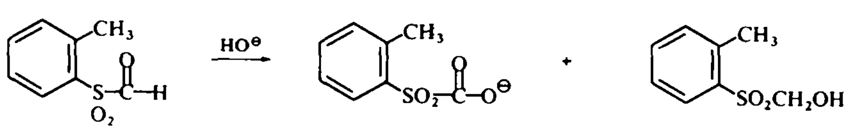

(9)

$$\text{I} + \text{II} \longrightarrow \text{PRODUCT} \qquad (10)$$

addition of hydroxide ion to the double bond, a prototropic shift, rearrangement of the alkoxide ion to a sulfonyl aldehyde and a Cannizzaro reaction to produce a carboxylate ion and an alcohol; both of which would be unstable under the present reaction conditions and decompose to a sulfinate ion. The sulfinate ion would undergo fusion to produce the *o*-cresol salt. Unreacted sulfinate ion would be readily oxidized to the sulfonate ion during work-up of the products. The unidentified products may be produced by a Diels Alder dimerization with subsequent loss of sulfur dioxide. This reaction has been observed by Bordwell *et al.*[15] in the absence of base at high temperatures.

The decomposition of the aliphatic sulfoxide and sulfone proceeds by a typical beta-elimination sequence. No isomerization of the terminal olefin was observed because it distilled out of the reaction flask as it was formed. The decomposition of diphenyl sulfoxide and sulfone proceeds by a complex series of cleavage, addition, and elimination reactions. A detailed discussion of these reactions is unjustified based on the present data. The phenolate salt is produced by the alkaline fusion of unstable sulfenate, sulfinate, and possibly sulfonate ions. In the case of the sulfoxide, some disproportionation to the sulfide and sulfone must occur. The sulfide probably undergoes reaction 1 to produce DBT.

EXPERIMENTAL

Materials. Dibenzothiophene, benzothiophene, n-octyl sulfide, diphenyl sulfoxide, diphenyl sulfone dibenzofuran, benzofuran, 2-phenylphenol, 2-methylphenol, sodium 2-phenylbenzene sulfonate, biphenyl, 1-octene, diphenyl sulfide, and n-hexadecane (olefin free) were purchased from either Matheson, Coleman, and Bell or Columbia Organic Chemicals as reagent grade materials and used without further purification. The white oil solvent (b.p. 250° plus) was obtained from the Humble Oil and Refining Company.

Dibenzothiophene dioxide (m.p. 236–237°) and dibenzothiophene monoxide (m.p. 186–187°) were synthesized from dibenzothiophene using the H_2O_2–AcOH oxidation procedure.[16] The observed m.ps were in satisfactory agreement with those reported in the literature. Benzothiophene dioxide (m.p. 142–143°; reported m.p.[17] 142–143°) was synthesized from benzothiophene using the H_2O_2–AcOH oxidation technique of Bordwell *et al.*[17] Di-n-octyl sulfoxide (m.p. 70–71°; reported m.p.[18] 71–72° and di-n-octyl sulfone (m.p. 76–77°, reported m.p.[18] 76·0–76·8°) were synthesized from the corresponding sulfide by a similar oxidation procedure. In all of the above oxidations, a short oxidation period at the reflux temp. of the soln favors the formation of monoxide or sulfoxide. The 2-phenylbenzene sulfonate salts (K and Na) were prepared by the controlled alkaline fusion of dibenzothiophene dioxide (2 to 3 min at 250°).[16] The salts were purified by repeated recrystallization from cold water. The structure of each salt was verified by conversion to the corresponding sulfonyl chloride (m.p. 102°, reported m.p.[10] 103°). Both salts were used to obtain qualitative and quantitative data on the products formed from the decomposition of dibenzothiophene monoxide and dioxide.

Procedure for decomposition studies. All decomposition reactions were carried out in a heavy-walled pyrex flask equipped with a N_2 bubbler, paddle stirrer, thermometer, Friedrich's condenser, self-sealing Neoprene diaphragm, and a dry-ice trap. In practice, the alkali metal hydroxide–white oil mixture was heated to the desired temp.; a small preheated soln of the reactant and internal standard in white oil was injected into the reaction flask by a syringe; agitation was initiated and maintained at 1000 rpm, and a constant temp. ($\pm 5°$) was maintained throughout the experiment by a Thermowatch temp regulator which was attached to the thermometer that was immersed in the white oil phase. On the average, about two decomposition runs were carried out in each flask and then the vessel was discarded. This is due to the fact that molten alkali readily attacks Pyrex glass. The reaction flask was thoroughly shielded during the course of each run as a safety precaution.

Product identification was accomplished by either gas chromotography (GC) or spectroscopic methods. These techniques were used to obtain both qualitative and quantitative data. Reaction products soluble in the white oil phase were identified by GC comparison of retention times with authentic samples using n-hexadecane as an internal standard. The quantity of each product formed was determined by measuring its peak area relative to that of n-hexadecane.[19] The amount of starting material which remained in the hydrocarbon phase was also determined in the same manner. The GC samples were analyzed on an F and M 609 Flame Ionization Gas Chromatograph equipped with a disc integrator, Minneapolis Honeywell recorder, and a 2 ft silicone gum rubber column (10 wt% an Chromasorb P). The block and injection port temps were maintained at 300°. The column temp. was varied from 75 to 275°. The He flow through the column was 100 ml/min when measured at room temp. with a flow meter. In several runs product analyses were obtained as a function of time. During the course of these runs, stirring was interrupted, the phases were allowed to separate, and an aliquot was withdrawn from the oil phase by a hypodermic syringe that was inserted through the Neoprene diaphragm. This operation usually required about 15 to 30 sec. Stirring was then reinitiated. The aliquot was analyzed by GC under the conditions described above. Low boiling materials, e.g. benzene, which distilled out of the reaction flask were collected in the dry-ice trap and added to the oil phase after the reaction was terminated and the mixture had cooled to room temp.

Attempts to analyze the molten caustic phase as a function of time proved to be both futile and hazardous. Thus, this phase was analyzed only after reactions were terminated. In general, the mixture was diluted with an equal volume of water; it was refluxed at 100° for 1 hr to dissolve the unreacted base and acid salts; the phases were separated; and the acid salts were identified by UV spectroscopy. The principal absorption bands for each product are summarized below.

Compounds*	λ Maximum
2-Phenyl benzene sulfonic acid	273
2-Phenyl phenol	307·5
Benzene sulfonic acid	262
Phenol	287
2-Methyl benzene sulfonic acid	261
2-Methyl phenol	288

* As the potassium and sodium salts.

Qualitative data were obtained from standard absorption curves which were constructed in the usual manner by the use of authentic compounds.

In addition to the above analytical techniques, a number of the products listed in Tables 1 through 4 were isolated at least once and identified by other techniques: (a) benzene was identified by its b.p. and characteristic IR spectrum (b) sodium 2-phenylbenzene sulfonate was isolated and converted to its corresponding sulfonyl chloride (m.p. 102°) and (c) 2-phenylphenol, phenol, and 2-methylphenol were extracted from acidified solns and identified by either IR or mass spectroscopy. Dibenzofuran, dibenzothiophene, diphenyl sulfide, and biphenyl, which were soluble in the oil phase, were identified by their parent ions in the mass spectrometer.

Identification of inorganic products. The inorganic products formed during the decomposition reactions were identified by standard methods. Sulfate content was obtained by initial acidification with HCl followed by addition of $BaCl_2$ to produce insoluble $BaSO_4$. The salt was heated to dryness and weighed. Carbonate was identified as CO_2 liberated during the acidification step. The gases were passed through a permanganate train to remove H_2S and SO_2, a H_2SO_4–Drierite medium to remove water, and the CO_2 was finally adsorbed on Ascarite which was weighed. Sulfide, sulfite, and thiosulfate were identified by titration techniques. A portion of the sample was treated with a suspension of zinc carbonate which precipitated sulfide and polysulfide. The ppt was filtered, dissolved in dilute acid, and titrated with I_2 to measure the sulfide sulfur content. The filtrate also contained sulfite and thiosulfate, both of which will react with I_2. It was divided into two portions and one portion was treated with formaldehyde. This compound forms a complex with the sulfite so that the latter will not react. Both portions were then titrated with iodine. One titration represented both the sulfite and thiosulfate content and, the other, thiosulfate only. The difference between the two, corresponds to the sulfide content.

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[1] M. G. Rudenko and V. N. Gromova, *Dokl. Akad. Nauk. SSSR* **81**, 207 (1951).

[2] P. Krumholz, *Heat Decomposition of Pyridine, Selecta Chim.* No. 8; p. 3 (1949); *Chem. Abstr.* **44**, 3992 (1950).

[3] For discussions see: [a] R. M. Acheson, *An Introduction to the Chemistry of Heterocyclic Compounds*, Chap. 3; pp. 50–126. Interscience, New York, N.Y. (1960); [b] H. D. Hartough, *Thiophene and Its Derivatives*. Interscience, New York, N.Y. (1952); [c] S. L. Meisel, G. C. Johnson, and H. D. Hartough, *J. Am. Chem. Soc.* **72**, 1910 (1950).

[4] J. F. W. McOmie and B. K. Bullimore, *Chem. Commun.* **4**, 63 (1965).

[5] G. W. Fenton and C. K. Ingold, *J. Chem. Soc.* 705 (1930) and pertinent Refs therein.

[6] T. J. Wallace, J. E. Hofmann and A. Schriesheim, *J. Am. Chem. Soc.* **85**, 2739 (1963).

[7] H. H. Szmant, *Organic Sulfur Compounds*—I, Chap. 16; pp. 163–164. Pergamon Press, New York, N.Y. (1960).

[8] H. Gilman and D. L. Esmay, *J. Am. Chem. Soc.* **74**, 265 (1952).

[9] R. Weissgerber and C. Seidler, *Ber. Dtsch. Chem. Ges.* **60**, 2088 (1927).

[10] C. Courtot and C. Chaix, *C.R. Acad. Sci., Paris* **192**, 1667 (1931).

[11] R. Weissgerber and O. Kruber, *Ber. Dtsch. Chem. Ges.* **53**, 1566 (1920).

[12] DBT has been employed as an abbreviation for dibenzothiophene in the Results and Discussion sections of this paper.

[13] J. L. Melles, *Recueil* **71**, 869 (1952).

[14] M. Katada, *J. Pharm. Soc. Japan* **67**, 53 (1947).

[15] F. G. Bardwell, W. H. McKellin and D. Babcock, *J. Am. Chem. Soc.* **73**, 5566 (1951).

[16] H. Gilman and D. L. Esmay, *J. Am. Chem. Soc.* **74**, 2021 (1952).

[17] F. G. Bordwell, B. B. Lampert and W. H. McKellin, *Ibid.* **71**, 1702 (1949).

[18] P. Allen, L. S. Karger, J. D. Haygood, and J. Shrensel, *J. Org. Chem.* **16**, 767 (1951).

[19] A. E. Messner, D. M. Rosie and P. A. Argabright, *Analyt. Chem.* **31**, 230 (1959).