

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, NORTHWESTERN UNIVERSITY]

The Reduction of Sulfones to Sulfides

BY F. G. BORDWELL AND W. H. MCKELLIN

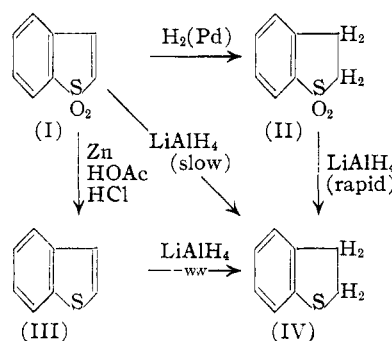
The classical resistivity to reduction of sulfones, like that of carboxylic acids, has been found to yield to the powerful action of lithium aluminum hydride. Five-membered cyclic sulfones were reduced to sulfides in ethyl ether at 35°, while higher temperatures were required for six-membered cyclic sulfones, open-chain aliphatic sulfones and phenyl sulfones. Benzo- thiophene 1-dioxide was reduced to benzothiophene by zinc, acetic acid and hydrochloric acid. In this respect, it is similar to tetraphenylthiophene 1-dioxide, but unlike other sulfones.

Beckmann¹ was apparently first to point out the marked stability of the sulfone grouping to the action of reducing agents. He observed¹ that neither aliphatic sulfones, nor ethyl phenyl sulfone was attacked by zinc and mineral acids, zinc dust (distillation), sodium or potassium amalgam, fuming hydroiodic acid or phosphorus pentachloride. Kraft and Vorster² found that phenyl sulfone did not react with red or yellow phosphorus at 250° or with zinc dust at the distillation temperature (379°), but when heated with sulfur it was converted in good yield to phenyl sulfide. The latter reaction is probably not a simple reduction, however, since phenyl sulfone when heated with selenium gave phenyl selenide,² and other aryl sulfones react with sulfur to give primarily products where the carbon-sulfur bonds have been broken.^{2,3}

The only straightforward reductions of sulfones to sulfides that have come to our attention are: (1) the reduction of (α,β -dibromoethyl) and (α,β -dichloroethyl) sulfones to the sulfides with hydrogen sulfide and hydrogen bromide in acetic acid solution,⁴ and (2) the reduction of tetraphenylthiophene 1-dioxide to tetraphenylthiophene by the action of zinc, acetic acid and hydrochloric acid.⁵ These reductions are probably limited in scope, and it appears that no general method for reducing sulfones to sulfides has been reported.

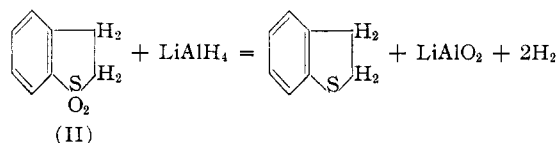
In view of its similarity to tetraphenylthiophene 1-dioxide, our attention was directed to the possibility of reducing the sulfone grouping in benzo- thiophene 1-dioxide (I). Catalytic low pressure hydrogenation with palladium-on-charcoal catalyst gave a smooth and rapid conversion of I to 2,3-dihydrobenzothiophene 1-dioxide (II).⁶ A similar reaction has been observed with zinc and sodium hydroxide,⁷ but zinc and acetic acid gave no reaction.⁷ With zinc, acetic acid and hydrochloric acid I gave benzothiophene (III). 2,3-Dihydrobenzothiophene 1-dioxide (II), dibenzothiophene 5-dioxide and thiacyclopentane 1-dioxide were not reduced under these conditions. It seems probable that the effectiveness of hydrochloric acid in promoting the reduction of the sulfone group in tetraphenylthiophene 1-dioxide and benzo- thiophene 1-dioxide (I) may be associated with the addition of a proton to the 2-3 double bond giving a positively charged intermediate, which is susceptible to the reducing action of zinc.

The reaction of benzo- thiophene 1-dioxide (I) with excess lithium aluminum hydride in ethyl ether solution yielded 33% of 2,3-dihydrobenzo- thiophene (IV) in one-half hour; 79% in 18 hours. Benzothiophene (III) was not reduced in measur- able quantity in 18 hours, whereas 2,3-dihydro- benzothiophene 1-dioxide (II) gave 92% of IV within 30 minutes. It is evident that III is not



an intermediate in the reduction of I to IV; the first stage of this reaction is probably a slow reduction of I to II.

In subsequent experiments it was found that an equimolar quantity of lithium aluminum hydride was sufficient to effect the reduction of 2,3-dihydro- benzothiophene 1-dioxide (II). Gas evolution was observed in this reaction, but an accurate deter- mination was not made. The present evidence suggests the equation shown, which is similar to those given for other lithium aluminum hydride reactions.⁸



Extension of the study of the reaction of lithium aluminum hydride to other types of sulfones re- vealed some remarkable differences in the ease with which reduction could be accomplished. Although the reduction of 2,3-dihydrobenzo- thiophene 1-dioxide (II) was essentially complete with 30 minutes when the reaction was carried out in refluxing ethyl ether solution, the open-chain analog, phenyl ethyl sulfone, gave no reaction under these conditions, and ethyl sulfone gave no re- action in twelve hours. The corresponding six- membered ring compound, 2,3-dihydro-1,4-benzo- thiapyran 1-dioxide gave no sulfide after two hours and only 9% after five hours. Apparently this

(8) Nystrom and Brown, *THIS JOURNAL*, **70**, 3738 (1948), and previ- ous papers.

(1) Beckmann, *J. prakt. Chem.*, [2] **17**, 439 (1878).

(2) Kraft and Vorster, *Ber.*, **26B**, 2813 (1893).

(3) Böseken, *Rec. trav. chim.*, **30**, 137 (1911).

(4) Kliger, *J. Gen. Chem. (U. S. S. R.)*, **3**, 904 (1933); *C. A.*, **28**, 3051 (1934).

(5) Hinsberg, *Ber.*, **48B**, 1611 (1915).

(6) Bordwell and McKellin, *THIS JOURNAL*, **72**, 1985 (1950).

(7) Challenger and Clapham, *J. Chem. Soc.*, 1615 (1948).

difference in reactivity of five- and six-membered ring sulfones is general since thiacyclopentane 1-dioxide and 2-methylthiacyclopentane 1-dioxide were reduced in good yield under these conditions within 30 minutes, whereas thiacyclohexane 1-dioxide gave only a trace of sulfide after 12 hours. The four-membered ring sulfone, thiacyclobutane 1-dioxide, was also readily reduced, while open-chain sulfones and phenyl sulfone were unreactive.⁹

By increasing the reaction temperature to 92° by the use of ethyl butyl ether as the solvent the reaction was extended to all sulfones tried except *t*-butyl sulfone. The results of the reduction with lithium aluminum hydride are summarized in Table I. From these data it appears that the reduction of five-membered ring sulfones is roughly one hundred times as rapid as that of six-membered ring sulfones and open-chain sulfones.

TABLE I

REDUCTION OF SULFONES TO SULFIDES WITH LITHIUM ALUMINUM HYDRIDE

Sulfone	LiAlH ₄ /sulfone	Temp., °C.	Time, hr.	Yield, %	Recovery, %
Benzothiophene 1-dioxide	9/1	35	0.5	33 ^a	
	9/1	35	18	79 ^a	
2,3-Dihydrobenzothiophene 1-dioxide	9/1	35	0.5	92	
	2/1	35	1	86	
2,3-Dihydrobenzothiophene 1-dioxide	1.1/1	35	1	83	
Phenyl ethyl sulfone	9/1	35	0.5	..	90
Phenyl ethyl sulfone	3/1	92	2	14	55
Phenyl ethyl sulfone	3/1	92	8	60	
2,3-Dihydro-1,4-benzothiazepyrane 1-dioxide	10/1	35	2	Trace ^b	
	3/1	35	5	9	90
2,3-Dihydro-1,4-benzothiazepyrane 1-dioxide	3/1	92	24	67	
Thiacyclohexane 1-dioxide	10/1	35	1	..	90
	3/1	35	12	Trace ^b	
Thiacyclohexane 1-dioxide	3/1	92	4	41	
Dibenzothiophene 5-dioxide	1.1/1	35	1	74	
Thiacyclopentane 1-dioxide	9/1	35	0.5	75	
2-Methylthiacyclopentane 1-dioxide	3/1	35	1	79	
Thiacyclobutane 1-dioxide	10/1	35	0.5	61	
Methyl sulfone	5/1	35	0.5	..	95
Methyl sulfone	3/1	35	12	Trace ^b	
Ethyl sulfone	3/1	35	12	..	80
Butyl sulfone	3/1	35	24	..	83
Butyl sulfone	3/1	92	2.5	26	28
Butyl sulfone	3/1	92	18	73	
<i>t</i> -Butyl sulfone	3/1	92	18	..	75
Phenyl sulfone	3/1	35	12	..	75
Phenyl sulfone	3/1	92	2	71	
Phenyl vinyl sulfone	3/1	92	2.5	12 ^c	
Phenyl vinyl sulfone	3/1	92	18	14 ^c	
Thiacyclopent-3-ene 1-dioxide	3/1	35	2	.. ^d	

^a 2,3-Dihydrobenzothiophene. ^b Sulfide odor. ^c Phenyl ethyl sulfide. ^d No sulfide was recovered from the dark-colored polymeric material obtained.

(9) Marvel and Caesar, *THIS JOURNAL*, **72**, 1033 (1950), recently reported the failure of phenyl sulfone to reduce under the usual conditions.

Recently Trevo and Brown¹⁰ have observed that most lithium aluminum hydride reductions can be considered as displacements of oxygen, nitrogen or halogen by hydrogen, the reactions probably being initiated by nucleophilic attack of aluminohydride ions on carbon. The reduction of organic sulfur compounds can be formulated in a similar manner, attack of aluminohydride ions occurring on sulfur¹¹ rather than on carbon. Thus, the reduction of disulfides,^{12,13} sulfonyl chlorides,¹³ sulfonyl thiocyanates,¹³ sulfonic acids,¹³ sulfoxides,¹⁴ sulfonyl chlorides,^{9,13} aryl sulfonates,^{13,15} thio-sulfonates¹³ and sulfones may be represented as displacement of chlorine, oxygen or sulfur by attack of aluminohydride ions on sulfur. An alternative representation, except for disulfides and sulfonyl thiocyanates would be an attack of aluminohydride ions on chlorine or oxygen. The inertness of *t*-butyl sulfone may be more easily rationalized, however, by assuming a steric (neopentyl-type) effect to attack of aluminohydride ions on sulfur. The resistance of *t*-butyl disulfide¹² to reduction is analogous. Using this view and an analogy with halide displacement reactions it is possible to account for the lower rate of reaction of six-membered ring sulfones as compared to five-membered ring sulfones, since displacement reactions of cyclohexyl halides are notoriously slow.¹⁶ However, the enhanced reactivity to reduction of five-membered cyclic sulfones vs. open-chain sulfones does not appear to have a counterpart in halide reactions,¹⁷ and there is no evidence that six-membered ring sulfones are more resistant to reduction than open-chain sulfones, as would be expected from the halide analogy.

Acknowledgment.—This work was supported in part by a grant from the Texas Company and in part by the American Petroleum Institute under Research Project 48B.

Experimental

Reduction of Benzothiophene 1-Dioxide with Zinc.—A mixture of 5.0 g. (0.030 mole) of benzothiophene 1-dioxide dissolved in 50 ml. of acetic acid, 12 g. of zinc (20 mesh granular) and 50 ml. of concd. hydrochloric acid was refluxed for three hours, 12 g. more of zinc and 50 ml. more of concd. hydrochloric acid being added after the first hour. The solution was steam distilled and the distillate made alkaline and extracted with ether. The ether extract was washed and dried; distillation gave 1.85 g. of benzothiophene, b.p. 111–112° (30 mm.), m.p. 30–31° (46% yield).

Preparation of Sulfones.—The sulfones were, for the most part, purchased, or synthesized by standard procedures. Thiacyclobutane, thiacyclopentane, 2-methylthiacyclopentane and *t*-butyl sulfide were kindly furnished by Dr.

(10) Trevo and Brown, *ibid.*, **71**, 1675 (1949).

(11) Nucleophilic displacements on sulfur have not been as generally recognized as those on carbon, but reactions of sulfonyl chlorides, sulfonyl thiocyanates, disulfides, sulfonyl chlorides and sulfonyl chlorides with amines, hydroxide ions, mercaptide ions, etc., are probably of this type.

(12) Arnold, Lien and Alm, *THIS JOURNAL*, **72**, 731 (1950).

(13) Strating and Backer, *Rec. trav. chim.*, **69**, 638 (1950).

(14) In contrast to the report of Strating and Backer,¹³ Dr. Burnett M. Pitt of this Laboratory has found that sulfoxides may be reduced to sulfides by lithium aluminum hydride at 35° in ethyl ether.

(15) Alkyl sulfonates, as might be anticipated, are usually attacked at carbon rather than sulfur.¹¹ However, see Karrer and Schmid, *Helv. Chim. Acta*, **32**, 1371 (1949), for certain exceptions.

(16) Conant and Hussey, *THIS JOURNAL*, **47**, 476 (1925); Bartlett and Rosen, *ibid.*, **64**, 543 (1942).

(17) Unpublished results of Dr. Glenn D. Cooper of this Laboratory.

Burnett M. Pitt. Oxidation of 10.2 g. (0.07 mole) of *t*-butyl sulfide in 45 ml. of acetic acid solution with 45 ml. (0.45 mole) of 30% hydrogen peroxide was effected by refluxing the solution for one hour. Neutralization of the acetic acid with aqueous sodium hydroxide, and ether extraction gave 9.5 g. (77%) of *t*-butyl sulfone, m.p. 129–130°. An analytical sample prepared by crystallization from water melted at 130–130.5°.

Anal. Calcd. for $C_8H_{18}O_2S$: C, 53.89; H, 10.18. Found: C, 53.73; H, 10.25.

2,3-Dihydro-1,4-benzothiapyran 1-dioxide (thiachromanone 1-dioxide) was prepared from thiachromanone¹⁸ by a modified Wolff-Kishner reduction,¹⁹ and oxidation of the crude sulfide with 30% hydrogen peroxide in acetic acid. Based on thiachromanone a 76% yield of sulfone, m.p. 87–89°, was obtained. It melted at 88–89° after crystallization from water; von Braun²⁰ reported 88.5°.

Phenyl vinyl sulfone was prepared from β -chloroethyl phenyl sulfone.²¹ A solution of 34.5 g. (0.2 mole) of β -chloroethyl phenyl sulfide²¹ in 50 ml. of acetic acid was treated with 100 ml. (1 mole) of 30% hydrogen peroxide. The reaction mixture was refluxed for ten minutes, cooled, diluted with 100 ml. of water and 500 ml. of benzene, and neutralized with sodium bicarbonate. The benzene layer was washed, dried by distilling a portion of the benzene, and treated with 500 ml. of triethylamine. The mixture was filtered and the filtrate evaporated to yield 36 g. of phenyl vinyl sulfone, m.p. 65–68° (80% over-all yield from thiophenol). After crystallization from petroleum hexane (b.p. 60–76°) the melting point was 67–68°.

(18) Krollpfeiffer and Schultze, *Ber.*, **56B**, 1819 (1923).

(19) Huang-Minlon, *THIS JOURNAL*, **68**, 2487 (1946).

(20) von Braun, *Ber.*, **43B**, 3220 (1910).

(21) Steinkopf, Herold and Stöhr, *ibid.*, **53B**, 1012 (1920).

Anal. Calcd. for $C_8H_8O_2S$: C, 57.12; H, 4.79. Found: C, 56.83; H, 4.47.

Reduction of Sulfones to Sulfides with Lithium Aluminum Hydride.—The sulfones were reduced in 2–6 g. quantities at the reflux temperature of ethyl ether or ethyl butyl ether.²² The reactions in which the molar ratios of lithium aluminum hydride were 9/1 or 10/1 were run by addition of ether solutions or suspensions of the sulfones to ether solutions of the hydride. In later experiments, where the ratio of hydride to sulfone was 3/1 or less, the solid sulfone and hydride were weighed into the reaction flask, and the ether added through the condenser with stirring (a magnetic stirrer was used). At the end of the reaction time the hydride was decomposed by drop-wise addition of water, and the precipitate dissolved in dilute hydrochloric acid. The ether and sulfide were usually separated from the metal salts by steam distillation, separation and drying of the ether layer, and stripping of the ether through a short helix-packed column. The sulfides were distilled from a 5-ml. Claisen flask. Identification was made on the basis of boiling points and also, in most instances, by oxidation to the sulfone (m.p. and mixed m.p.). Thiacyclobutane, thiacyclopentane and 2-methylthiacyclopentane were separated from the ether-sulfide distillate by means of mercuric chloride, the yield of sulfide being calculated on the assumption that a mercuric chloride salt, $R_2S \cdot HgCl_2$, was obtained. Phenyl sulfide and dibenzothiophene were isolated from the reaction mixture by ether extraction. Recovery of the sulfones was made by evaporation of the steam distillation residues with the aid of a current of air, extraction with benzene and evaporation.

(22) Kindly furnished by Dr. R. W. McNamee, Carbide and Carbon Chemicals, Charleston, W. Va.

EVANSTON, ILLINOIS

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Ultraviolet Absorptions of Some 2,5-Diphenylfurans and Related Compounds¹

BY SPENCER M. KING,^{2a} CARL R. BAUER^{2b} AND ROBERT E. LUTZ

The ultraviolet absorptions of 2,5-diphenylfuran and twenty-five derivatives and analogs, including 2,5-diphenylthiophene and three 2,5-diphenylpyrroles, have been measured and found to resemble those of the 1,4-diphenylbutadienes. Absorption at the longer wave length is suppressed by substitution of mesityl groups for the 2,5-phenyls, and increased by substitution of *p*-xenyl groups.

Furan does not absorb in the near ultraviolet above 220 $m\mu$ but does so when the conjugation is increased by even one α -ethylene linkage³ or a phenyl group.^{3b} Diphenylfuran (Ia) and a number of its derivatives (Ib–q) have now been studied and have been found to possess two distinctive bands, one in the range 226–235 $m\mu$ and the other (and stronger) in the range 312–340 $m\mu$. Illustrations are given in Figs. 1–3 and the data are tabulated. These absorptions are similar to those of the 1,4-diphenylbutadienes,⁴ $C_6H_5CH=CHCH=CHC_6H_5$. The λ_{max} (324 $m\mu$) of the longer-wave length band of 2,5-diphenylfuran itself is intermediate between the maxima of the main long wave length bands of the all-*cis* and all-*trans* diphenylbutadienes but it is closer to that of the all-*trans* isomer; and the extinction coefficient (29.2×10^3) is not far below that of the all-*cis* isomer but it is about half that of the strongly-absorbing all-*trans* isomer. On the

whole it may be said that the absorption of 2,5-diphenylfuran more closely resembles that of the all-*cis* diphenylbutadiene than that of the all-*trans* isomer. It should be noted, however, that, configurationally, 2,5-diphenylfuran is not strictly comparable with either the all-*cis* or the all-*trans* diphenylbutadiene system because, although it corresponds to all-*trans* with respect to the double bonds, it has a *cis* arrangement of the molecule as a whole with respect to the 3,4-furan bond, a condition which does not exist in either of the diphenylbutadienes.

In the case of the mono and disubstituted diphenylfurans Ib–m there is no doubt as to structures; in certain of the others, In–q, the comparability of the ultraviolet absorptions supports the furan structures given⁵ and excludes the conceivable though most unlikely 2-substituted-3-methylene-2,5-diphenyl-2,3-dihydrofuran formulations.

2,4-Diphenylfuran (II, Fig. 1) which does not contain the 1,4-diphenylbutadiene system, has a quite different ultraviolet absorption from that of the 2,5-diphenyl compounds; the two peaks ob-

(1) Taken from Doctorate Dissertations of the first two authors, University of Virginia, July, 1950.

(2) (a) Experiment, Inc., Richmond, Va.; (b) du Pont Co. Fellow, 1949–1950, now at University of Virginia Medical School.

(3) (a) Hughes and Johnson, *THIS JOURNAL*, **53**, 737 (1931); (b) Johnson, *J. Chem. Soc.*, 895 (1946).

(4) Sandoval and Zechmeister, *THIS JOURNAL*, **69**, 553 (1947).

(5) Lutz and Bailey, *ibid.*, **67**, 2229 (1945).