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# SYNTHESIS AND PROPERTIES OF A NAPHTHOTHIETE SULFONE
## (3,8-DIPHENYL-2H-NAPHTH[2,3-b]THIETE-1,1-DIOXIDE)[1,2]

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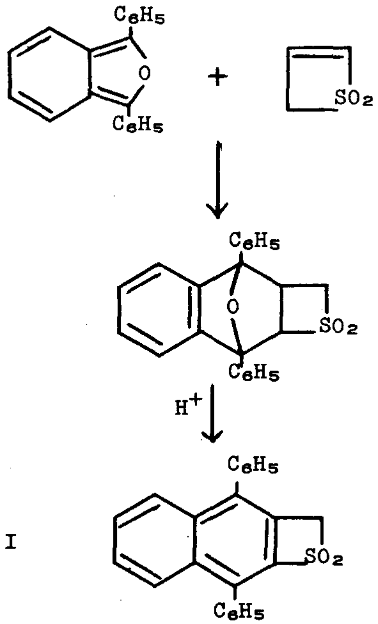
Although various thiete (thiacyclobutene) sulfones have been prepared recently,[3] no thiete derivative has been reported which has the double bond as part of an aromatic ring system.[4] We wish to report the synthesis of 3,8-diphenyl-2H-naphth [2,3-b] thiete-1,1-dioxide (I), an example of this class of compounds, and some of the reactions which it undergoes.

The synthesis involves the Diels-Alder addition of 1,4-diphenyl-2,3-benzofuran to thiete sulfone in refluxing benzene and subsequent aromatization of the adduct by treatment with sulfuric acid or with polyphosphoric acid. The intermediate ether, obtained in 89% yield, is a white, crystalline solid, m.p. 221°. Anal. Calcd. for $C_{23}H_{18}O_3S$: C, 73.78; H, 4.85; S, 8.55. Found: C, 73.88; H, 4.84; S, 8.55. The thiete sulfone, I, is prepared in yields of about 90% by treatment of the ether with concentrated sulfuric acid or with polyphosphoric acid at room temperature. It could be obtained also by treatment of the crude ether with ethanolic hydrogen chloride. The sulfone is isolated by pouring the reaction mixture into ice water.

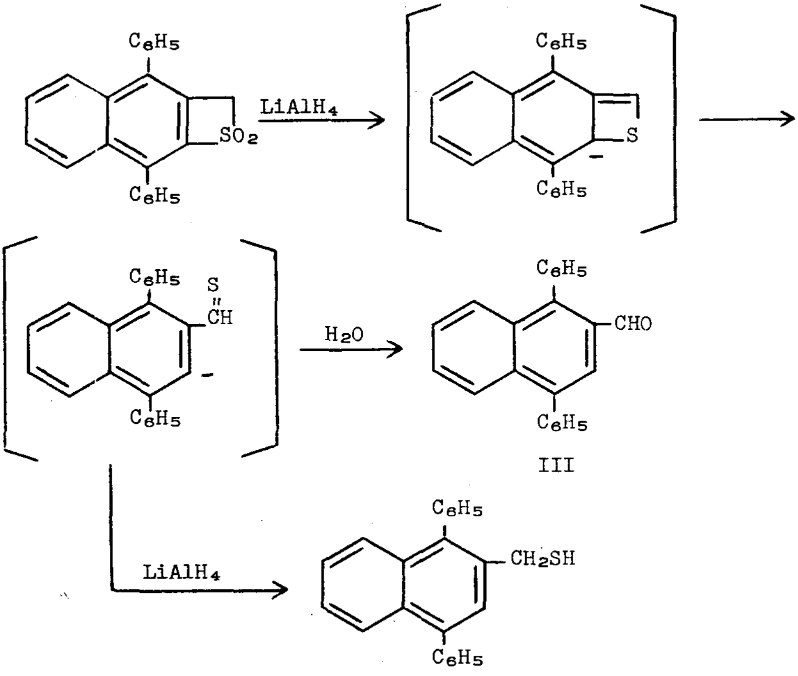


I

3,8-Diphenyl-2H-naphth[2,3-b] thiete-1,1-dioxide is a white, crystalline solid, m.p. 259°, which fluoresces a brilliant blue-white. <u>Anal</u>. Calcd, for $C_{23}H_{16}O_2S$: C, 77.51; H, 4.53; S, 8.98; molecular weight, 356. Found: C, 77.70; H, 4.50; S, 8.69; molecular weight, 350. The infrared spectrum shows absorption at 1130 and 1298 $cm^{-1}$ for the sulfone group, and the proton magnetic resonance spectrum (in $CDCl_3$ at 60 Mc relative to tetramethylsilane) shows two absorptions at 5.10 and 7.64 $\delta$ whose areas are in the ratio 2:14. The ultraviolet spectrum in acetanitrile has three maxima at 241 ($\varepsilon$ 5.3 x $10^4$), 315 ($\varepsilon$ 1.2 x $10^4$) and 338 mμ ($\varepsilon$ 9.1 x $10^3$).

Reduction of I with lithium aluminum hydride in ether at 0° yields 1,4-diphenyl-2-mercaptomethylnaphthalene, II, m.p. 138°.

Anal. Calcd. for $C_{23}H_{18}S$: C, 84.63; H, 5.56; S, 9.81; molecular weight 326. Found: C, 84.40; H, 5.70; S, 9.55; molecular weight 338. The proton magnetic resonance spectrum of the mercaptan (in $CDCl_3$ at 60 Mc relative to tetramethylsilane) has absorption at 1.65, 3.66, and 7.50 δ in the ratio of 1:2:15. It decolorizes an iodine solution. When the reduction is done at -78°, 1,4-diphenyl-2-naphthaldehyde, III, m.p. 147°, is obtained as the major product along with some II. The aldehyde is identified by a mixture melting point with an authentic sample and by comparison of infrared, ultraviolet and proton magnetic resonance spectra with those of an authentic sample prepared by an independent route[5]. Work is in progress on the determination of the mechanism of this reduction. A possible rationalization involves the formation of a thiete anion which, with 14 π-electrons, obeys the Hückel 4 n + 2 rule where n=3. A deep purple color is observed during the reduction which may be due to the anion or to the thioaldehyde. At low temperatures the anion may be more stable and on work up of the reaction mixture it yields the thioaldehyde which is hydrolyzed to the naphthaldehyde[6]. At higher temperatures, the anion may decompose to the thioaldehyde which is reduced to the mercaptan.



III

II

When I is heated for 5 min. at 400°, carbon monoxide and several organic products, two of which have been partially characterized, are obtained. One, a bright red compound, m.p. 271°, has a tentative empirical formula of $C_{23}H_{13}OS$, a carbonyl absorption in the infrared at 1750 $cm^{-1}$ and ultraviolet maxima in chloroform at 272 and 315 mμ. The second compound is white, m.p. 237°, has a tentative empirical formula of $C_{23}H_{14}S$, and has ultraviolet maxima in chloroform at 253, 311, 350 and 368 mμ.

The thermal decomposition of I seems to be unprecedented oxidation-reduction reaction involving a sulfone in which the sulfone is reduced and a carbon is oxidized. Work is in progress on the elucidation of the structures of the pyrolysis products and on the chemistry of aromatic thiete derivatives.

## REFERENCES

(1) This research was supported by Grant GP 726 from the National Science Foundation.

(2) Reported in part at the 148th Meeting, American Chemical Society, Chicago, Illinois, Sept., 1964, Abstracts of Papers, p. 69S.

(3) D. C. Dittmer and M. E. Christy, J. Org. Chem., **26**, 1324 (1961); W. E. Truce, J. R. Norell, J. E. Richman and J. P. Walsh, Tetrahedron Letters, 1677 (1963); W. E. Truce and J. R. Norell, J. Am. Chem. Soc., **85**, 3236 (1963); R. H. Hasek, P. G. Gott, R. H. Meen, and J. C. Martin, J. Org. Chem., **28** 2496 (1963); G. Opitz and H. Schempp, Z. Naturforsch, **19b**, 78 (1964).

(4) Dr. Leo Paquette has kindly informed us that several such derivatives have been prepared recently in his laboratory.

(5) R. Weiss and A. Abeles, Monatsh. Chem., **61**, 165 (1932).

(6) Thiocarbonyl groups are hydrolyzed to their oxygen analogs: Houben Weyl's Methoden der Organischen Chemie-Schwefel-, Selen-, Tellur- Verbindungen, Vol. IX, p. 723. Georg Thieme, Stuttgart, (1955).