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SYNTHESIS AND REACTIONS OF 1,2-BENZOXATHIAN-4-ONE 2-OXIDES

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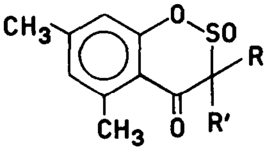
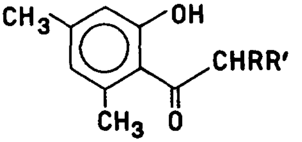
1,2-Benzoxathianes form a little known class of substances(1): the synthesis of 1,2-benzoxathian 2-oxide has only recently been reported by Givens and Hamilton, who described it as a pretty unstable compound(2) and no accounts have so far appeared on the synthesis of 1,2-benzoxathian-4-one 2-oxide, a cyclic ester of a δ-hydroxy-β-ketosulfinic acid(3).

We wish to report here the synthesis and some reactions of a group of stable, crystalline 1,2-benzoxathian-4-one 2-oxides (I, II, III), which can be easily obtained by refluxing the corresponding hydroxy ketones (IV, V, VI) with four parts of $SOCl_2$ for 1 hr(4).



I R=R'=H
II R=H R'=CH_3
III R=R'=CH_3



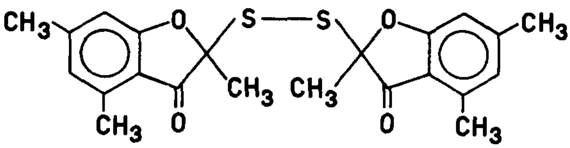
IV R=R'=H
V R=H R'=CH_3
VI R=R'=CH_3

Treatment of IV with $SOCl_2$ yielded a compound $C_{10}H_{10}O_3S$ (I), m.p. 113° (EtOH), whose IR spectrum shows strong bands at 1685 (carbonyl) and 1135 cm^{-1} (sulphinate group)(5). The PMR spectrum ($CDCl_3$) shows the expected AB pair of doublets (3.69 and 4.15 δ; J_{gem} = 15.1 Hz), since the geminal protons are non-equivalent owing to the presence of the chiral SO group. Oxidation of I with H_2O_2 in AcOH(2) afforded the 2,2-dioxide, m.p. 141°, whose IR spectrum shows three strong sulfonyl bands at 1380, 1180 and 1150 cm^{-1}(2). The PMR spectrum ($CDCl_3$) shows a singlet at 4.31 δ(2H) due to the two, now equivalent, geminal protons.

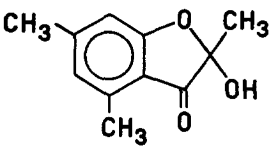
Treatment of VI with $SOCl_2$, likewise yielded III, m.p. 56° (pet. ether) (IR bands at 1685 and 1135 cm^{-1}), whose PMR spectrum shows the presence of two non-equivalent aliphatic CH_3 groups ($CDCl_3$; 1.51 and 1.57 δ).

Treatment of V with $SOCl_2$, followed by crystallization from EtOH, gave II A, m.p. 117° whose PMR spectrum shows the expected signals for the $CHCH_3$ group ($CDCl_3$; CH_3: d, 1.49 δ; CH : q, 4.10 δ). From the mother liquors a minor component, m.p. 86-89°, was isolated: its PMR spectrum shows that this compound is a 1:1 mixture of II A and its epimer II B ($CDCl_3$; CH_3: d, 1.58 δ; CH: q, 3.56 δ). On attempted separation of the two epimers by chromatography on Al_2O_3, complete decomposition occurred: one white crystalline compound $C_{22}H_{22}O_4S_2$, m.p. 164°, was isolated from the first chromatographic fractions and to it structure VII was assigned on the following grounds. The IR spectrum shows a band at 1705 cm^{-1} (conjugated CO in a strained ring) and no OH bands; the UV spectrum shows maxima at 272 and 334 nm, unchanged by addition of NaOH; the PMR spectrum ($CDCl_3$) shows, besides the Ar-CH_3 signals at 2.33 and 2.51 δ, a singlet at 1.66 δ, assigned to the two C^{IV}-CH_3 groups.

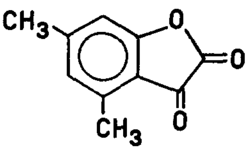
Although the 1,2-benzoxathian-4-one 2-oxides are relatively stable in protic solvents, they are easily decomposed by bases. Treatment of III with NaOH/EtOH at room temp gave VI and Na_2SO_3, whereas II yielded, beside some V and Na_2SO_3, a white crystalline compound $C_{11}H_{12}O_3$, m.p. 122-124°, to which structure VIII(6) has been assigned on the basis of the UV (λmax 268 and 333 nm; unchanged by addition of NaOH), IR (CH_2Cl_2; 3570 (OH) and 1720 cm^{-1} (CO, aromatic)(7)) and PMR ($CDCl_3$; s, 1.62 δ, C^{IV}-CH_3) spectra. Treatment of I with NaOH or piperidine, at reflux temp, yielded, besides some sulfur, a compound $C_{10}H_8O_3$, m.p. 145-147°, to which the structure of 4,6-dimethylcoumaran-2,3-dione (IX) (lit.(9) m.p. 145°) has been assigned on the basis of the PMR ($CDCl_3$; 2.45 and 2.56 δ, Ar-CH_3 groups; 6.84 and 6.91 δ, aromatic protons) and IR (1820 cm^{-1}, strained lactone; 1730 cm^{-1}, five-member ring ketone; no OH bands) spectra.



VII



VIII



IX

REFERENCES AND NOTES

1) D.S. Breslow and H. Skolnik; "Multi-sulfur and sulfur and oxygen five- and six-membered heterocycles" (A. Weissberger ed.) Interscience Publishers, New York, p. 792 (1966).

2) E. N. Givens and L.A. Hamilton, J. Org. Chem., 32, 2857 (1967).

3) W.L. Truce and C.W. Vriesen (J. Am.Chem. Soc., 75, 2525 (1953)) were unsuccessful in obtaining a β-chetosulfinic acid by reduction of ω.acetophenonesulfonyl chloride.

4) Yields decrease considerably by using a larger excess of $SOCl_2$ or longer reaction time. Simple o.acyl phenols, such as o.hydroxyacetophenone yield a very complex mixture and although the presence of 1,2-benzoxathian-4-one 2-oxide can be detected in the PMR spectrum ($CDCl_3$; dd at 3.77 and 4.34 δ; J_{gem} 14.0 Hz), we have been unable to isolate a pure product.

5) D. Darwish and E.A. Preston, Tetrahedron Letters, 113 (1964).

6) K.V. Auwers and W. Müller (Ber., 50, 1149 (1917)) report m.p. 115-117°.

7) A strong band is also present at 1610 cm^{-1}. A similar, unexplained band, has been previously reported(8) in the case of coumaranone.

8) A.K. Bose and P. Yates, J.Am.Chem.Soc. 74, 4703 (1952).

9) K. Fries and Bartens, Liebigs Ann.Chem. 442, 265 (1925).