The Behaviour of the 1,2-Dithiolium Cation towards Selected Nucleophiles

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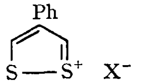
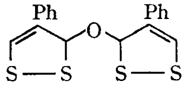
THE behaviour of the 1,2-dithiolium cation towards nucleophilic agents has been little explored.[1,2b] We report here our observations on the behaviour of this cation, as represented by 4-phenyl-1,2-dithiolium hydrogen sulphate (I), in[1a] dimethyl sulphoxide–water and towards the following nucleophiles: hydroxide ion in aqueous sodium hydrogen carbonate and aqueous sodium hydroxide, hydrogen sulphide and aqueous ammonia.


(I) X=HSO_4^-
(II) X=ClO_4^-

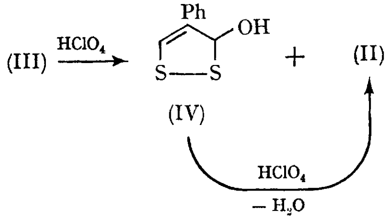

(III)

Dimethyl Sulphoxide–Water—The protons on the dithiolium ring (10·9δ) undergo exchange in

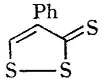
Me_2SO-D_2O with a half-life of *ca.* 30 min.[2] (followed by n.m.r.).

Aqueous $NaHCO_3$.—A yellow crystalline solid was obtained in 46% yield by treating an aqueous solution of (I) with an excess of sodium hydrogen carbonate at room temperature for 30 min., followed by trituration of the water-insoluble product with ether. The analytical data of the product (m.p. 107—111° decomp.) and its molecular weight (345) were consistent with its formulation as the ether (III), λ_{max}(Nujol) 6·30 μ (M) (C=C); λ_{max}(MeOH) *ca.* 340 (ϵ 5600) (plateau), 304 (ϵ 19,000), and 230 mμ (ϵ 16,000). Its n.m.r. spectrum [in $CDCl_3-(CD_3)_2SO$ *ca.* 3 : 1] consisted of a single unsymmetrical multiplet which appeared between 7·58 and 7·25 δ.

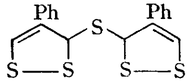
Additional support for the assigned structure follows from the behaviour of the product towards acid. Treatment of the compound with 70% perchloric acid in methylene chloride–ether resulted in the instantaneous precipitation of (II)[1a] in 87% yield [based on a calculated yield of 2 moles of (II) from one of (III)]. The high yield of this conversion indicates that the initially formed hydroxydithiolene (IV) is further transformed under the reaction conditions.



2N-*Sodium Hydroxide*.—Treatment of (I) with an excess of 2N-NaOH (pH of mixture ⩾ 13) gave a water-insoluble amorphous solid from which the trithione (V)[1a,3] could be obtained (15% yield) by chromatography on alumina. In view of the foregoing results, the previous report[1a] that upon exposure to even a weak base the 1,2-dithiolium cation decomposes with the liberation of sulphur would have to be amended.



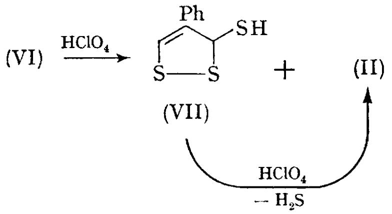
(V)

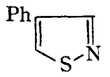


(VI)

Hydrogen Sulphide.—Treating an aqueous solution of (I) with hydrogen sulphide resulted in the immediate separation of a yellow solid, m.p. 143—145° decomp., after trituration with acetone. The product (obtained in 85% yield) is formulated as the thioether (VI) on the basis of its analysis and molecular weight. The infrared spectrum (Nujol) of (VI) was extremely simple showing two weak peaks at 6·40 and 6·50 μ, a strong peak at 13·15 μ and a medium-intensity one at 14·60 μ. The 6·0 μ region was completely transparent [*cf.* (III)]. Its ultraviolet spectrum was virtually the same as that of (III): λ_{max}(MeOH) *ca.* 350 (ϵ 3620) (plateau), 303 (ϵ 19,500) and 228 mμ (ϵ 17,500). Its n.m.r. spectrum [in $CDCl_3-(CD_3)_2SO$ *ca.* 3 : 1] showed a singlet at 6·45 δ and an unsymmetrical multiplet between 7·17 and 7·75 δ; relative intensities 1 : 6. Since replacing the ether oxygen in (III) with sulphur [as in (VI)] would be expected to predominantly affect the chemical shift of the adjacent proton, the 6·45 δ signal is attributed to the ring proton situated between the *endo*- and *exo*-cyclic sulphurs in (VI). The diamagnetic shift observed is in accord with the previously observed increase in shielding with decreased substituent electronegativity.[4]

Consistent with the assigned structure was the conversion of the product on treatment with 70% perchloric acid in methylene chloride–ether into (II) in 85% yield, hydrogen sulphide (detected by odour) also being formed. As in the case of (III), the high yield of (II) obtained is indicative of the further transformation of the mercaptodithiolene (VII) under the reaction conditions, as is, additionally, the formation of hydrogen sulphide.





(VIII)

Aqueous Ammonia.—On treatment of an aqueous solution of (I) (1 g.) with aqueous ammonia in the presence of ammonium chloride (pH of reaction mixture *ca.* 8) at room temperature (5 min.), there was obtained an orange, water-insoluble solid which was transformed into a yellow solid melting at 145—147° decomp. (0·35 g.) on trituration with acetone. Its analysis and its infrared, ultraviolet, and n.m.r. spectra showed it to be identical with the product previously obtained from (I) and hydrogen sulphide, *viz.* (VI). The other organic products formed in the reaction (isolated from the acetone wash above and extracted from the aqueous phase; total 0·2 g.) were shown (by thin-layer-chromatographic comparison with authentic specimens) to be predominantly the trithione (V) and the isothiazole (VIII).[2b,5] Analyses were performed by L. Brancone and his staff; ultraviolet and n.m.r. spectra were determined by W. Fulmor and his staff.

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[1] (a) E. Klingsberg, *J. Amer. Chem. Soc.*, 1961, **83**, 2934; (b) E. Klingsberg, *J. Org. Chem.*, 1963, **28**, 529.

[2] Exchange of the 1,2-dithiolium ring protons has been independently observed by (a) H. Prinzbach, E. Futterer, and A. Lütrringhaus (*Angew. Chem. Internat. Edn.*, 1966, **5**, 513 and (b) R. A. Olofson, J. M. Landesberg, R. O. Berry, D. Leaver, W. A. H. Robertson, and D. M. McKinnon, *Tetrahedron*, 1966, **22**, 2119.

[3] (a) B. Bottcher and A. Lüttringhaus, *Annalen*, 1947, **557**, 89; (b) E. K. Fields, *J. Amer. Chem. Soc.*, 1955, **77**, 4255.

[4] See L. M. Jackman, "Application of Nuclear Magnetic Resonance. Spectroscopy in Organic Chemistry," Pergamon, London, 1959, p. 54.

[5] F. Hubenett and H. D. Hofman, *Angew. Chem. Internat. Edn.*, 1963, **2**, 325.