A Ready Acid-catalyzed Cyclodeamination of a γ-Hydroxy-*NN*-dimethylsulphonamide to form a Sultone

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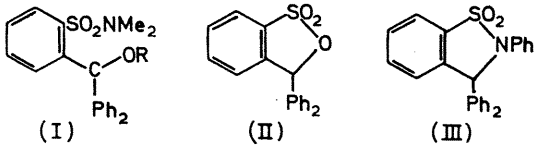
ATTEMPTED preparation of αα-diphenyl-*o*-(*NN*-dimethylsulphamoyl)benzyl methyl ether (I; R = Me) by addition of the hydroxy-sulphonamide (I; R = H) in cold, concentrated sulphuric acid to methanol,[1] gave the sultone (II) (90%). However at −78° the reaction gave the ether (I; R = Me) (77%). The structure of the ether (I; R = Me) was supported by its analysis and absorption spectra. That the sultone (II) was not produced in the concentrated sulphuric acid was shown by recovery of 90% of the hydroxy-sulphonamide (I; R = H) when the acid solution was added to water. Apparently the formation of the ether (I; R = Me) is kinetically controlled and that of sultone (II) is thermodynamically controlled, as indicated by the conversion of the ether (I; R = Me) into sultone (II) in acidic methanol.



(I) (II) (III)

The ready cyclodeamination of the hydroxy-sulphonamide (I; R = H) in methanolic sulphuric acid is novel,

since sulphonamides undergo hydrolysis and alcoholysis in the presence of acid or base only with difficulty.[2] The success of this alcoholysis of the sulphonamide group is evidently due to its intramolecular nature, as *NN*-dimethylbenzenesulphonamide fails to undergo alcoholysis or hydrolysis with methanolic sulphuric acid under similar conditions; this would have involved an intermolecularly-assisted deamination.

Although the hydroxy-sulphonamide (I; R = H) is presumably converted initially into the corresponding carbonium ion by concentrated sulphuric acid, as shown by the formation of the ether (I; R = Me), the carbonium ion appears to acquire a hydroxy-moiety again from the acidic medium to form (I; R = H) in order to yield the sultone (II). The cyclization reported here may involve protonation of the sulphonamide nitrogen of (I; R = H) and an intramolecular displacement of dimethylamine by the hydroxy-group of (I; R = H). Moreover, acids weaker than concentrated sulphuric such as protonated methanol seem to be required for the cyclodeamination.

The present synthesis of the sultone (II) is superior to earlier methods involving thermal cyclodeamination of the hydroxy-sulphonamide[3] (I; R = H) or treatment of the amide (I; R = H, NHPh for NMe_2) with concentrated sulphuric acid on a steam-bath,[4] which afforded the sultone (II) in yields of 30 and 18%, respectively. The mechanisms of both reactions are probably different from that of the present cyclization. A more characteristic acid-catalyzed reaction of the amide involves cyclodehydration to form the sultam (III) in good yield.[4] This cyclization which may be considered to involve a carbonium-ion intermediate is to be distinguished from the present cyclodeamination in which a carbonium ion is not the active intermediate.

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[1] For such a preparation of methyl triphenylmethyl ether see H. A. Smith and R. J. Smith, *J. Amer. Chem. Soc.*, 1948, **70**, 2400.
[2] (a) See C. R. Noller, "Chemistry of Organic Compounds," 3rd ed., W. B. Saunders, Philadelphia, 1965, p. 510; (b) W. Marckwald and A. F. von Droste-Huelshoff, D.R.P. 105,870/Jan. 12, 1897; *Chem. Zentr.*, 1900, **71**, I, 524; (c) H. R. Snyder and R. E. Heckert, *J. Amer. Chem. Soc.*, 1952, **74**, 2004, 4864.
[3] H. Watanabe, R. A. Schwarz, C. R. Hauser, J. Lewis and D. W. Slocum, *Canad. J. Chem.*, in the press.
[4] H. Watanabe, R. L. Gay and C. R. Hauser, *J. Org. Chem.*, 1968, **33**, 900.