Cycloaddition of Keten and Imines to Sulphur Dioxide

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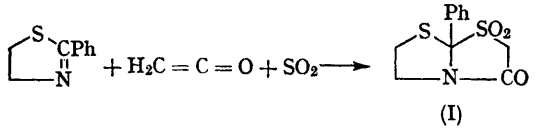
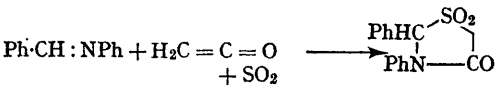
THE use of liquid sulphur dioxide as a solvent for ionic reactions has long been recognized.[1] Johnson and his co-workers have postulated an explanation for the ionizing influence of this solvent.[2] Smrt, Béranek and Šorm[3] reported that liquid sulphur dioxide was an outstanding solvent for the

reactions of keten with activated acid chlorides, and their results were confirmed in our laboratory.[4] We then decided to use this solvent during a study of the reactions of keten with imines to obtain



(I)

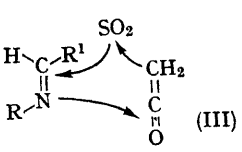


(II)

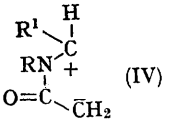
azetidinones. However, instead of the expected azetidinones, products containing sulphur dioxide were isolated in good yields. These structures result from what appears to be a novel cycloaddition reaction of sulphur dioxide.

Both products are white solids; dihydro-7a-phenyl-7a*H*-thiazolo[2,3-*b*]thiazol-3(2*H*)-one 1,1-dioxide (I) was obtained in 80% yield, m.p. 116·5° and 2,3-diphenylthiazolidin-4-one 1,1,-dioxide (II) was in 52% yield, m.p. 181—182°. Analytical and physical data indicated that both compounds contained a sulphur group. The i.r. spectrum of (I) (KBr) showed absorptions at 1700 (cyclic amide), and at 1350, 1325, and 1142 cm.$^{-1}$ (sulphone). The n.m.r. spectrum in deuterated dimethyl sulphoxide showed a multiplet (5 H) centred at 7·45, a multiplet centred at 4·35 (2 H), and a multiplet centred at 1·92 p.p.m. (4 H). The i.r. spectrum of (II) (KBr) showed absorptions at 1678 (amide), and at 1325, and 1135 cm.$^{-1}$ (sulphone). The n.m.r. spectrum in deuterated dimethyl sulphoxide showed a multiplet (10 H) centred at 7·45, a singlet at 6·80 (1 H), and a singlet at 4·65 (2 H) p.p.m.

This cycloaddition may proceed through a concerted mechanism (III) or through the reaction of a 1,4-dipole intermediate, formed from keten and the imine with sulphur dioxide (IV). The latter course seems more probable since the reaction appears to yield only one product and keten is known to react with imines in the absence of sulphur dioxide.[5]



(III)



(IV)

The extrusion of sulphur dioxide from (I) and (II) and the identification of the products formed are being investigated. The scope and mechanism of this cycloaddition are also being studied.

(*Received, August* 1*st*, 1967; *Com.* 809.)

[1] P. Walden, *Ber.*, 1899, **32**, 2862.
[2] R. E. Johnson, T. H. Norris, and J. L. Huston, *J. Amer. Chem. Soc.*, 1951, **73**, 3052.
[3] J. Smrt, J. Béranek, and F. Šorm, *Coll. Czech. Chem. Comm.*, 1955, **20**, 285.
[4] D. K. Wald and M. M. Joullié, *J. Org. Chem.*, 1966, **31**, 3369.
[5] H. Staudinger, *Ber.*, 1917, **50**, 1035; R. Pfleger and A. Jöger, *Chem. Ber.*, 1957, **90**, 2460.