Addition of Sulphenes to Thioamide Vinylogues: Substituted 5,6-Dihydro-1,2-dithiin 1,1-Dioxides and 1,2-Dithiin 1,1-Dioxides

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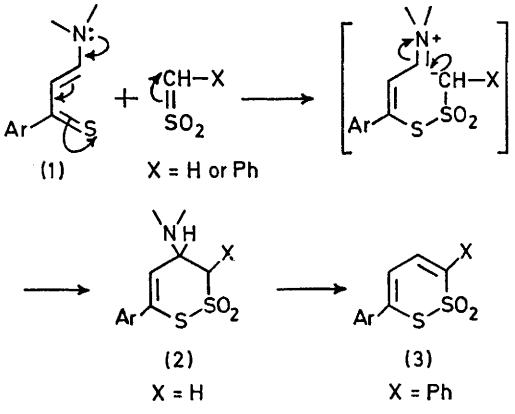
Summary Syntheses of substituted 1,2-dithiin 1,1-dioxides *via* the addition of sulphenes to thioamide vinylogues are described.

THE thioamide vinylogues ArC(S)CH=CHN< (**1**)[1] may lead to 1,4-cycloaddition products[2] involving the group S–C=C. Earlier papers[3] describe the reaction of sulphene, $CH_2{=}SO_2$, with amide vinylogues to give 4-amino-3,4-dihydro-1,2-oxathiin 2,2-dioxides. The sulphenes are produced by dehydrochlorination of sulphonyl chlorides with triethylamine.

We have found that the compounds (**1**) react with sulphene to give the 5-amino-3-aryl-5,6-dihydro-1,2-dithiin 1,1-dioxides (**2**) (see Scheme). Triethylamine (3 cm³) is added dropwise to a stirred mixture of (**1**) (2 g) and an excess of methanesulphonyl chloride (2 cm³) in 200 cm³ of dry benzene at room temperature. The mixture is stirred for 2 h and filtered. The mother liquor is washed with water and dried over anhydrous sodium sulphate, filtered, and concentrated to a pale yellow oil, which is crystallized from a mixture of ethanol–benzene to give (**2**)† in 41—61% yield (Ar = phenyl, *p*-bromophenyl, *p*-methylphenyl, and *p*-methoxyphenyl; –N< = morpholino, piperidino, *o*-anisidino). Analytical samples are prepared by chromatography on silica gel using benzene and mixtures of benzene–ethyl acetate as an eluant.



SCHEME

The thioamide vinylogues (**1**) react with phenylsulphene similarly, but the 1,4-addition is always followed by the elimination of amine (see Scheme) to give the 3-aryl-6-phenyl-1,2-dithiin 1,1-dioxides (**3**). Yields of (**3**) of 37—53% were obtained for Ar = phenyl, *p*-bromophenyl, *p*-chlorophenyl, and *p*-methoxyphenyl.

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† Satisfactory analytical data and spectra (i.r., n.m.r.) were obtained for all compounds described.

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[3] G. Opitz and E. Tempel, *Angew. Chem.*, 1964, **76**, 921; *Angew. Chem. Internat. Edn.*, 1964, **3**, 754; *Annalen*, 1966, **699**, 74; W. E. Truce, D. J. Abraham, and P. Son, *J. Org. Chem.*, 1967, **32**, 990.