Tetrahedron Letters No.47, pp. 4863-4864, 1968. Pergamon Press. Printed in Great Britain.

The reaction of N,N-dichloro-N',N'-dimethylsulphamide with phenylethylenes

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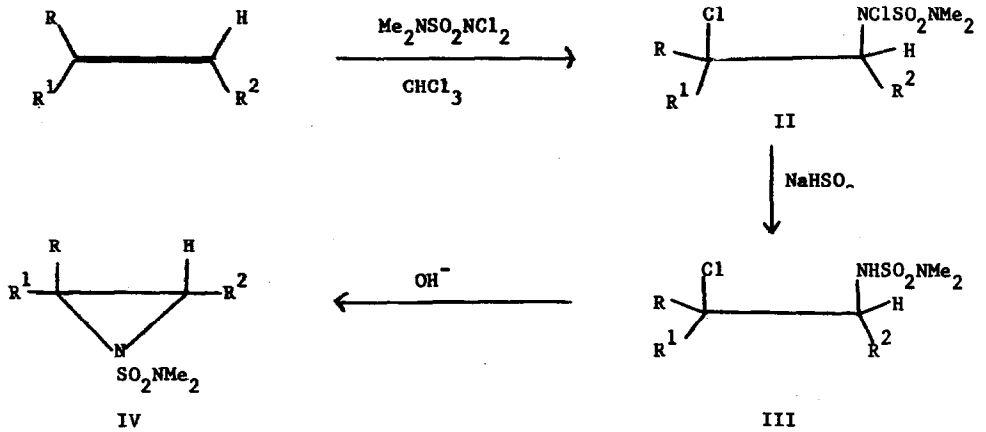
(Received in UK 25 July 1968; accepted for publication 16 August 1968)

The functionalisation of olefins with N,N-dichlorourethane[1], N,N-dichlorotoluene-p-sulphonamide[2], and O,O-diethyl N,N-dichlorophosphoramidate[3] have been described recently. We wish to report the preparation of the novel pseudo-halogen, N,N-dichloro-N',N'-dimethylsulphamide (I), and its free radical addition to a number of phenylethylenes.

Addition of N,N-dimethylsulphamide to excess 4N. sodium hypochlorite solution at 0° followed by acidification with acetic acid to pH6 and chloroform extraction, gave in 68% yield the dichlorinated product (I), as a yellow oil (b.p. 68-70° /0.3 mm.), which seemed quite stable at room temperature. The crude oil on thin layer chromatography, I.R. and N.M.R. examination was deemed pure enough to be used without distillation. The pseudo-halogen (I) reacted exothermically with phenylethylenes in chloroform solution to give the free radical addition products (II), which are readily reduced with sodium bisulphite solution to the corresponding N-(β-chloroethyl)-N',N'-dimethylsulphamides (III). Styrene gave a 76% yield of (III, R = Ph, R^1, R^2 = H), m.p. 70-71° (from ether/petroleum ether).



The 100 Mc./sec. N.M.R. spectrum ($CDCl_3$) showed the CH_2 group as a triplet, which collapsed to a doublet on D_2O treatment, demonstrating the anti-Markownikoff nature of the addition. Cyclisation utilising sodium hydroxide gave the aziridine (IV, R, = Ph, R^1,R^2 = H), m.p. 43° (from petroleum ether) in 85% yield. Similarly 1,1-diphenylethylene furnished (III, R,R^1 = Ph, R^2 = H), m.p. 153° (from ether/petroleum ether), in 30% yield, isolated after column chromatography (silica/benzene), which readily cyclised to the aziridine, m.p. 109° (from ether) on treatment with alkali.

Reaction of (I) with anethole proved more complicated, a mixture of erythro and threo forms of (III, R = p-$MeOC_6H_4$, R^1 = H, R^2 = Me), m.p. 73-75° being obtained in 55% yield after column chromatography (silica/benzene ether mixture). Cyclisation of the isomer mixture with sodium hydroxide gave a mixture of the cis and trans aziridines (IV, R = p-$MeOC_6H_4$, R^1 = H, R^2 = Me) in a ratio of 1.25 to 1. The 100 Mc./sec. N.M.R. spectrum ($CDCl_3$) of the isomer mixture showed two methyl doublets centred at 8. 36τ and 8.97τ , which were assigned to the trans and cis isomers respectively by analogy with the specta of cis and trans 1-phenyl-2-methylaziridines[4]. This cis-isomer of the 2-methylaziridine is reported to have its methyl doublet at higher field than that of the trans isomer due to the shielding effect of the aromatic ring. Confirmation of this assignment was provided by separation of the cis isomer by column chromatography (silica/benzene) and the observation that the coupling constant for its vicinal ring protons was 7 c.p.s. compared with 4.2 c.p.s. for the trans isomer. This complies with the reported general stereospecificity of vicinal coupling for styreneimines, that $J_{cis} > J_{trans}$ regardless of the nature of the ring substituents[4].

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