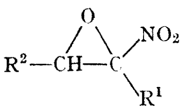
α-Nitro-epoxides, a New Class of Compounds

By HOWARD NEWMAN* and ROBERT B. ANGIER

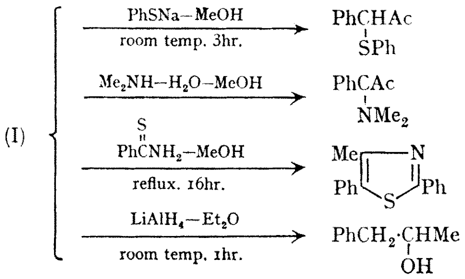
(*Organic Chemical Research Section, Lederle Laboratories, American Cyanamid Company, Pearl River, New York,* **10964**)

Summary The first examples of α-nitro-epoxides have been prepared; some chemical properties are reported.

WE report the preparation and chemical properties of α-nitro-epoxides, generated from nitro-olefins in methanol with hydrogen peroxide-dilute sodium hydroxide (*cf.* αβ-unsaturated ketones[1]). β-Methyl-β-nitrostyrene gave (I) [67%: light yellow liquid, b.p. 77—78°/0·1 mm: λ_{max} (film) 6·47s μm. (-NO_2); λ_{max} (MeOH) 290br (ϵ 450), 230br nm. (4500), and end absorption: n.m.r. δ 7·40 (finely split s, 5H, ArH), 4·58 (s, 1-H), and 1·83 p.p.m. (s, 2-CH_3)]; cis-α-nitrostilbene gave (II) [85%: colourless crystals (from MeOH),† m.p. 108—110°: λ_{max} (Nujol) 6·45s μm. (s, NO_2); (MeOH) 290 br (800), 232br (6000), and end absorption: n.m.r. δ 7·35—7·00 (m, 10H, ArH) and 4·75 p.p.m. (s, 1H)]; and 2-cyclohexyl-1-methyl-1-nitroethylene gave (III) [91%: colourless liquid, b.p. 68—71°/0·1 mm.: λ_{max} (film) 6·40s (NO_2); (MeOH) end absorption only: n.m.r. δ 3·17 (m, 1-H), 1·93 (sharp s, 2-Me), and 1·9—1·1 p.p.m. (br m, cyclohexyl H)].



(I) R^1=Me, R^2=Ph
(II) R^1=R^2=Me
(III) R^1=Me, R^2=cyclohexyl



Substitution on the carbon bearing the nitro-substituent appears necessary for the success of the reaction since, under the same conditions, β-nitrostyrene gave only benzaldehyde and starting material.

The behaviour of (I) towards nucleophiles (Scheme)† parallels that previously observed for epoxides with electronegative substituents at the carbon furthest from the epoxy-group: this is rationalized in terms of an S_N2 transition state in which the reacting carbon centre bears a residual positive charge. The similarity in behaviour of (I) to an α-halogeno-ketone makes (I) a useful alternative to those highly lachramatory compounds.

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† Satisfactory analytical data were obtained for all new compounds.

[1] E. Weitz and A. Scheffer, *Ber.* 1921, **59**, 2327.

[2] R. E. Parker and N. S. Isaacs, *Chem. Rev.*, 1959, **59**, 737.

[3] The reaction of $LiAlH_4$ and α-halogenoketones gives initially the halohydrin which, in the presence of an excess of hydride, can be further reduced to the alcohol: R. E. Lutz, R. C. Wayland, jun., and H. G. France, *J. Amer. Chem. Soc.*, 1950, **72**, 5511.