Methylene Nitrones, a New Type of Nitrone

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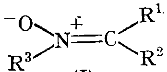
ALL the nitrones known up to the present time bear at least one *C*-substituent (I; R^1 and/or R^2 = alkyl, aryl, or other residue), the unsubstituted compounds, the methylene nitrones (I; $R^1 = R^2 = H$) being unknown.[1,2] We have discovered that diazomethane reacts rapidly and quantitatively at room temperature with t-nitroso-monomers (II) to provide methylene nitrones. The blue t-nitroso-monomers were obtained by melting the labile dimers and dissolving the product in warm ether. These solutions could be titrated with the yellow ethereal diazomethane solution, removal of the solvent affording the product. The dimeric nitroso-compounds were, in their turn, conveniently accessible by oxidation of the parent amines with *m*-chloroperbenzoic acid in chloroform.[3] The combination of these two procedures thereby constitutes a simple preparation of the methylene nitrones. Several examples were prepared (see Table). The structures of these compounds are defined by their spectral properties, *e.g.* (I; R^3 = 1-ethylcyclohexyl) exhibited ν_{max} (liquid film) 1550 cm.$^{-1}$; λ_{max} (ethanol) 241 mμ (ϵ 6535); n.m.r. AB quartet τ 3·61, 3·33 (*J* 7·5 c./sec.); molecular weight 155 (mass spectral), 159 (cryoscopic), and by the formation of formaldehyde 2,4-dinitrophenylhydrazone. Finally, their rapid oxidative cleavage with sodium periodate back to the parent nitroso-compound confirmed the assignment.[4]

TABLE

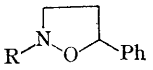
Methylene nitrones (I; $R^1 = R^2 = H$)

R^3 = 1,1,3,3-Tetramethylbutyl
R^3 = 1-Ethylcyclopentyl
R^3 = 1-Ethylcyclohexyl
R^3 = 1-Cyclohexylcyclohexyl
R^3 = 2,4,6-Trimethylphenyl

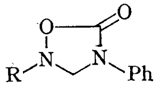


(I)

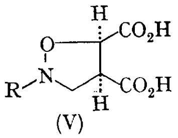
RNO
(II)



(III)

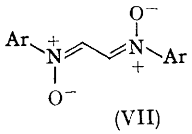


(IV)



(V)

RNH·CHS
(VI)



(VII)

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We have investigated the chemical reactions of this new class of compounds and find that, like other nitrones,[1,2] they readily undergo 1,3-dipolar additions.[5] Thus styrene and phenyl isocyanate provided the adducts (III) and (IV; R = 1-ethylcyclohexyl) and maleic anhydride gave the diacid derivative (V; R = 1-ethylcyclohexyl). Carbon disulphide, however, gave the thioformamide (VI; R = 1-ethylcyclohexyl) in good yield, probably the result of a two-stage mechanism, as already suggested for similar processes.[6,7]

Finally it should be mentioned that the reaction of diazomethane with several nitrosobenzenes has long been known to yield the dinitrones (VII).[8] We reasoned that the more hindered 2,4,6-trimethylnitrosobenzene (reported to give an oily hydroxylamine[8]) might yield a stable *N*-arylmethylene nitrone, and have found this to be so. This compound (I; $R^1 = R^2 = H$, R^3 = 2,4,6-trimethylphenyl) may be isolated as a crystalline solid, m.p. 102—104°, whose u.v. absorption, λ_{max} (ethanol) 241 mμ (ϵ 7432), indicates absence of conjugation with the aromatic group. On storage, and more quickly on heating in cyclohexene, it is transformed to the dinitrone (VII), m.p. 136—138°; λ_{max} 349 mμ (ϵ 10,200) and mass peak 324 *m/e* units.

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