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THE 1,3-DIPOLAR CYCLOADDITION OF BENZONITRILEOXIDE TO CONJUGATED IMINES

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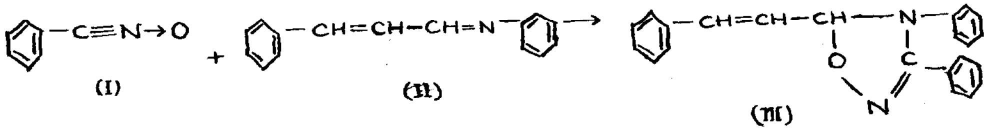
Dipolar cycloadditions of nitrileoxides to carbon-carbon multiple bonds,carbon-nitrogen multiple bonds,carbon-oxygen,carbon-sulphur double bonds (1) nitrogen-sulphur double bonds (2) and nitrogen-nitrogen double bonds (3) have been effected.

Cycloaddition of benzonitrileoxide to the conjugated imines which forms the subject of this communication does not appear to have been reported in literature.

Benzhydroxamoyl chloride was prepared by the methods of Benn (4) and Piloty and Steinbock (5). Benzonitrileoxide (I) produced from benzhydroxamoyl chloride in situ by the methods of Benn (4) and of Wiley and Wakefield (6) was made to react with equivalent quantities of cinnamylidene aniline (II). The residue left on removal of the solvent,on crystallization from a mixture of benzene-petroleum ether yielded a 1:1 addition product in 90% yield.



The structure of the adduct indicated as (III) is supported by the elemental analysis,U.V.Spectrum,Infrared spectrum, N.M.R.spectrum(determined at 60 Mc), and the mass spectrum. Benzonitrileoxide has preferentially added to the C=N rather than the C=C bond of the conjugated imine. The presence of a CH=CH trans bond in cycloadduct (III) is indicated in the infrared absorption spectrum at 970 cm^{-1} and by the two protons signals in the N.M.R.spectrum in the region 3.2τ to 3.5τ as these are shown in other 1,2 adducts of conjugated imines (7). One proton in the 1,2,4-oxadiazoline ring is indicated as a doublet at 3.8 τ . The mass spectrum of the cycloadduct (III) gave a base peak at m/e 326, (Calc.M.Wt.326) and other major fragment ion peaks including the ions at m/e 104 assigned to $(C_6H_5CH{=}CH_2)^+$, m/e 131 assigned to $(C_6H_5CH{=}CH{-}C{=}O)^+$ and m/e 180 assigned to $(C_6H_5C{=}N{-}C_6H_5)^+$. Seven analogous 1,2,4-oxadiazoline cycloadducts having substituents in the aromatic ring of aniline were similarly prepared in 60 to 90% yield and characterized. The addition of two moles of benzonitrileoxide yielded the same cycloadduct, and this reagent did not add to the other 1,2-adducts of conjugated imines prepared in our laboratory.

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