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THE DIPOLAR CYCLOADDITION OF 3-NITROBENZONITRILEOXIDE TO DIETHYL AZODICARBOXYLATE

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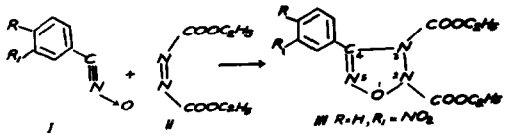
Dipolar cycloadditions of nitrileoxides to Carbon-Carbon multiple bonds (1,2), Carbon-Nitrogen multiple bonds (3,4), Carbon-Oxygen (5) and Carbon-Sulphur double bonds (6) and Nitrogen-Sulphur double bond (7) have been effected.

Cycloaddition of a nitrileoxide to the Nitrogen-Nitrogen double bond, which forms the subject of this communication, has to the best of our knowledge not so far been reported in literature.



a) R=H, R_1=NO_2
b) R=Cl, R_1=H
c) R=R_1=Cl

When a dried solution of 3-nitrobenzonitrileoxide (Ia) in ether was treated with a molar equivalent of diethyl azodicarboxylate (II) an exothermic reaction slowly developed and the reddish-

brown oily product (obtained by removal of ether from the clear reaction mixture after a two-hour reflux) furnished, on extraction with a hot mixture of n-hexane and benzene (5:1) and cooling, 2,3-dicarbethoxy-4-(3-nitrophenyl)- Δ^4-1,2,3,5-oxatriazoline (III), m.p. 68-70° (uncorr.) in about 48% yield. On recrystallisation from a large quantity of n-hexane, III was obtained as glistening yellow plates having a deep orange fluorescence, m.p. 69-71° (uncorr.). (Calculated for $C_{13}H_{14}O_7N_4$: C = 46.16; H = 4.17; N = 16.56%. Found: C = 46.26; H = 4.29; N = 16.33%).

When 4-chloro- and 3,4-dichlorobenzonitrileoxides (Ib and Ic respectively) were used in the place of 3-nitro-benzonitrileoxide (Ia), exothermic reactions did occur but the products, which were reddish-brown oils in both cases, were difficult to purify decomposing rapidly on distillation even under a high vacuum.

The assignment of the structure III to the cycloadduct is in agreement with its infrared spectrum which has bands at 1768 cm^{-1} ($>N-COOC_2H_5$), 1525 and 1348 cm^{-1} (aromatic nitro function) and 850 and 860 cm^{-1} (two pairs of adjacent aromatic H's) and the N.M.R. spectrum (determined at 60 mc in Varian A60 with TMS as internal standard), which, besides confirming the total number of protons present (fourteen), exhibits signals corresponding to the aromatic protons in the region δ = 8.6 to δ = 7.5 ppm and carries two pairs of quartets centred at δ = 4.6 ppm and δ = 4.37 ppm (J = 7 cps) assignable to the methylene protons of the two carbethoxy groups at 2 and 3 positions respectively and two pairs of triplets at δ = 1.5 ppm and δ = 1.38 ppm (J = 7 cps) assignable to the methyl protons of the two carbethoxy groups at respectively the same positions.

1,2,3,4-Oxatriazole has been described in literature (8) but not the 1,2,3,5-oxatriazole system. Hence III represents a new class of heterocyclic compounds.

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