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DIPOLAR ADDITION REACTIONS OF NITRILEOXIDES VI. REACTION OF BENZONITRILEOXIDES WITH DIAZOMETHANE*

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In the wake of a recent communication[1] in this journal, we would like to publish our observations on the course of the reaction between benzonitrileoxides and diazomethane. Treatment of an ethereal solution of benzonitrileoxide with an ethereal solution of diazomethane afforded in 25% yield a light yellow crystalline solid, m.p. 151-152° (dec.) of the molecular formula $C_9H_9N_3O$ (analysis, mass spectrum). This product was obviously not compound II that we hoped to obtain by methylene addition to the nitrileoxide. Reductive acetylation of the product in dioxane containing acetic anhydride in the presence of 10% Pd-C yielded, after the slow uptake of 1 mole of hydrogen, a colourless crystalline compound, $C_{12}H_{12}N_2O$, m.p. 132-134°, (λmax 286 mμ, ϵ 23,000) which was identified as N-acetyl-3-phenyl-Δ^2-pyrazoline[2]. $LiAlH_4$ reduction of the diazomethane product afforded an oil, which was eventually characterized as

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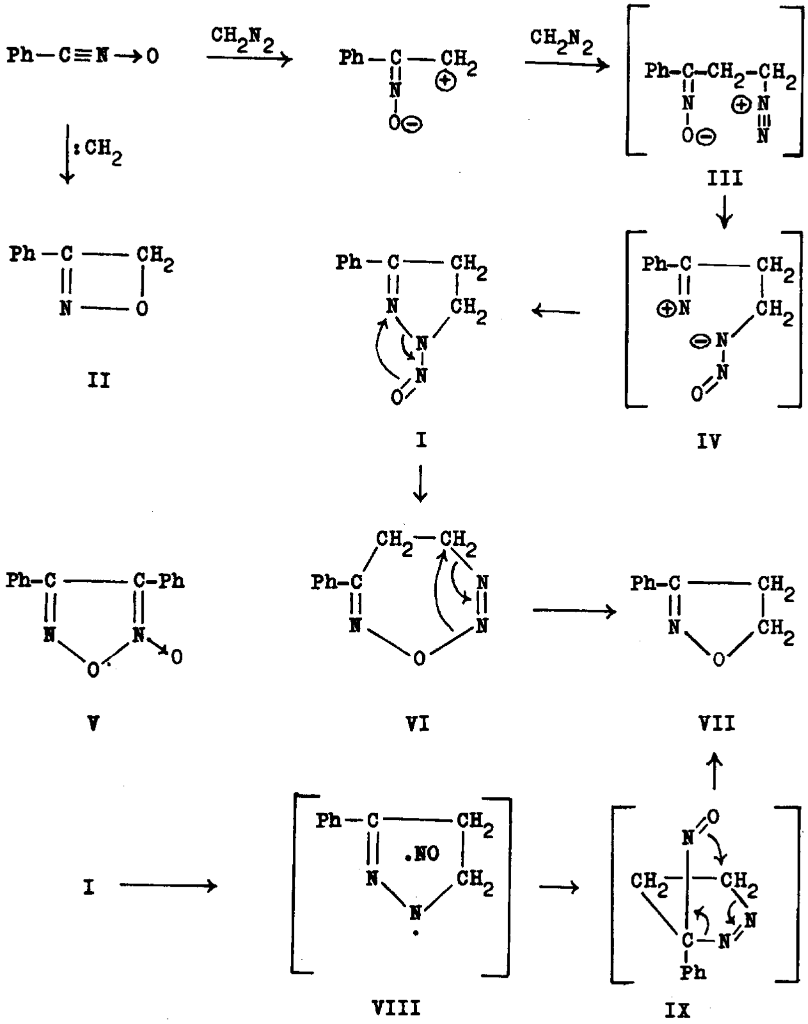
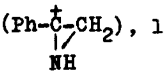
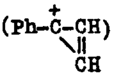


the known 3-phenylpyrazole through its picrate[3], m.p. 171-172°. The compound was unaffected by acetic anhydride in dioxane or by PCl_3 or triphenylphosphine in benzene. These data constitute independent support for the identification of the diazomethane product as 1-nitroso-3-phenyl-Δ^2-pyrazoline (I)[1].

The NMR spectrum[4] of the nitroso derivative I in $CDCl_3$ showed a triplet with fine structure and about 8 cps spacing for 2 protons centred at 3.34 ppm $(=\underset{|}{C}-CH_2)$, a similar triplet for 2 protons at 3.70 ppm $(-\underset{|}{N}-CH_2)$, and a multiplet for the aromatic protons at 7.3 - 8.1 ppm. The relative sharpness of the several signals signified that structure I in solution had almost exclusively one orientation of the nitroso-group only or that thermal energy at ambient temperature was in excess of the barrier to the free rotation of the N-nitroso bond[5].

The mass spectrum of I exhibited, besides the molecular ion peak at m/e 175, major peaks at m/e 145 (loss of NO), 118  $(Ph-\overset{+}{C}-CH_2)$ with NH below, 115  $(Ph-\overset{+}{C}-CH)$ with CH below, 103 ($Ph-C\equiv N$ ion) and 91 (tropylium ion). The formation of the ions at m/e 145 from 175, 118 from 145 and 91 from 118 was supported by the appearance of metastable peaks at m/e 113, 91 and 70.2 respectively. The presence of an ion at m/e 103 appears, from other studies in this laboratory, to be characteristic of the mass spectra of systems containing a $Ph-\underset{|}{C}=N-$ grouping.

The formation of 3-aryl-1-nitroso-Δ^2-pyrazolines in the reaction between an aromatic nitrileoxide and diazomethane is found to be a general phenomenon. The accompanying table summarises data on the products we have obtained with p-chloro, p-bromo and m-bromobenzonitrileoxides. With the exception of the m-bromo compound, the others are already reported in the literature from the nitrosation of appropriate pyrazolines. Catalytic reductive acetylation of the p-chlorophenyl derivative gave the corresponding N-acetyl-Δ^2-pyrazoline, m.p. 153-155° (λmax. 290-300 mμ, ϵ25800).

1-Nitroso-Δ^2-pyrazoline	m.p. °C	u.v. λmax mμ	ϵ max
3-Phenyl[1]	151-152° dec.	298	25,900
3-p-Chlorophenyl[6]	156-158° dec.	300	24,150
3-m-Bromophenyl	155-157° dec.	298	21,930
3-p-Bromophenyl[7]	161-162° dec.	302	27,100

The reaction between diazomethane and benzonitrileoxide leading to the formation of I has been postulated[1] to proceed via the species III and IV. We feel that the possibility of species III forming the 7-membered ring VI is also worthy of consideration. The rearrangement of VI to form I is easily visualized.

We have looked carefully into the complex mixture of products formed in the reaction between benzonitrileoxide and diazomethane. It was of special interest to find out whether 3-phenyl-Δ^2-isoxazoline (VII) was formed in this reaction, as III may be expected to lead predominantly to VII by the displacement of the diazonium group by the oxide anion. The formation of VII in the reaction between benzonitrileoxide and dimethyloxosulphonium methylide has been recorded recently and follows a similar pathway[8]. Silica gel chromatography of the residual oil left after the isolation of I did indeed afford VII but only in minute quantity. A significant and the only other crystalline product isolated in 17% yield was the furoxan V[9], m.p. 108-110°, known to be formed in benzonitrileoxide reactions especially with poor dipolarophiles.

We would like to report on an interesting reaction of 1-nitroso-3-phenyl-Δ^2-pyrazoline (I) which was encountered early and which in fact led us to consider structure VI as a strong possibility for the diazomethane product. Pyrolysis of I at 160-170° in a nitrogen combustion tube afforded upto 0.8 mole of nitrogen and in about 10% yield (isolated after chromatography), the isoxazoline VII, m.p. 68-70°, (λmax, 262 mμ, ϵ11,560) identical with an authentic sample. An improved yield (35%) was realized when I was refluxed in o-dichlorobenzene for 90 min. and the mixture chromatographed on silica gel. This seems to be a general reaction as 3-(p-chlorophenyl)-1-nitroso-Δ^2-pyrazoline also yielded, on similar treatment, the corresponding isoxazoline, m.p. 116°, (λmax, 267 mμ, ϵ15,910).

In considering the mechanism of formation of VII from I, one remote possibility that the nitrosation of 3-phenyl-Δ^2-pyrazoline might lead to VI with ring expansion was taken into account. This had to be abandoned as X-ray crystallographic studies[10] on 3-(m-bromophenyl) and 3-(p-bromophenyl)-1-nitroso-Δ^2-pyrazolines have established their structures conclusively. It is possible that I undergoes thermal rearrangement to VI and thence, with loss of nitrogen, to VII by simple shifts of electrons as shown. Alternately, a homolytic cleavage of I at the N-nitroso bond to give a diradical cage (VIII) can be visualized. Recombination can afford the C-nitroso intermediate IX which can then lose nitrogen to form VII. The use of nitrogen-labelled substrates would help distinguish between the two mechanisms.

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