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# REACTION OF DIAZOMETHANE WITH BENZONITRILE OXIDE

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It is well known that nitrile oxides react easily with compounds containing unsaturated bonds of different kinds, e.g. $-C\equiv C-$ (1), $>C=C<$ (2), $-C\equiv N$ (3), $>C=O$ (4), $>C=C=O$ (5), $>C=C=C<$(6), $-N=O$ (7).

We thought therefore it was interesting to investigate the behaviour of nitrile oxides toward other highly reactive unsaturated molecules, isosteric with ketenes, such as phenyl isocyanate, ethyl diazoacetate, diazoacetophenone, diazomethane and some of its higher homologues. All these products proved however to be inert toward benzonitrile oxide, at least in the experimental conditions we used, with the exception of diazomethane.

Diazomethane and benzonitrile oxide in ether react readily at room temperature, with nitrogen evolution, giving a light-yellow product (I), sparingly soluble in ether, m.p. 155°-156° (8).(Found : C, 61.71; H, 5.34; N, 24.08; M.w. 175. $C_9H_9ON_3$ requires : C, 61.70; H, 5.18; N, 23.99; M.w. 175.19).

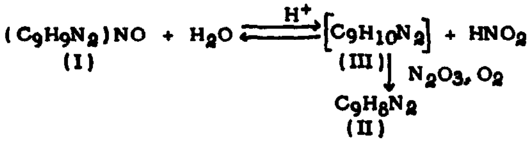
The same product we obtained also on treatment with diazomethane of benzohydroxamic chloride in ether solution.

Its molecular formula indicates that the product takes its origin from one molecule of nitrile oxide and two molecules of diazomethane, as shown by the empirical equation :

$$C_7H_5ON + 2\ CH_2N_2 \longrightarrow C_9H_9ON_3 + N_2$$

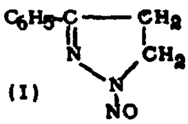
When refluxed with dilute mineral acids or acetic acid compound (I) loses nitrous acid. Extraction with ether of the solution filtered from some unchanged starting material and alkalized yields a sticky product, from which traces of a basic compound (II), $C_9H_8N_2$, were isolated in the form of picrate, m.p. 171°.

If the refluxing with acids is carried out at reduced pressure or in a slow stream of $CO_2$ in order to remove the nitrogen oxides as soon as they are formed, a solution is obtained which contains a compound (III) that on addition of sodium nitrite in the cold gives again the starting product (I), m.p. 155°-156°.

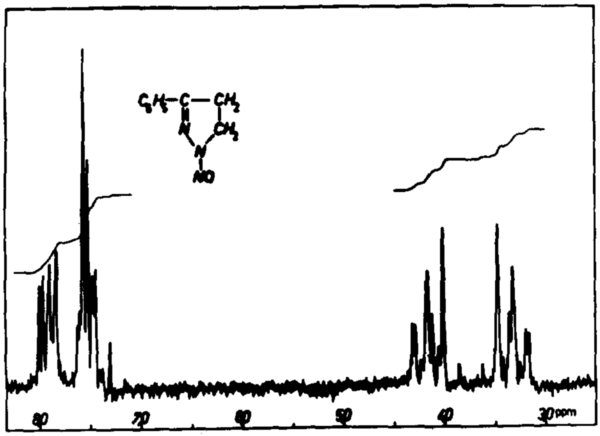


$$\begin{array}{lcl} (C_9H_9N_2)NO + H_2O & \overset{H^+}{\rightleftharpoons} & [C_9H_{10}N_2] + HNO_2 \\ \quad (I) & & \ (III) \big\downarrow N_2O_3, O_2 \\ & & C_9H_8N_2 \\ & & \ (II) \end{array}$$

This indicates that (I) is a N-nitrosoderivative of (III), and that compound $C_9H_8N_2$ (II) results from the oxidation of (III) by the nitrogen oxides set free during the hydrolysis. Since compound (II) (picrate m.p. 171°) has proved to be identical with 3-phenylpyrazole (9), to the product (I) can be assigned the structure of 1-nitroso-3-phenyl-2-pyrazoline. Further evidence in favour of this structure was supplied by the NMR spectrum ($CDCl_3$) of (I), which shows a typical

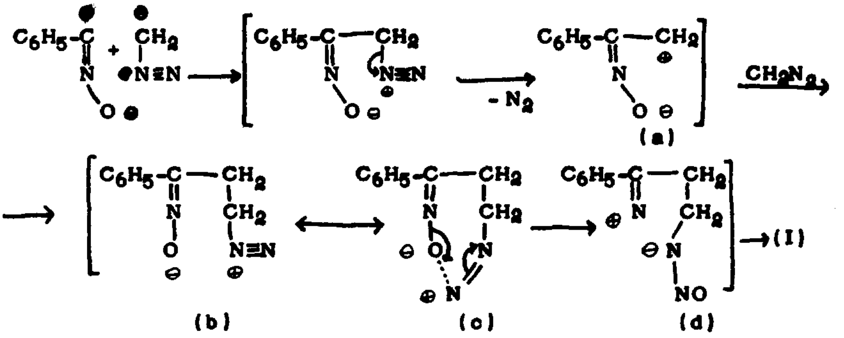


(I)



$A_2B_2$ sistem due to two adjacent methylene groups (centered at δ= 3.75 ppm., area 4) and a multiplet at 7.35 - 8.05 ppm. (area 5) attributable to the aromatics protons. Finally, com parison of product (I) with an authentical sample of the known 1-nitroso-3-phenyl-2-pyrazoline (10) confirmed the identity of the two substances.

About the m ode of formation of (I) from benzonitrile oxide and diazomethane, we suggest as possible the following reaction mechanism :



Nucleophylic attack of benzonitrile oxide by diazomethane followed by nitrogen elimination would give the highly reactive dipolar ionic species (a) (11); further attack of (a) by a second molecule of diazomethane would lead, through the possible intermediates (b), (c) and (d), to the nitrosophenylpyrazoline (I).

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8) Total yield generally amounted to 45-50 % based on benzonitrile oxide available. The viscous residue obtained from mother liquor did not contain diphenylfuroxane. We are at present studying the composition of this residue.

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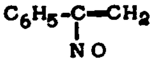
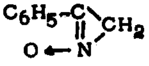
11) It cannot be excluded that intermediate ( a ) may actually exist as α-nitrosostyrene ( $a_1$ ) or in one of the cyclic forms ( $a_2$ ) and ( $a_3$ ) :



$C_6H_5-\underset{\displaystyle NO}{\underset{|}{C}}=CH_2$

( $a_1$ )

( $a_2$ )



( $a_3$ )