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1,3-Addition Reactions of the Benzonitrile Oxide with Acid Anions

Evidence for 1,4- Acyl Migration from Oxygen to Oxygen

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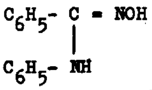
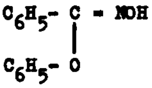
Benzonitrile oxide reacts with nucleophilic reagents(1,2) such as aniline and phenol and gives through 1,3-addition the corresponding substituted oximes I, II.



$$C_6H_5-\underset{\underset{C_6H_5-NH}{|}}{C}=NOH$$

I



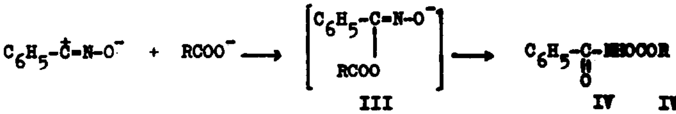
$$C_6H_5-\underset{\underset{C_6H_5-O}{|}}{C}=NOH$$

II

In the reaction of the benzonitrile oxide with phenol, it has been found that the yield of the product II is remarkably increased by using phenol anion instead of phenol. This observation led us to investigate the reaction of the benzonitrile oxide with acid anions.

The reaction takes place at room temperature by the addition of a 70% ethanolic solution of the sodium salt of the acid to an ether solution of benzonitrile oxide; the pH of the reaction mixture has to be < 8 in order to avoid decomposition of the reaction product.

On the basis of the formation of the products I and II, the present reaction should give an analogous product III. However, the final product is an ester of



$$C_6H_5-\overset{+}{C}=N-O^- + RCOO^- \longrightarrow \left[\begin{matrix}C_6H_5-C=N-O^- \\ | \\ RCOO\end{matrix}\right] \longrightarrow C_6H_5-\underset{\underset{O}{\|}}{C}-NHOCOR$$

III

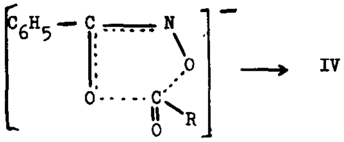
IV

IVA R= C_6H_5-
IVB R= *p*-CH_3-C_6H_4
IVC R= CH_3 -

benzohydroxamic acid IV, the formation of which is readily explained assuming that an 1,4-acyl migration from oxygen to oxygen is involved in the intermediate III. The reaction products of the benzonitrile oxide with sodium benzoate, *p*-toluate and acetate were identified by a comparison of their infrared spectra with those of the compounds IVA, IVB, IVC, prepared from benzohydroxamic acid and the corresponding acid chloride (3,4); furthermore their melting points were in agreement with those of the literature (5). The infrared spectra of these compound in Nujol showed absorptions in the regions 3225-3165 (NH), 1800-1780 (CO ester) and 1675-1660 cm^{-1} (CO amide).

It is well known (6) that systems with an imino anhydride structure like III undergo at room temperature (7) rearrangement, which involves an 1,3-acyl migration from oxygen to nitrogen. However, in the present case an 1,4-acyl migration should probably give a more stable product. An analogous 1,4-benzoyl migration (8) from oxygen to nitrogen was implied in the formation of N,N'-dibenzoylphenylhydrazine from 2,5-diphenyltetrazole and benzoic acid at 170°. Grünanger and Finzi (9), during their study of the reaction of benzonitrile oxide with unsaturate acids to form substituted Δ^2-isoxazoline-4-carboxylic acids, found that some unsaturated acids give esters of benzohydroxamic acid, but they did not consider the possibility that in this reaction an 1,4-acyl migration was involved.

Concerning the mechanism of this rearrangement there are several possibilities; one of them assumes a five center cyclic transition state V, which directly gives



V

the final product IV. This suggestion is in agreement with Tamelen's (10) mechanis proposed for the rearrangement of N-acyl-1,2-aminoalcohols. However, in the preser case is by no means impossible that the product of an 1,3-acyl migration rearranges to IV through an 1,2-acyl migration. On the other hand the reactions with benzoate and p-toluate gave small amounts of the coresponding ethyl esters identified by vapor phase chromatography and this fact suggests that at least part of reaction is of intermolecular character. The mechanism of this rearrangement is under further investigation.

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