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DIPOLAR ADDITION REACTIONS OF NITRILEOXIDES. V*.

THE ACTION OF CARBETHOXYNITRENE ON SOME BENZONITRILEOXIDES.

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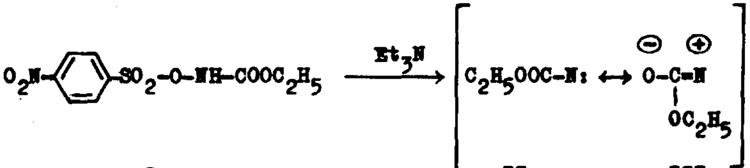
The facile method of generating 'carbethoxynitrene' (II) (or 'carbethoxyazene' as Huisgen (1) prefers to call it) from N-4-nitrobenzenesulphonyloxyurethane (I) recently described by Lwowski and Maricich (2) led us to examine the action of this reactive species (II) on a few benzonitrileoxides. 'Carbethoxynitrene' can react as the electronically neutral 'nitrene' (II) or as the dipolar 'ketoazene' (III).



I II III

When a stirred ether solution containing equimolar proportions of benzhydroximoyl chloride (IV) and N-4-nitrobenzenesulphonyloxyurethane (I) was treated with two molar equivalents of triethylamine added dropwise and the product

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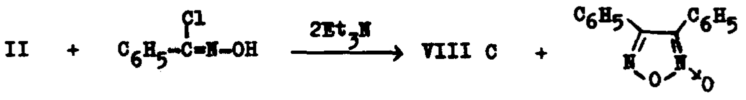
worked up, two crystalline compounds, one major and the other minor, were obtained. The former, which was colourless, was identified as the 3,4-diphenylfuroxan (V) by comparison with an authentic specimen. The latter, yellow in colour, analysed (3) for $C_{10}H_{10}N_2O_3$ which would correspond to a product resulting from the interaction of benzonitrileoxide with 'carbethoxynitrene' (II) in a 1:1 ratio. Molecular weight determination by Simon's vapourometric method (found: 394, 399) indicated that this substance was dimeric. Its I.R. spectrum (KBr disc) exhibits a carbonyl absorption at 1790 cm^{-1} and its N.M.R. spectrum (4) carries, besides a five-proton multiplet in the aromatic region, a triplet centred at 1.4 ppm and a quartet centred at 4.4 ppm ascribable to methyl and methylene protons, respectively, of a carbethoxy group. These spectral data suggest a) that no substitution of any kind on the benzene ring of the benzonitrileoxide has occurred, b) that 'carbethoxynitrene' has reacted in the nitrene form (II) and not as the ketoazene (III) as otherwise there would be no absorption in the carbonyl region of the infrared spectrum and c) that the carbethoxy group has, in all probability, migrated from the nitrogen for the carbonyl absorption for compounds of the type >N-COOR falls in the region 1740-1690 cm^{-1} and the observed value (1790 cm^{-1}) is higher.

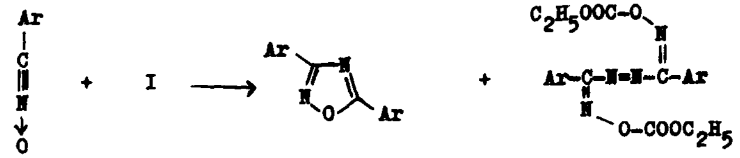


IV

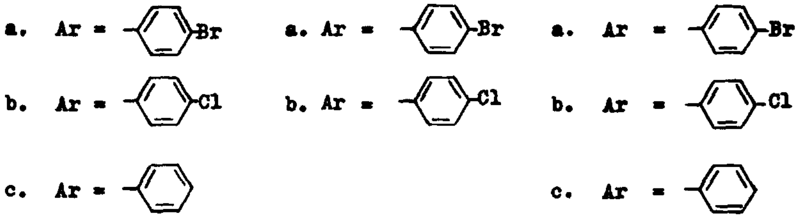
V

Similar yellow compounds were obtained, again in extremely poor yields, from the reaction of 'carbethoxynitrene' with 4-bromo (VIa) and 4-chlorobenzonitrileoxides (VIb). However, in these two cases the other isolable products were the colourless oxadiazoles (VIIa) and (VIIb) respectively.

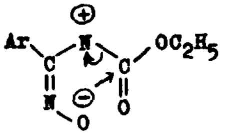
Since the chemical investigation of these yellow dimeric compounds was limited by their formation in almost insignificant yields, the 4-bromophenyl derivative was submitted to Dr. G. Kartha of the Centre for Crystallographic Research, Roswell Park Memorial Institute, Buffalo, N.Y. in October 1965, for X-ray crystallographic analysis the results of which (5) have led to the assignment of the structure VIIIa for this compound. It follows, then, that the other two related substances should be represented by VIIIb and VIIIc respectively.



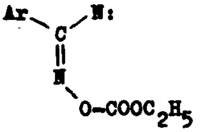
VI VII VIII



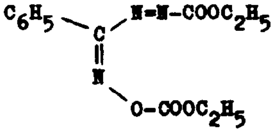
One of the possible mechanisms of formation of the compounds of the type VIII is depicted below :



IX



X



XI

The intermediate IX formed by the attack of 'carbethoxynitrene' (II) at the nucleophilic centre of the dipolar nitrileoxide (VI) can rearrange through a five-centred transition state to the 'nitrene' X which can then dimerise yielding compounds of the type VIII.

While the X-ray crystallographic analysis was in progress, Huisgen and coworkers (6) published a paper on the reaction of benzonitrileoxides with azodicarboxylic esters in which they have assigned structure VIIIc to a by-product formed by the action of excess of benzonitrileoxide (VIc) on diethyl azodicarboxylate. Comparison of the physical properties of this compound of theirs with those of the minor product we had isolated from the reaction of benzonitrileoxide (VIc) with 'carbethoxynitrene'(II) leaves no doubt that they are one and the same. This might lead to the speculation that carbethoxynitrene (II) could dimerise first to form diethyl azodicarboxylate which could then react with benzonitrileoxide (VIc) in the manner described by Huisgen <u>et al</u> (6) furnishing VIIIc. However, the fact that we have not been able to isolate the

1:1 adduct (XI) described by Huisgen *et al* (6) from our reactions involving 'carbethoxynitrene' (II) suggests that this is not likely.

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References

1. R. Huisgen, *Angew. Chem. Intl. Ed.*, **2**, 565 (1963).
2. W. Lwowski and T.J. Maricich, *J. Am. Chem. Soc.*, **87**, 3630 (1965).
3. Elemental analyses of all the new compounds described herein are in accord with the theoretical values.
4. The N.M.R. spectrum was determined in a Varian A60 instrument with $CDCl_3$ as solvent and TMS as internal standard.
5. To be published elsewhere by Dr. G. Kartha in the near future.
6. R. Huisgen, H. Blaschke and E. Brunn, *Tetrahedron Letters*, **1966**, 405.