Tetrahedron Letters No 39, pp 3801 - 3804, 1973 Pergamon Press Printed in Great Britain

THE INTERACTION OF N-HEXYL AZIDE AND CARBETHOXYNITRENE

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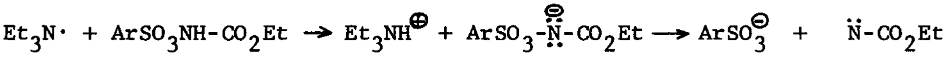
(Received in USA 9 July 1973, received in UK for publication 7 August 1973)

As part of a research program designed to explore the interaction of organic azides and reactive intermediates[1], we have examined the reactions of organic azides with nitrenes. Previously, the formation of azo compounds from the decomposition of carbamoyl and aryl azides[2,3,4,5] in solution has been rationalized either by the attack of a nitrene on an azide or by nitrene dimerization[5,6]. Lwowski observed the formation of an azo compound from the decomposition of ethyl azidoformate, but presented data indicating that the azo compound was formed by a mechanism not involving a nitrene intermediate[7] In the thermal decomposition of 1,2-diazidobenzene, intramolecular attack of a nitrene on an adjacent azido group was suggested[8]. Although other studies of decomposition of neighboring azido groups could be rationalized by interactions of nitrenes with azides[9], the work with 1,2-diazidobenzene is the only reported example of an intramolecular nitrene-azide interaction supported by experimental data. We wish to report the first recorded example of an intermolecular reaction between an organic azide and a nitrene intermediate.

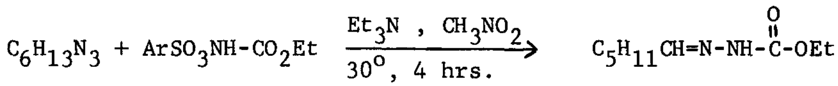
The problem in establishing the intermediacy of nitrenes when thermally or photolytically generated from azides is that various excited states of azides may also act as reactive intermediates[7]. In order to circumvent this problem we have used the method of Lwowski and Maricich to generate carbethoxynitrene from N-p-nitrobenzenesulfonoxyurethane (I) by alpha-elimination[7].



$$Et_3N\cdot + ArSO_3NH\text{-}CO_2Et \rightarrow Et_3NH^{\oplus} + ArSO_3\text{-}\overset{\ominus}{\underset{\cdot\cdot}{\ddot{N}}}\text{-}CO_2Et \longrightarrow ArSO_3^{\ominus} + \ddot{N}\text{-}CO_2Et$$

I II

When carbethoxynitrene is generated by alpha-elimination in a nitromethane solution of n-hexyl azide at room temperature, the azide is decomposed and n-hexaldehydecarbethoxy hydrazone (III) is isolated in good yield. Using equimolor amounts of urethane (I) and azide (0.20 M), 20% of the azide is

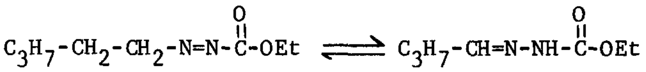


$$C_6H_{13}N_3 + ArSO_3NH\text{-}CO_2Et \xrightarrow[30^{\circ},\ 4\ hrs.]{Et_3N\ ,\ CH_3NO_2} C_5H_{11}CH{=}N\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}OEt$$

I III

decomposed, generating the hydrazone in 90% yield, based on decomposed azide. (The azide decomposition can be followed using infrared analysis at 2190 cm^{-1}.) Alternatively, this same hydrazone is isolated from the product mixture resulting from the thermal decomposition of ethyl azidoformate in a refluxing nitromethane solution of hexyl azide.

One might expect the interaction of an azide and a nitrene to generate an azo compound. However, alkyl azo compounds bearing an alpha-hydrogen readily isomerize to the corresponding hydrazone[10]. Even with a carbonyl group adjacent to the azo linkage, isomerization at room temperature has been observed for ethyl n-butylazocarboxylate (IV)[11]. The same behavior would be expected for



$$C_3H_7\text{-}CH_2\text{-}CH_2\text{-}N{=}N\text{-}\overset{\overset{O}{\|}}{C}\text{-}OEt \rightleftharpoons C_3H_7\text{-}CH{=}N\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}OEt$$

IV

ethyl n-hexylazocarboxylate, prepared by oxidation of 1-n-hexyl-2-carbethoxyhydrazine.* Ethyl n-hexylazocarboxylate does isomerize to n-hexaldehydecarbethoxy hydrazone (III) at room temperature in ethanol (half-life = 3 days), or much more rapidly in the presence of a small amount of triethylamine.

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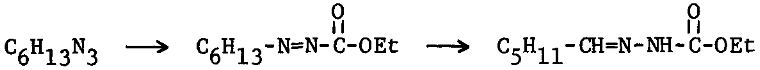
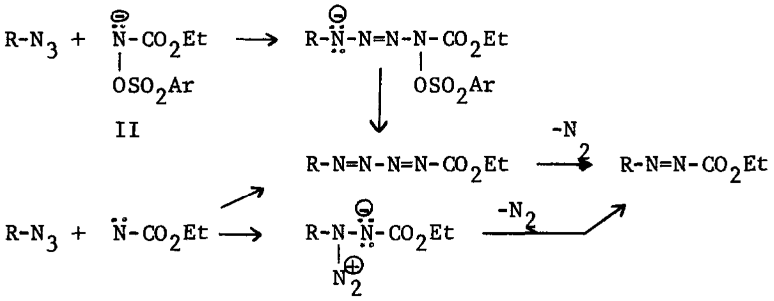
*Both 1-n-hexyl-2-carbethoxyhydrazine and n-hexaldehydecarbethoxy hydrazone were characterized by the usual spectral methods as well as by satisfactory elemental analysis Bromine and water was used as the oxidizing agent. The isomerization of the azo compound can be followed by ultraviolet analysis (380 mm) or by infrared analysis, as the azo compound has a strong carbonyl absorption at 1760 cm^{-1} while the hydrazone absorbs at 1735 cm^{-1}.

These data are best interpreted by the general scheme below, involving the conversion of the azide initially to an azo compound, which readily isomerizes to the isolated hydrazone. However, there are at least two pathways by which



$$C_6H_{13}N_3 \longrightarrow C_6H_{13}\text{-N=N-}\overset{O}{\overset{\|}{C}}\text{-OEt} \longrightarrow C_5H_{11}\text{-CH=N-NH-}\overset{O}{\overset{\|}{C}}\text{-OEt}$$

the azide might be converted to the azo compound, as shown below. The first pathway involves attack upon the azide by the anion II preceding the nitrene.



The second involves attack by carbethoxynitrene on either the terminal or substituted nitrogen of the azide group, either of which may lead to the azo compound. In order to distinguish between attack upon the azide by anion II or by carbethoxynitrene, we added cyclohexene to the system, a compound previously shown to be reactive toward carbethoxynitrene, but not the anion preceding it[12]. If the anion were the intermediate reacting with the azide, addition of cyclohexene would have no effect on the decomposition of the azide. Conversely, one would expect cyclohexene to compete with n-hexyl azide if carbethoxynitrene were reactive toward both compounds. From the results in Table I it is apparent that

TABLE I

Azide Decomposition Results in the Presence of Cyclohexene
(initial azide conc. = 0.355 M)

Cyclohexene conc., M	% azide decomposed
.00	16
.70	12
1.40	9
2.10	5

the azide and cyclohexene are indeed competing for a common intermediate, namely carbethoxynitrene. Thus a major reaction pathway in this system involves the reaction of n-hexyl azide and carbethoxynitrene to generate ethyl n-hexylazocarboxylate, which isomerizes to n-hexaldehydecarbethoxy hydrazone. This example of an intermolecular reaction between an organic azide and a nitrene intermediate opens the possibility of such a reaction in many other different but related systems. Future work here will be concerned with exploring the scope of this reaction as well as various mechanistic details.

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The support of this work by a research grant (AD-311) from The Robert A. Welch Foundation is gratefully acknowledged.