

CURTIUS-REARRANGEMENT OF "RIGID" AZIDES

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Since 1914, the organic azides have been divided into two classes: Rigid azides, which do not rearrange upon decomposition, and non-rigid azides which undergo rearrangement.<sup>1, 2, 3</sup> The classic example for the latter class are the carbonyl azides,  $\text{>C-CO-N}_3$ . Upon decomposition by heat or light, they rearrange to isocyanates,  $\text{>C-NCO}$ . A number of aryl-substituted carbamoyl azides,  $\text{ArRN-CO-N}_3$ , also rearrange.<sup>2, 3</sup> Typical rigid azides are the arylsulfonyl azides,  $\text{Ar-SO}_2\text{-N}_3$ , the azidoformates,  $\text{RO-CO-N}_3$ , and certain carbamoyl azides, such as  $\text{Ar-NH-CO-N}_3$ ,<sup>4</sup>  $\text{R-NH-CO-N}_3$ , and  $\text{R}_2\text{N-CO-N}_3$ .<sup>2, 3</sup> No convincing explanation for the different behavior of these azides as yet been given.

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1. T. Curtius, Z. Angew. Chem., 27, 111, 213 (1914).
  2. A. Bertho, J. prakt. Chem., 120, 89 (1928).
  3. F. L. Scott, Chem. and Ind., 1954, 959.
  4. T. Curtius and A. Burkhardt, J. prakt. Chem. 58, 205 (1898).

We have studied members of these three groups of "rigid" azides. Photolysis (using a low pressure mercury arc) in hydrocarbon solvents did not lead to rearrangement, but photolysis in methanol gave products derived from the addition of solvent to the isocyanates, R-X-NCO. So far, we have not found a member of these three classes of azides that fails to rearrange when photolyzed in methanol.

When ethyl azidoformate was photolyzed in hydrocarbon solution,<sup>5</sup> no products derived from rearrangement could be detected. Photolysis in methanol at  $-10^{\circ}$ , however, gave a mixture of the product from insertion into the O-H bond, EtO-CO-NH-OCH<sub>3</sub>, and the isomeric product from methanol addition to ethoxyisocyanate:



The yields of the insertion product was 44%, that of the rearrangement product 13% of the theory - reaction with the OH group predominated by a factor of 3.4. Urethane, EtOOC-NH<sub>2</sub>, was formed in 20% yield. Higher urethane yields are produced at higher temperatures. The two isomeric alkoxy carbamates could be separated by vapour phase chromatography on a 15' cyanosilicon column. Mixtures can be analyzed by comparing the methyl peaks of the two compounds in the n. m. r. spectrum. Structure proof was provided by elemental analyses, n. m. r. and IR spectra and independent synthesis.

The quantum yield of the photolysis of ethyl azidoformate was found to be about 0.35 in cyclohexane and nearly 1 in methanol. The

5. W. Lwowski and T. W. Mattingly, Jr., Tetrahedron Letters, 1962, 277; and work to be published.

azide decomposition in methanol could be induced by large amounts (1/2 mole) of diethyl peroxydicarbonate, but this reaction produced a 78% yield of urethane  $\text{EtO}-\text{CONH}_2$ , and no alkoxy carbamates.

Monophenyl-, monoethyl- and diethyl carbamoylazide, were irradiated in hydrocarbon solvents (cyclohexane, cyclohexene and benzene). The products were of high molecular weight. According to their IR spectra, they contained little, if any, groups derived from the solvent. In methanol, however, the addition products to the corresponding alkylaminoisocyanates were obtained.

Phenylcarbamoyl azide,  $\text{C}_6\text{H}_5-\text{NH}-\text{CO}-\text{N}_3$ , gave a 65% yield of N-phenyl-N'-carbomethoxy-hydrazine,  $\text{C}_6\text{H}_5-\text{NH}-\text{NH}-\text{COOCH}_3$ . Ethylcarbamoyl azide,  $\text{C}_2\text{H}_5-\text{NH}-\text{CO}-\text{N}_3$ , gave N-ethyl-N'-carbomethoxyhydrazine,  $\text{C}_2\text{H}_5-\text{NH}-\text{NH}-\text{COOCH}_3$  in 57% yield and diethyl carbamoyl azide,  $(\text{C}_2\text{H}_5)_2\text{N}-\text{CO}-\text{N}_2$  produced 63% of the theoretical yield of N-diethyl-N'-carbomethoxyhydrazine. The products were identified by their elemental analyses, n. m. r. and IR spectra. N-Phenyl-N'-carbomethoxyhydrazine was also compared with an authentic sample.<sup>6</sup>

Photolysis of diethylcarbamoyl azide in an aqueous emulsion gave 26% of the theory of N,N-diethyl hydrazine, isolated as the oxalate and identified by comparison with an authentic sample. Apparently, rearrangement of the azide, followed by addition of water, gives  $\text{Et}_2\text{N}-\text{NH}-\text{COOH}$ , which then decarboxylates. Interestingly, photolysis in a 1:1 acetone-water solution did not yield rearrangement products. It appears that the

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6. G. Heller, Ann. 263, 281 (1891).

organic component forms a closed solvate shell around the azide, preventing hydrogen bonding to the water.

When pure benzenesulfonylazide,  $C_6H_5-SO_2-N_3$ , of the melting point  $10.5 - 11.5^\circ$ , was irradiated in methanol, a complex mixture of products was formed. Hydrolysis, followed by chromatography on silica gel, gave 28% yield of aniline, weighed as its 3,5-dinitrobenzoyl derivative. We have not yet been able to isolate the presumed intermediates,  $C_6H_5-NSO_2$  and  $C_6H_5-NH-SO_2-OCH_3$ . The latter has evaded synthesis by other investigators, probably because of instability.<sup>7</sup>

The results can be explained by assuming that a hydrogen-bonded azide is the rearranging species. It could decompose to a hydrogen-bonded nitrene, or rearrange synchronously with the loss of nitrogen. The results with diethylcarbamoyl azide in water and in water-acetone seem to indicate that the reaction is not one of a free nitrene that forms hydrogen bonds after its formation and then rearranges. Our observations show the barrier between "rigid" and "nonrigid" azides to exist only for the reactions in non-hydroxylic solvents. Further study of the factors that influence the rearrangement is expected to shed light on the nature of the transition state in the Curtius rearrangement.

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7. L. S. Yaguzhinskii and A. Ya. Berlin, J. Gen. Chem. USSR, 33, 3078 (1963); and references cited therein.