

CHEMISTRY OF AZIDES. I.

REACTION WITH OLEFINS

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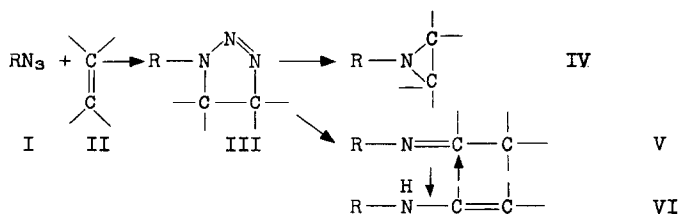
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The reaction of aryl azides with certain olefinic compounds is known<sup>1</sup> to give stable triazolines (III) which, in some cases, can be pyrolyzed to aziridines (IV) and imines (V or VI).



In contrast to these results we have found that azides of type I ( $R=C_6H_5SO_2-$ ,  $p-CH_3C_6H_4SO_2-$ ,  $CH_3SO_2-$  ( $C_6H_5$ )<sub>2</sub>PO-, ( $C_2H_5$ )<sub>2</sub>NSO<sub>2</sub>-, and  $N_3SO_2C_6H_4OC_6H_4SO_2-$ ) react with bicyclic olefins (norbornene, dicyclopentadiene, 3,6-endomethylenetetrahydro phthalic anhydride, and 3,6-endooxytetrahydrophthalic anhydride) to yield aziridines and imines directly. Nitrenes<sup>2</sup> or unstable triazolines may be intermediates in this reaction but no evidence for the existence of the latter has been found.

<sup>1</sup> S. J. Davis and C. S. Rondestvedt, Jr., Chem. Ind. 845, (1956) and references therein.

<sup>2</sup> P. Walker and W. A. Waters, J. Chem. Soc., 1632, (1962).

When maleic anhydride, N-phenylmaleimide, divinyl sulfone, mesityl oxide, cyclohexene<sup>3</sup>, cyclopentene, styrene, vinyl acetate and p-quinone were each added to benzenesulfonylazide and heated (steam bath) for one hour no measurable gas evolution occurred. Infrared measurements showed no change in the concentration of sulfonyl azide.

The following example is typical of the conditions employed.

Benzenesulfonyl azide was mixed with a 100 mole percent excess of bicyclo [2,2,1]hept-2-ene (norbornene) in acetonitrile at 55-60° for two-three hours or until a sample showed no azide infrared absorption at 4.7 $\mu$ . The solvent was removed to give an ether insoluble adduct (64% yield) melting at 106-7°.

Calc. for C<sub>13</sub>H<sub>15</sub>NO<sub>2</sub>S: C, 62.6; H, 6.06; N, 5.61; S, 12.9; M.W. 249. Found: C, 62.3, 62.6; H, 6.17, 6.4; N, 5.69; S, 12.7; M. W. 257.

The ether soluble portion of the reaction mixture gave an oil (35%), the infrared spectrum of which showed bands for NH, at 3 $\mu$  (w), and C=N, at 6.1 $\mu$  (vs). This fraction is believed to be a crude mixture containing isomeric structures of type IV, V and VI.

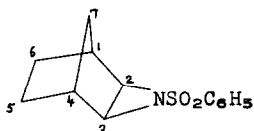
The infrared spectrum (CHCl<sub>3</sub>) of the solid product showed the following bands; 6.8 (w), 6.92 (m), 7.4 (s), 7.6 (vs), 7.8 (m),

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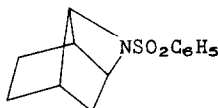
<sup>3</sup> The photodecomposition of ethyl azidoformate in the presence of cyclohexene has recently been reported<sup>4</sup> to give an aziridine. Under the same conditions we found that nitrogen was evolved from a mixture of cyclohexene and benzenesulfonylazide but no aziridine could be isolated from the tarry reaction mixture.

<sup>4</sup> W. Lwowski and T. W. Mattingly, Tetrahedron Letters, 277 (1962).

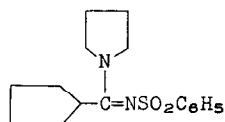
8.6 (vs), 8.87 (m), 9.18 (vs), 9.67 (s), 10.2 (vs), 10.7 (m), 10.95 (vs), 11.35 (s), 12.1 (w), 13.85 (s), and 14.08 (s)  $\mu$ . The absence of absorption in the  $6\mu$  region argues against a structure of type V and, with the absence of  $3\mu$  absorption, against a type VI structure. This adduct did not decolorize  $\text{Br}_2$  or permanganate. Reaction with either HBr or acetic acid gave oils which showed characteristic NH absorption bands in the infrared. These data support the aziridine type structure (VII).



VII



VIII



IX

The possibility of rearrangement<sup>5</sup> to give a structure such as VIII cannot be ruled out on the evidence thus far cited. In order to shed light on this problem, *exo*-2,3-epoxynorbornane was prepared<sup>6</sup> and the proton NMR spectrum ( $\text{CDCl}_3$ ) compared with that of our product (VII). Identical chemical shifts were observed (except for the aromatic hydrogens). The following assignments were made: bridge  $\text{CH}_2$  group 7, two doublets one at 9.2 - 9.4  $\uparrow$  the other at 8.8-8.9  $\uparrow$ ; ring  $\text{CH}_2$  groups 5 and 6, multiplet at 8.6 - 8.7  $\uparrow$ ; bridgehead

<sup>5</sup> G. D. Brindell and S. J. Cristol, Organic Sulfur Compounds Vol. I, pp. 121-133. Edited by N. Kharasch. Pergamon Press 1961 and references cited therein.

<sup>6</sup> H. M. Walborsky and D. F. Loncrini, J. Am. Chem. Soc. 76, 5396 (1954). See also S. B. Soloway and S. J. Cristol, J. Org. Chem. 25, 327 (1960) for structural confirmation.

CH at C-1 and C-4, 7.6  $\tau$ ; ring CH at C-2 and C-3, 7.1  $\tau$ ; aromatic H, complex band at 2.0 - 2.5  $\tau$ . Structure VII is, therefore, strongly supported with regard to exo configuration as well as presence of the aziridine ring.

In a similar fashion reaction of p-toluenesulfonyl azide with endo-methylenetetrahydrophthalic anhydride gave a product, m.p. 242° (d), in 64.6% yield. Calc. for  $C_{18}H_{15}NO_5S$ : C, 57.65; H, 4.53; N, 4.20. Found: C, 57.4; H, 4.6; N, 4.0. The infrared spectrum was in agreement with the aziridine type structure.

Enamines have recently been reported to react with sulfonyl azides to give rearranged products.<sup>7</sup> Our results, obtained before this paper appeared confirm these observations. For example, 1-(1-cyclohexen-1-yl)-pyrrolidine and benzenesulfonyl azide gave the formamidine IX, m.p. 92-93°, (72%). Calc. for  $C_{18}H_{22}N_2O_2S$ , C, 62.7; H, 7.25; N, 9.15. Found: C, 62.4; H, 7.2; N, 9.37. Acid hydrolysis yielded cyclopentane carboxylic acid (65%) in agreement with the report of R. Fusco<sup>7</sup>

It has now been found that vinyl ethers such as butyl vinyl ether, dihydropyran, and 2,3-dihydro-2-methoxypyran also react with azides of type I. Although the infrared spectra of the enamine and vinyl ether products are similar, characterization of the latter materials is not complete. The mechanisms of these reactions will be discussed in a later paper.

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<sup>7</sup> R. Fusco, G. Bianchetti and D. Pocar, Gazz. chim. ital, 91, 933 (1961). Chem. Abstr. 56, 14020 (1962).