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AZABICYCLOBUTANES. FORMATION OF AN AZABICYCLO[1.1.0]BUTANE *VIA* IRRADIATION OF AN ALLYLIC AZIDE

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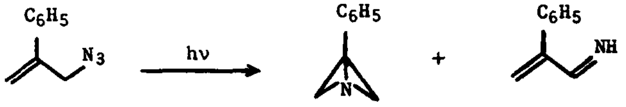
We wish to record the first observation of the formation of a 1-azabicyclo[1.1.0]butane *via* photo-induced decomposition of an allylic azide.(1,2)



1 2 3

1-Azido-2-phenylprop-2-ene (1)(3,4) (0.200 g) in cyclohexane (200 ml; purged with argon for 30 min) containing 0.025 ml of pyridine-d_5(5) was irradiated at 10-20° for 1.2 hr (time required for almost complete disappearance of 1) using a 450 watt high-pressure Hanovia 679A-36 mercury vapor lamp and a 1.5 mm Corex 9700 filter sleeve in a quartz immersion well. Removal of most of the cyclohexane *in vacuo* at 25° yielded a viscous oil. The nmr spectrum of the total crude product in CCl_4 ($\sim$1:1) exhibited identical A_2X_2 multiplets at δ_{TMS} 1.28 and δ 2.52 indicative of the presence of 3-phenyl-1-azabicyclo[1.1.0]butane (2).(6) The product also exhibited three peaks of *ca.* equal area at δ 5.53, 5.73 (partially resolved doublets, 1 H ea, *J* $\sim$1.3 Hz) and δ 8.16 (s (br)) which were believed to arise from the presence of 2-phenylpropenal imine (3); further indication of the presence of 3 came from the observation of nmr signals due to 2-phenylpropenal ($\delta^{CCl_4}_{TMS}$ 6.05, 6.52 (doublets, 1 H ea, *J* = 0.8 Hz) and 9.75 (s, 1 H))(7) in the spectrum of the total crude product obtained by acid-catalyzed hydrolysis(8) of the photolysate. Finally, in addition to the nmr peaks cited for 2 and 3, and a band due to Ar-H at δ 7.2-7.9, broad absorption also occurred throughout the spectrum, with a small increase in intensity in the region of δ 5.2-5.9. The yields of 2 and 3 in several experiments were consistently found to be 3.2% and 5.0% respectively by nmr assay.(9)

Identical experiments in which a Pyrex filter sleeve was employed led to decomposition of 75% of 1 and yielded 2.6% of 2 and 7.6% of 3.(10,11) Evaporative distillation (bath temp 35-48° (2mm)) of the products obtained by irradiation of 1.0 g of 1 in this manner allowed recovery of about one-half the amount of 2 formed, but none of the suspected imine 3 could be obtained. Large amounts of polymeric material were also present.

Although the observed formation of 2 and 3 from 1 can be compared with the formation of bicyclobutane and 1,3-butadiene from allyl carbene,(12) the intermediacy of an allyl nitrene, possibly homoallylically-stabilized, would be difficult to establish.(13)

Extension of this study to other allylic azides is in progress.(14)

REFERENCES AND FOOTNOTES

1. The photolysis of allyl azide yields the imine of acrolein, isolated in 52% yield as its 2,4-DNP derivative: D.H.R. Barton and L.H. Morgan, Jr., J. Chem. Soc., 622 (1962).
2. Attempts to form 1-azabicyclo[1.1.0]butane by pyrolysis of allyl azide have been reported: A. Logothetis, J. Am. Chem. Soc., 87, 749 (1965). Any bicyclic amine formed in these experiments would probably have been destroyed in the isolation procedure (cf. ref. 6).
3. Obtained by treatment of 1-bromo-2-phenylprop-2-ene(4) with sodium azide in dimethylformamide at 25° for 16 hr. The structure of 1 was confirmed by a satisfactory combustion analysis and ir, nmr, and uv (max at 241.5 mμ; ε 8280) spectral data.
4. H. Pines, H. Alul and M. Kolobielski, J. Org. Chem., 22, 1113 (1957).
5. Addition of pyridine-d_5 had no measurable effect on the yields obtained in its absence, but was done to assure consistent results since both 2 and 3 were very sensitive to traces of acid. Base-washed glassware was used for all manipulations.
6. A.G. Hortmann and D.A. Robertson, J. Am. Chem. Soc., 89, 5974 (1967).
7. An authentic sample of 2-phenylpropenal used for comparison was obtained via MnO_2 oxidation of the corresponding alcohol formed from $C_6H_5(MgBr)C = CH_2$ and formaldehyde.
8. Studies on the kinetics of the acid-catalyzed hydrolysis of 2 under similar conditions (J.L. Kurz, B.K. Gillard and D.A. Robertson, unpublished results) indicate that, using the nmr assay described, no detectable amount of 2-phenylpropenal is formed from 2.
9. This analysis was done by comparing the integrated areas of the signals at δ 1.28, 2.52, 5.53, 5.73 and 8.16 with the area under the methyl signal arising from a weighed amount of p-nitrotoluene added as an internal standard; estimated accuracies are 0.2% for 2, and 0.5% for 3. Compound 2 does not undergo appreciable decomposition under the conditions stated for the irradiation of 1.
10. Similar experiments using a 1.5 mm uranyl oxalate filter sleeve (cut-off at ∿330 mμ) and 1% benzophenone as a photosensitizer led to complete disappearance of the azide in less than 0.5 hr; the product (which was not investigated in detail) exhibited two broad and intense nmr absorption bands at δ 0.7-1.9 which were not exhibited by the products obtained in the absence of sesitizer. No detectable amounts of 2 and 3 were formed in these experiments.
11. Pyrolyses of 1 performed in cyclohexane (containing pyridine-d_5) using sealed tubes at temps ranging from 120-180° led to decomposition of 1; compounds 2 and 3 could not be detected.
12. D.M. Lemal, F. Menger and G.W. Clark, J. Am. Chem. Soc., 85, 2529 (1963). See also P.A.S. Smith, Open-Chain Nitrogen Compounds, Vol 2, p. 215, W.A. Benjamin, Inc., New York (1966).
13. S. Linke, G.T. Tisue, and W. Lwowski, J. Am. Chem. Soc., 89, 6308 (1967).
14. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support (Grant No. 3032-A1) of this research.