Reactions of Phosphoryl Azides with Norbornene. Formation of a Novel Phosphorylated Triazoline

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CURRENT interest in the reaction of strained alkenes with organic azides is apparent.[1–4] The reaction of alkyl and aryl azides with norbornene (I) has been reported to give triazolines[1,2] in the case of alkyl or aryl azides and aziridines[1,2] when acyl azides were employed. Decomposition of the triazolines under photolytic conditions resulted in high conversions into the corresponding aziridines.[1] In contrast pyrolyses of triazolines gave primarily imines.[1] The aziridines were stable under the conditions used to pyrolyze the triazolines.[1] In the experiments with acyl azides, the triazolines, if formed, were unstable and could not be isolated by ordinary techniques. In fact, it was postulated that the aziridine is formed directly from benzenesulphonyl azide and (I).[3]

We have found that the reaction of diethyl phosphorazidate (II)[5] with excess of (I) at 40—45° gives diethyl (3a,4,5,6,7,7a-hexahydro-4,7-methano-1*H*-benzotriazol-1-yl)phosphonate (III).

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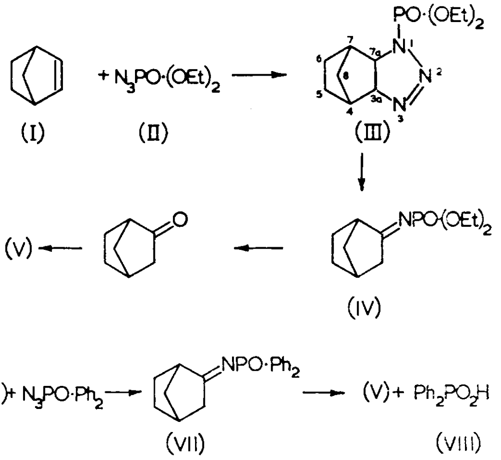
[1] P. Scheiner, *J. Org. Chem.*, 1965, **30**, 7.
[2] J. E. Franz and C. Osuch, *Tetrahedron Letters*, 1963, 837.
[3] J. E. Franz, C. Osuch, and M. M. Dietrich, *J. Org. Chem.*, 1964, **29**, 2922.
[4] L. H. Zalkow, A. C. Oehlschlager, G. A. Cabat, and R. L. Hale, *Chem. and Ind.*, 1964, 1556.
[5] F. L. Scott, R. Riordan, and P. D. Morton, *J. Org. Chem.*, 1962, **27**, 4255.

Although (III) was not isolated because of its instability, support for its structure was afforded by n.m.r. analysis. Thermal decomposition of (III) in boiling toluene resulted in stoicheiometric loss of nitrogen and in the formation of the corresponding imide [95·6% based on (II)] diethyl 2-norbornylidenephosphoramidate (IV). The imide (IV) was characterized by hydrolysis with 10% hydrochloric acid to give ammonia, phosphoric acid, and norcamphor which was isolated[6] as its 2,4-dinitrophenylhydrazone (V).

Important evidence for (III) is afforded by n.m.r. analysis which shows an AB quartet centred at δ 4·10 (J = 8·5 c./sec.) and absorptions at δ 2·5 and 2·65 which are assigned in the non-equivalent C-4, C-7 bridgehead protons. The AB quartet at δ 4·01 is assigned at the C-3a, C-7a protons of the triazoline (III). Absorption at δ 2·61 and 2·73 in the n.m.r. spectrum of the triazoline from phenyl azide and (I) is similar for the bridgehead protons at C-4, C-7. Infrared absorption for (III) at 7·88 μ was assigned to the $P\rightarrow O$ group. The infrared spectrum of compound (IV) (b.p. 119°/2 mm) does not show absorption near 3 μ (N–H) or at 6·6 μ, but strong bands are visible at 5·98 μ (C=N) and 7·94 μ ($P\rightarrow O$). The n.m.r. of (IV) is also consistent with the structure.

The condensation of diphenylphosphinic azide (VI)[7] with excess of (I) for 18 hours at 90° gave only *N*-2-norbornylidene-*PP*-diphenylphosphinic amide (VII) [63% based on (VI)], b.p. 190/1 mm. The infrared spectrum has strong absorption at 5·97 μ (C=N) and at 8·26 and 8·36 μ (doublet for $P\rightarrow O$). Structure (VII) was characterized by acid hydrolysis to give diphenylphosphinic acid (VIII) and norcamphor, which was again isolated as the 2,4-dinitrophenylhydrazone (V). Since the condensation required a higher temperature than was needed with the previous phosphoryl azide, the suspected triazoline intermediate in this reaction apparently does not survive.

Attempts to decompose the triazoline (III) or to cause either (II) or (VI) to react with (I) under photolytic conditions yielded only complex mixtures and tars in both cases. The results recorded here support the triazoline (III) as an intermediate in this particular azide–alkene condensation. The triazoline obtained from (I) and ethyl azidoformate was reported recently but only a maximum in the ultraviolet spectrum was given in support of the structure.[1] In any event, the latter data[1] and that found in our studies appear to contain the only examples of identifiable triazolines in the norbornene system which have an electron-withdrawing group attached to nitrogen in the triazoline ring. The phosphoryl azide (II) appears to be intermediate in reactivity between benzenesulphonyl azide[2,3] (the more reactive azide where no triazoline is isolated) and phenyl azide from which the triazoline is a solid, stable at its melting point.[1]



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[6] Phosphoric acid was determined by the method described in W. J. Blaedel and V. W. Moloche, "Elementary Quantitative Analysis," Harper and Row, New York, 1963, p. 371.

[7] R. A. Baldwin and R. M. Washburn, *J. Amer. Chem. Soc.*, 1961, **83**, 4466.