86. *The Reaction of Bicyclo*[2,2,1]*heptadiene with Methylphosphonous Dichloride.**

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Bicycloheptadiene and methylphosphonous dichloride readily form a 1 : 1 adduct, which on hydrolysis or reaction with sulphur dioxide gives a novel phosphine oxide. The structure of the adduct was established as a substituted nortricyclene by chemical transformations and physical measurements.

BICYCLO[2,2,1]HEPTADIENE reacts with the Lewis acids boron trichloride,[1] phenylboron dichloride,[1] stannic chloride,[2] phenyltin trichloride,[2] and germanium tetrabromide [2] to give nortricyclenes. Bicyclo[2,2,1]heptadiene also reacts to form substituted nortricyclenes on reaction with other electrophilic reagents,[3] on irradiation,[4] and in reactions

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* Cf. *Proc. Chem. Soc.*, 1963, 177.

[1] Joy and Lappert, *Proc. Chem. Soc.*, 1960, 353.

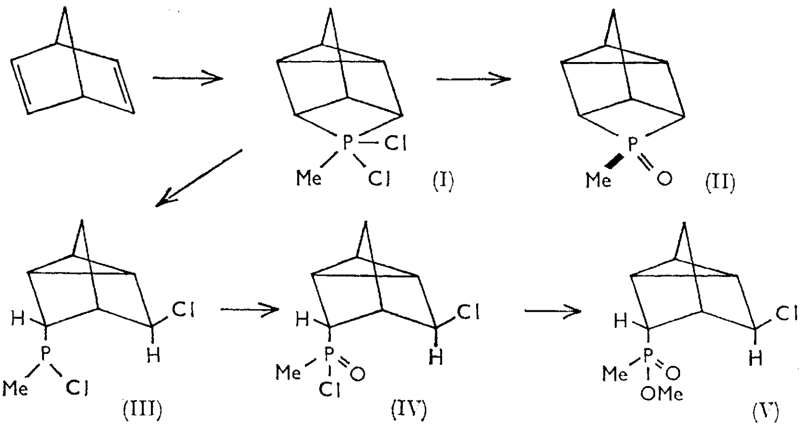
[2] Rabel and West, *J. Amer. Chem. Soc.*, 1962, **84**, 4169.

[3] Winstein and Shatavsky, *J. Amer. Chem. Soc.*, 1956, **78**, 592.

[4] Cristol and Snell, *J. Amer. Chem. Soc.*, 1958, **80**, 635.

with dienophiles.[5] These abnormal reactions can be attributed to the importance of a homoconjugative effect.[6]

It has now been found that methylphosphonous dichloride reacts with bicyclo[2,2,1]heptadiene in the absence of light and oxygen to give a crystalline 1 : 1 adduct (I). This adduct on oxidation with sulphur dioxide or on hydrolysis with aqueous sodium hydrogen carbonate gave a neutral phosphine oxide (II), $C_8H_{11}PO$ ($\nu_{max.}$ 3·25, 8·40, and 12·55 μ), that resisted hydrogenation. Pyrolysis of the adduct (I) gave a liquid isomer (III), $C_8H_{11}PCl_2$, which reacted with chlorine and then sulphur dioxide to give thionyl chloride and a liquid phosphonyl chloride (IV), $C_8H_{11}POCl_2$ ($\nu_{max.}$ 3·25, 8·1, and 12·55 μ). This phosphonyl chloride (IV) reacted readily with an excess of methanol, which replaced only one chlorine atom to give a phosphinate ester (V), $C_9H_{14}PO_2Cl$, [$\nu_{max.}$ 3·25, 8·25 (P = 0), and 12·55 μ].



The presence of peaks at 3·25 and 12·55 μ and the absence of absorption between 5·0 and 6·9 μ suggested[7] that compounds (II—V) are substituted nortricyclenes. Overlap of peaks prevented a detailed analysis of the proton magnetic spectra of compounds (II) and (III), however, the absence of peaks assignable to olefinic hydrogens and other features suggested that these compounds have nortricyclene structures.

The spectrum of the phosphine oxide (II) contained four groups of protons with area ratios of 1·95, 2·8, 3·4, and 3. A doublet, J 11·4 c./sec. at τ 8·76 with area ratio 3·4, collapsed into a singlet and a simplification of a multiplet of area ratio 1·95 occurred on application of the spin-decoupling technique to the phosphorus-31 atom. This doublet can be assigned to the group Me·P(:O). This shows that the Me·P group in methylphosphonous dichloride remains intact in the reaction with bicyclo[2,2,1]heptadiene.

The proton spectrum of the liquid phosphorus chloride (III) contained a singlet at τ 5·66, which showed no evidence of splitting under conditions of high resolution. The chemical evidence proves that (III) is a chloride of tervalent phosphorus, which contains one chlorine atom attached to carbon. This is supported by the p.m.r. spectrum of (III), since the singlet at τ 5·66 can be assigned to the CHCl group.

The chemical and physical observations can be explained on the basis of the tricyclo[2,2,1,0]heptane structures formulated. The presence of the CHCl group as a singlet in the p.m.r. spectrum of (III), and the known[8] dependence of the coupling constant

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[5] Ullman, *Chem. and Ind.*, 1958, 1173; Blomquist and Meinwald, *J. Amer. Chem. Soc.*, 1959, **81**, 667.

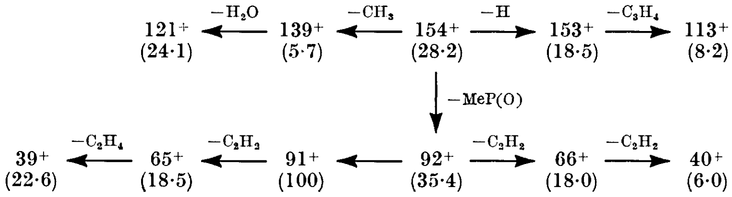
[6] Winstein and Shatavsky, *Chem. and Ind.*, 1956, 59.

[7] Pollard, *Spectrochim. Acta*, 1962, **18**, 837.

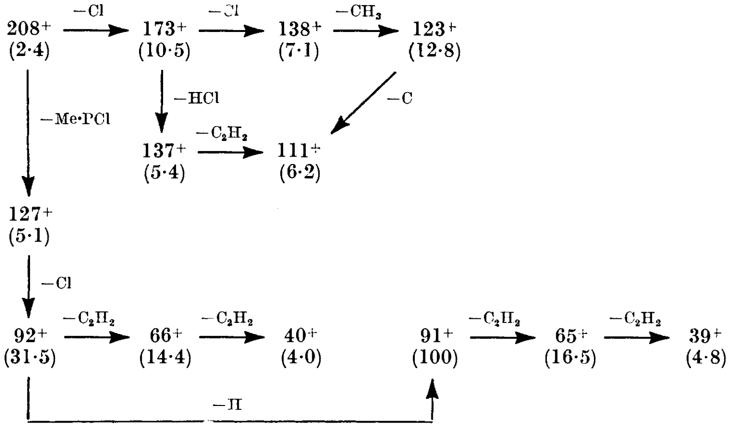
[8] Karplus, *J. Chem. Phys.*, 1959, **30**, 11; Anet, *Canad. J. Chem.*, 1961, **39**, 789.

between vicinal hydrogen atoms on the dihedral angle suggests a structure (III) in which the chlorine atom of the CHCl group occupies an *exo*-position.

The mass spectrum of the phosphine oxide (II) and the phosphonous chloride (III) have been examined. The spectra confirm the molecular formulæ determined on the basis of elemental analyses and molecular weight measurements. The spectra also provide general support for the suggested structures. The most characteristic peaks of the mass spectra of compounds (II) and (III) are illustrated in schemes 1 and 2, respectively.



Scheme 1.



Scheme 2.

It is of interest that in both compounds fragmentation of the parent ion occurs to an ion of *m/e* 92. This ion then breaks down by two competing paths, which have also been observed [9] for a number of other molecular ions derived from C_7H_8 isomers such as cycloheptatriene and bicyclo[2,2,1]heptadiene.

The chemical and physical evidence presented provides general support for the structures (I)—(V). The extremely ready reaction of methylphosphonous dichloride with bicyclo[2,2,1]heptadiene is clearly related to the known [10] reaction of isoprene with phenylphosphonous dichloride. These reactions are of particular interest because normally phosphonous chlorides do not react with olefins except in the presence of Lewis acids [11] or under free-radical [12] conditions.

EXPERIMENTAL

The mass spectra were measured on an A.E.I. MS.2H spectrometer.

Reaction of Methylphosphonous Dichloride with Bicyclo[2,2,1]*heptadiene.*—Methylphosphonous dichloride (11·7 g.) was added in an atmosphere of dry oxygen-free nitrogen to freshly distilled

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[9] Meyerson, McCollum, and Rylander, *J. Amer. Chem. Soc.*, 1961, **83**, 1401.
[10] McCormack, *Chem. Abs.*, 1955, **49**, 7601, 7602.
[11] Jungermann, McBridge, Clutter, and Mais, *J. Org. Chem.*, 1962, **27**, 606.
[12] Frank, *Chem. Reviews*, 1961, **61**, 401.

bicyclo[2,2,1]heptadiene (13·8 g.). After 24 hr. at room temperature the solid (I) 2,2-*dichloro-*2-*methyl-*2-*phospha*(V)*tetracyclo*[3,2,1,$0^{3,6}$,$0^{4,7}$]*octane* (18·0 g.) (Found: Cl, 33·8. $C_8H_{11}PCl_2$ requires Cl, 33·9%) was filtered off in a dry box.

Reaction of the Phosphorane (I) *with Sulphur Dioxide.*—(I) (2·0 g.) was placed in a heavy Pyrex tube, the tube evacuated, and sulphur dioxide (5·0 g.) condensed onto (I). The tube was sealed and allowed to warm to room temperature. After 2 hr. at room temperature the contents were examined. Thionyl chloride (1·0 g.) and unchanged sulphur dioxide (4·2 g.) were obtained, together with a crystalline product, 2-*methyl-*2-*phosphatetracyclo*[3,2,1,$0^{3,6}$,$0^{4,7}$]*octane* 2-*oxide* (1·35 g.) had m. p. 157° (from carbon tetrachloride) [Found: C, 62·1; H, 7·1; P. 19·9%; *M*(benzene), 161. $C_8H_{11}OP$ requires C, 62·3; H, 7·2; P, 20·1%; *M*, 154]; $\nu_{max.}$ 3·25, 8·40 (P = 0), and 12·55 μ. The proton magnetic resonance spectrum measured at 60 Mc/sec, in benzene showed peaks at (τ 8·07, 8·13) multiplet, τ 8·43 multiplet, (τ 8·66, 8·85) doublet, (τ 8·89, 8·93) multiplet, with area ratios 1·95, 2·8, 3·4, 3, respectively. The spectrum measured in carbon tetrachloride showed no peak assignable to olefinic hydrogens. The mass spectrum showed a parent ion *m*/*e* 154 and the characteristic peaks shown in Scheme 1.

Reaction of the Phosphorane (I) *with Aqueous Sodium Hydrogen Carbonate.*—The adduct (I) (2·0 g.) was shaken with aqueous sodium hydrogencarbonate solution (2·0 g. in 100 c.c.) for 1 hr. The product was filtered off, dried, and crystallised from carbon tetrachloride; it (1·26 g.) had m. p. 157° and was identical (i.r. spectrum) with the phosphine oxide (II).

Pyrolysis of the Phosphorane (I).—The adduct (I) (9·0 g.) was heated at 180°/0·1 mm. The product, exo-3-*chloro*-endo-5-*methylchlorophosphinotricyclo*[2,2,1,$0^{2,6}$]*heptane*, (III) distilled, and on redistillation had b. p. 100°/0·2 mm. (5·0 g.) [Found: C, 46·2; H, 5·2; Cl, 33·7; P, 14·6%; *M*(benzene), 207. $C_8H_{11}Cl_2P$ requires C, 46·0; H, 5·3; Cl, 33·9; P, 14·8%; *M*, 209]; $\nu_{max.}$ 3·25 and 12·55 μ. The proton magnetic resonance spectrum measured at 60 Mc/sec, in benzene had peaks at τ 5·66 singlet, (τ 7·79, 7·97) multiplet, τ 8·31 singlet, τ 8·76 multiplet, τ 8·90 multiplet, and τ 9·04 multiplet, with ratios 0·85, 1·26, 1·0, 2·93, 3·94, and 0·96, respectively. The spectrum measured in carbon tetrachloride showed no peak assignable to olefinic hydrogens. The mass spectrum showed a parent ion *m*/*e* 208 with $M + 2$ and $M + 4$ isotope peaks with intensities (relative to the parent ion) of 63·8 and 10·6%, respectively, demonstrating the presence of two chlorine atoms in the compound. The other characteristic peaks are shown in Scheme 2.

The Oxidation of the Phosphonous Chloride (III).—Chlorine (1·8 g.) was bubbled with ice-cooling into a carbon tetrachloride solution (50 c.c.) of the phosphonous chloride (III) (5·0 g.). Sulphur dioxide was then bubbled through the suspension of the chlorine adduct until a clear solution was obtained. After removal of solvent exo-3-*chloro*-endo-5-*methylchlorophosphinyltricyclo*[2,2,1,$0^{2,6}$]*heptane* (IV) (5·0 g.) distilled, b. p. 130°/0·2 mm. [Found: C, 42·4; H, 4·8; Cl, 31·7%; *M*(benzene), 220. $C_8H_{11}Cl_2OP$ requires C, 42·7; H, 4·9; Cl, 31·5%; *M*, 225]. Gas chromatography showed that the solvent carbon tetrachloride contained thionyl chloride.

Reaction of the Phosphinic Chloride (IV) *with Excess of Methanol.*—The phosphinic chloride (IV) (4·0 g.), in dry ether (10 c.c.) was added dropwise to methanol (5·0 c.c.) at 0°. The excess of methanol was removed under vacuum and exo-3-*chloro*-endo-5-*methoxymethylphosphinyltricyclo*[2,2,1,$0^{2,6}$]*heptane* (V) (3·6 g.) distilled, b. p. 121°/0·1 mm. [Found: C, 49·2; H, 6·3; Cl, 15·9%; *M*(benzene), 223. $C_9H_{14}ClO_2P$ requires C, 49·0; H, 6·4; Cl, 16·1%; *M*, 220).

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