

816. *The Reactions of Organic Derivatives of Elements Capable of Valency-shell Expansion. Part II.* Unsaturated Quaternary Phosphonium Salts.*

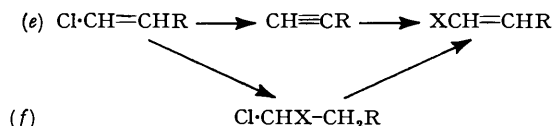
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The preparation and reactions of derivatives of trialkylpropenephosphonium and hexa-alkylpropenylene-1 : 3-diphosphonium salts are reported. The probability of the occurrence of tautomerism in the latter compounds is discussed.

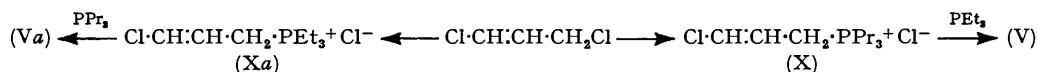
THIS paper reports an extension of investigations on unsaturated quaternary ammonium salts (Ingold and Rothstein, *J.*, 1929, 8; 1931, 1666; Rothstein, *J.*, 1940, 1560) to the corresponding quaternary phosphonium salts. The conclusions reached in Part I indicate

* Part I, preceding paper.

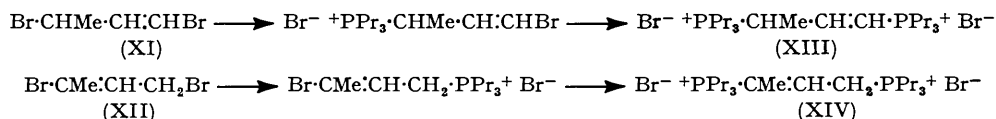
Although the isomeric substances (V) and (Va) should have been formed, repeated fractional crystallisation failed to yield more than one individual. Unequivocal syntheses of each of the isomers were difficult to devise. In the case of the ammonium salts the method followed (Ingold and Rothstein, *loc. cit.*) was ${}^+R_3N \cdot CH_2 \cdot CHCl \cdot CH_2 \cdot NR'_2 \longrightarrow {}^+R_3N \cdot CH : CH \cdot CH_2 \cdot NR'_2 \longrightarrow {}^+R_3N \cdot CH : CH \cdot CH_2 \cdot NR'_3{}^+$, but a major difficulty in using a similar route for phosphorus compounds is the absence of a method for the preparation of pure secondary phosphines in quantity. Advantage, however, was taken of a recent observation of one of us (unpublished) that although halogen attached to a vinyl group is usually unreactive in ethanol or *tert.*-butanol, in certain cases replacement can be effected in amyl alcohol. Amongst reasons for believing that the process is direct replacement, and neither elimination followed by addition (*e*), nor addition followed by elimination (*f*), is



that anions are added to these olefinic derivatives at the 2-position, and the same is likely for acetylenic compounds. Application of this reaction to propenyl derivatives afforded the chloroallylphosphonium salts (X) and (Xa), which should yield the diphosphonium salts (V) and (Va) respectively:



In fact, (X) and (Xa) furnished the same product, and the presumption is that this is due to interconversion of (V) and (Va) since, if mobility is decreased by the use of the dibromobenzenes (XI) and (XII), the two distinct isomerides (XIII) and (XIV) can be isolated:

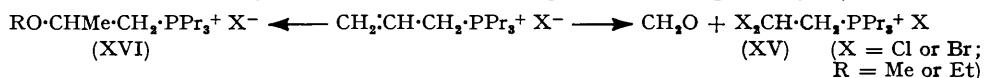


The triethyltripropylpropenylenediphosphonium picrates obtained from the chloro-derivatives (X) and (Xa) had melting points which differed from that of the picrate (m. p. 151—152°) of the compound obtained by dehydration of the hydroxytrimethylenediphosphonium chloride (IV), although there was no depression of the m. p. on admixture (such depressions do occur for totally different diphosphonium picrates; *e.g.*, all the above picrates depress the m. p. of hexa-*n*-propylpropenylenediphosphonium picrate). The melting points of the picrates derived from chloroallyl chloride varied from 154° to 183° according to the number of recrystallisations but all the specimens gave correct analytical data and afforded intermediate melting points when mixed with one another. The identity of the two picrates of m. p. 183° was confirmed by measuring their solubilities in acetone (*cf.* Ingold and Rothstein, *loc. cit.*) which was constant both for the single substances and their mixtures. The compounds may be mixtures of tautomerides having widely separated melting points but in the absence of methods for ascertaining the position of the double bonds this cannot be confirmed and geometrical isomerism is not precluded.

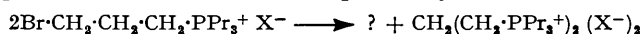
Attempts to alkylate the diphosphonium salts (II) with alkyl halide and sodium alkoxide led to the production of what appeared to be isomerides. The same transformation occurred with piperidine in acetone. Owing to the small quantities available the structures of the new compounds have not yet been determined.

Trialkylallylphosphonium Derivatives.—These were obtained by condensation of allyl bromide with the corresponding tertiary phosphine. The structure of allyltri-*n*-propylphosphonium halide was shown by its reduction to tetra-*n*-propylphosphonium halide and

by fission by ozone, but in the latter reaction the fragment including the phosphonium portion was, not the aldehyde, but the corresponding dichloro-compound (XV) :

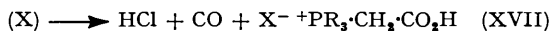


Unlike the diphosphonium salts, the allyl derivatives showed considerable double-bond activity, reaction with sodium alkoxide yielding the 2-alkoxy-derivative (XVI) although mild alkali did not react. This may be compared on the one hand with allyltrimethyl- and trimethylprop-1-enyl-ammonium salts which are unreactive to dilute alkali or alkoxide, and on the other with alkyl prop-1-enyl sulphone which adds water or alcohol in the presence of traces of alkali (Rothstein, *J.*, 1934, 684). The last-mentioned addition also occurs with alkyl allyl sulphones but is preceded by isomerisation to the prop-1-enyl compound (Backer and De Jong, *Rec. Trav. chim.*, 1948, 67, 884). It has not yet been possible to isomerise allylphosphonium compounds and therefore at what stage addition occurs has yet to be determined. It is significant, however, that, although elimination of hydrogen halide from the 2-halogenopropyl derivative leads, in the case of ammonium salts and sulphones (Rothstein, *loc. cit.*), to the prop-1-enyl compounds $\text{Me}\cdot\text{CHX}\cdot\text{CH}_2\text{R} \longrightarrow \text{Me}\cdot\text{CH}\cdot\text{CHR}$ ($\text{R} = \cdot\text{NMe}_4, \cdot\text{SO}_2\cdot\text{CH}_2\text{Ph}$), 2-chloropropyltri-*n*-propylphosphonium chloride yields the allylphosphonium salt. In the first two cases it is certain that the primary product is not the allyl compound, and it seems therefore that, if the prop-1-enyl-phosphonium salt is formed, it is rapidly converted into the allyl isomeride. The absence of addition to the unsaturated ammonium salts may be explained by the relatively high energy of a structure such as $\text{Me}\cdot\overset{+}{\text{C}}\text{H}\cdot\text{CH}\cdot\text{NMe}_3\overset{-}{\text{H}}\text{X}$ compared with those corresponding for the sulphone and the phosphonium salts where the postulated formation of a π -bond by utilisation of the *d* orbitals is possible. It has already been mentioned that trialkyl-3-chloropropylammonium salts yield the allyl derivative quite smoothly. The phosphonium derivatives do not under similar conditions lose hydrogen halide but a hexa-*n*-propyltrimethylenediphosphonium salt is formed accompanied by a faint odour of phosphine :



and in this respect they resemble 3-chloro-sulphones which however yield the hydroxy-derivative with alkalis.

The chloroallylphosphonium salts (X and Xa) were similar in their reactions to the unsubstituted compounds, but here ozonolysis yielded the normal products, namely, the trialkylcarboxymethylphosphonium salt (XVII), hydrogen chloride, and carbon monoxide :



EXPERIMENTAL

Preparation of Trialkylphosphines.—Trimethylphosphine. The preparation from methylmagnesium bromide and phosphorus trihalide, under various conditions, always gave poor yields, owing to the easy formation of tetramethylphosphonium salts. Pure trimethylphosphine was obtained by warming the silver iodide derivative, $(\text{Me}_3\text{P}\cdot\text{AgI})_4$, in a stream of oxygen-free nitrogen (Mann and Wells, *J.*, 1938, 702) but the method was unsuitable for the preparation of any quantity of the substance and in spite of the exclusion of air the phosphine was always contaminated with impurities arising from its oxidation and alkylation.

Triethylphosphine. This was obtained in nearly 50% yield by the addition of an excess of ethereal ethylmagnesium bromide to phosphorus tribromide (70 g.) in ether (100 c.c.) (Hibbert, *Ber.*, 1906, 39, 161; Fenton and Ingold, *J.*, 1929, 2342; Slotta, *Ber.*, 1927, 60, 298). It was stored under carbon dioxide and transferred either to a vertical nitrogen-filled pipette or to the reaction vessel by pressure of purified nitrogen. Preparation of triethylphosphine on the scale used for the *n*-propyl compound was on the whole unsuccessful.

*Tri-*n*-propylphosphine.* The preparation was a modification of that used by Davies, Pearse, and Jones (*J.*, 1929, 33, 1262). *n*-Propylmagnesium bromide (4 mols.), prepared in two portions from a total of *n*-propyl bromide (592 g.), magnesium (96 g.), and ether (2 l.), was placed in a 5-l. 3-necked flask fitted with a heavy mercury-sealed spiral stirrer, a reflux condenser, and a nitrogen inlet. Ethereal (250 c.c.) phosphorus trichloride (122 g., 0.88 mol.) was cautiously

added during 5 hr. to the above solution cooled in ice-salt, oxygen-free nitrogen being passed through the liquid. The mixture was then heated under reflux for 0.5 hr. and aqueous ammonium chloride (600 g. in 2 l.) was slowly added. This addition occupied 4 hr. and was at first accompanied by a vigorous reaction but could be accelerated after a quarter of the ammonium chloride solution had been added. The product was siphoned into a separating funnel in an atmosphere of carbon dioxide, the useful device described by Dyke, Davis, and Jones (*J.*, 1930, 463) being employed. The ethereal extract was dried (Na_2SO_4) and distilled in nitrogen. The product had b. p. $77^\circ/13$ mm. (80–85 g., 56%). Occasionally the presence of a fine precipitate in suspension prevented the use of a siphon; in such cases all operations were carried out in a large box filled with carbon dioxide and fitted with a glass observation window and protected arm-holes.

The phosphines could also be isolated in the forms of their addition products with carbon disulphide, $\text{R}_3\text{P}\cdot\text{CS}_2$ (Hofmann, *Annalen*, Suppl., 1861, 1, 26), but a satisfactory method for decomposition of these could not be found. Decomposition by heat was attended by sublimation and by recombination of the gaseous components.

Preparation of 2-Hydroxytrimethylene diphosphonium Salts.—(a) A solution of 1:3-dibromohydrin (15 g.) in absolute ethanol (25 c.c.) was boiled for 5 hr. under reflux with tri-*n*-propylphosphine (25 g.). Addition of dry ether to the cooled solution precipitated a viscous oil which quickly crystallised to a white hygroscopic solid; this was dried over phosphoric oxide. An aqueous solution of the bromide was mixed with an excess of silver oxide, and the filtered liquid mixed with aqueous-alcoholic sodium iodide. The precipitated 2-hydroxy-PPPP'P'P'-hexa-*n*-propyltrimethylene-1:3-diphosphonium di-iodide separated from dry ethanol in colourless leaflets, m. p. 277° (Found: C, 39.7; H, 7.5; I, 39.7, 39.9. $\text{C}_{21}\text{H}_{48}\text{OP}_2\text{I}_2$ requires C, 39.9; H, 7.6; I, 40.2%). The monostyphnate crystallised from 90% ethanol in feathery needles, m. p. 214° (slow decomp.) (Found: C, 52.2; H, 7.9; N, 6.7. $\text{C}_{27}\text{H}_{49}\text{O}_9\text{N}_3\text{P}_2$ requires C, 52.2; H, 7.9; N, 6.8%), the dipicrate in lemon-yellow needles (from dilute ethanol), m. p. 135 – 136° (Found: C, 47.7; H, 6.5; N, 10.6. $\text{C}_{33}\text{H}_{52}\text{O}_{15}\text{N}_6\text{P}_2$ requires C, 47.5; H, 6.3; N, 10.1%), and the very sparingly soluble monochloroplatinate from a large quantity of aqueous ethanol in orange-fawn crystals, m. p. 215° (decomp.) (Found: C, 31.9; H, 6.1; Pt, 24.1. $\text{C}_{21}\text{H}_{48}\text{OCl}_6\text{P}_2\text{Pt}$ requires C, 32.1; H, 6.1; Pt, 24.8%).

(b) 2-Hydroxy-3-iodopropyl-PPP-tri-*n*-propylphosphonium iodide was prepared by boiling under reflux an alcoholic solution of 1:3-di-iodohydrin (excess) with tri-*n*-propylphosphine for 3 hr. The product crystallised from the cooled solution and recrystallised from absolute ethanol as prisms, m. p. 132 – 134° (Found: C, 30.8; H, 5.8; I, 53.1. $\text{C}_{12}\text{H}_{27}\text{OI}_2\text{P}$ requires C, 30.5; H, 5.7; I, 53.8%). Addition of ether to the original mother-liquors precipitated a small amount of an unidentified substance, m. p. 138 – 139° (Found: C, 34.7; H, 6.6; I, 51.9%). The monostyphnate of the hydroxy-iodo-compound was only moderately soluble in hot water and did not crystallise well, tending to separate as an oil which solidified to a flaky solid. After four recrystallisations from ethanol it still possibly contained a small quantity of distyphnate. The m. p. was then 104 – 105° (Found: C, 39.5; H, 5.9; N, 4.2. Calc. for $\text{C}_{30}\text{H}_{55}\text{O}_{10}\text{N}_3\text{P}_2\text{I}_2$: C, 38.6; H, 5.9; N, 4.5%).

(c) Tri-*n*-propylphosphine (16 g.) was boiled for 4 hr. under reflux with 3-chloro-1-iodopropan-2-ol (23.0 g.) (Reboul, *Annalen*, Suppl., 1861, 1, 225, 228) in ethanol (40 c.c.), affording mainly 3-chloro-2-hydroxy-*n*-propyltri-*n*-propylphosphonium iodide, prisms (from ethanol-ether), m. p. 145° (25 g., 66%) (Found: C, 36.6; H, 7.0. Calc. for $\text{C}_{12}\text{H}_{27}\text{OPClI}$: C, 37.8; H, 7.1%). The low figures for carbon in this and the analysis below suggest that partial replacement of chlorine by iodine had occurred since subsequent condensation to the diphosphonium derivatives yielded satisfactory products. The above iodide was sparingly soluble in ethyl acetate and much more so in ethanol. The picrate could not be obtained crystalline, whilst the chloroplatinate (crude, m. p. 129°) was practically insoluble in all common solvents. The monostyphnate, needles (from ethanol), m. p. 112 – 113° , had the low carbon content mentioned above (Found: C, 46.5; H, 7.2; N, 5.3. Calc. for $\text{C}_{30}\text{H}_{55}\text{O}_{10}\text{N}_3\text{P}_2\text{Cl}_2$: C, 48.0; H, 7.3; N, 5.6%).

(d) A mixture of triethylphosphine (11.8 g., 0.1 mol.), dry ethanol (30 c.c.), and 1-chloro-3-iodopropan-2-ol (23 g., 0.11 mol.) was boiled under reflux for 2 hr. Two layers were formed, the lower depositing colourless crystals which after two recrystallisations from ethanol had m. p. 119 – 121° . Further recrystallisations gave m. p. 133 – 136° . Excess of dry ether added to the original mother-liquors precipitated 3-chloro-PPP-triethyl-2-hydroxypropylphosphonium iodide, slowly separating from ethanol in colourless crystals, m. p. 141° (Found: C, 31.1; H, 6.0. $\text{C}_9\text{H}_{21}\text{OPClI}$ requires C, 31.9; H, 6.2%). It appeared that the lower-melting substance

was a mixture of the 3-iodo-salt with a small quantity of the chloro-derivative since different samples gave analyses intermediate between those required for either derivative (Found : C, 25.7, 27.5; H, 4.6, 5.3. Calc. for $C_9H_{21}OPI_2$: C, 25.1; H, 4.8%). This was probably true of the other salts also. The *picrate* had m. p. 82—84° (Found : C, 34.2, 34.1; H, 4.3, 4.4; N, 7.8, 7.4. $C_{15}H_{23}O_8N_3PI$ requires C, 33.9; H, 4.3; N, 7.9%) and the *monostyphnate*, orange-yellow prisms, m. p. 142° after three recrystallisations from aqueous ethanol (Found : C, 34.2; H, 5.2; N, 4.5. $C_{24}H_{43}O_{10}N_3P_2I_2$ requires C, 33.9; H, 5.1; N, 4.9%).

(e) The foregoing 3-chloro-*PPP*-triethyl-2-hydroxypropylphosphonium iodide (10 g.) was boiled under reflux for 6 hr. with tri-*n*-propylphosphine in alcoholic solution. The extremely deliquescent diphosphonium salt was precipitated with ether, the semi-liquid product crystallising after several days in a vacuum-desiccator over phosphoric oxide. Heating a solution of the compound with a solution of sodium styphnate precipitated *PPP*-triethyl-2-hydroxy-*P'P'P'*-tri-*n*-propyltrimethylenediphosphonium distyphnate (cf. VI) which separated from aqueous ethanol in needles, m. p. 143—144° (decomp.) (Found : C, 44.0; H, 5.5; N, 10.1%; *M*, 773. $C_{30}H_{46}O_{17}N_6P_2$ requires C, 43.7; H, 5.6; N, 10.2%; *M*, 824). The main product obtained when the solution was cooled was the *monostyphnate* (cf. VII), which was deposited after several hours. It crystallised from aqueous ethanol in a fine powder, m. p. 213° (decomp.) (Found : C, 49.6; H, 7.3; N, 7.4. $C_{24}H_{43}O_9N_3P_2$ requires C, 49.7; H, 7.4; N, 7.3%). The identical styphnate (as VII) (m. p. and mixed m. p.) was obtained from triethylphosphine and 3-chloro-2-hydroxypropyl-*PPP*-tri-*n*-propylphosphonium iodide (Found : C, 50.2; H, 7.6; N, 7.7%). The *dipicrate* separated from ethanol in bright yellow needles, m. p. 151° (Found : C, 45.4; H, 5.8; N, 11.1. $C_{30}H_{46}O_{15}N_6P_2$ requires C, 45.5; H, 5.8; N, 10.6%).

Reaction of 2-Hydroxypropyldiphosphonium Salts with Phosphorus Pentachloride.—(a) Phosphorus pentachloride (4.4 g.) was added gradually to a solution of the above triethylhydroxytripropylphosphonium dibromide (7.5 g.) in chloroform (25 c.c.). Little reaction was evident in the cold and no hydrogen chloride was evolved until the liquid was boiled. After 1 hr. the cooled solution was extracted twice with water. The chloroform layer yielded a thick oil, affording a styphnate which crystallised with difficulty, but separated from ethanol as a fine powder, m. p. 94°, containing halogen. After repeated crystallisations it finally was deposited in the form of prisms, m. p. 134° (Found : C, 42.3; H, 5.6; N, 7.9; Cl, 10.8%). It was unsaturated to permanganate but the chlorine content was too high even for the saturated 2-chloro-derivative.

The aqueous layer yielded *PPPP'P'P'*-hexa-*n*-propylpropenylene-1 : 3-diphosphonium distyphnate which after repeated recrystallisation separated from aqueous ethanol in shining flakes, m. p. 167—168° (Found : C, 46.5; H, 5.9; N, 10.0. $C_{33}H_{50}O_{16}N_6P_2$ requires C, 46.8; H, 5.9; N, 9.9%). It was also obtained from ethyl acetate as thick yellow prisms, m. p. 177° (Found : C, 46.7; H, 6.0; N, 9.8%).

(b) The above experiment was repeated with phosphorus pentachloride (4.7 g.), the phosphonium bromide (8.1 g.), and chloroform (20 c.c.). In this case after the reaction was complete, the product was mixed with water and the chloroform distilled off. The residual aqueous liquid was made just alkaline with sodium hydroxide and evaporated to dryness on the steam-bath. The residue was kept over sulphuric acid for some days and then extracted with ethanol, the extract on removal of the solvent affording a hygroscopic solid. This yielded the *diphosphonium picrate* which was sparingly soluble in alcohol and ethyl acetate and separated from these solvents in orange-yellow prisms, m. p. 156—157° (yield, 6.5 g.) (Found : C, 48.9; H, 6.0; N, 10.3. $C_{33}H_{50}O_{14}N_6P_2$ requires C, 48.5; H, 6.1; N, 10.3%). Potassium permanganate was decolorised by both the styphnate and the picrate, but bromine water was unaffected.

(c) The product of the reaction between tri-*n*-propylphosphine (5 g.) and 3-chloro-*PPP*-triethyl-2-hydroxypropylphosphonium iodide (9 g.) was converted into the chloride by successive treatment with silver oxide and dilute hydrochloric acid, followed by evaporation to dryness. The white semi-solid so obtained (after final desiccation over sulphuric acid) still contained traces of hydrogen chloride, and its aqueous solution was therefore neutralised with sodium carbonate solution and again evaporated. The residual brown mass was extracted with ethanol, the liquid filtered, and the filtrate concentrated, affording a neutral residue which was dried over phosphoric oxide in a vacuum. This material (4 g.) was treated in chloroform (20 c.c.) with phosphorus pentachloride (3.1 g.), the product affording *PPP*-triethyl-*P'P'P'*-tri-*n*-propylpropenylene-1 : 3-diphosphonium dipicrate which crystallised from ethyl acetate in large prisms, m. p. 151—152° (Found : C, 46.8; H, 5.9; N, 10.8. $C_{30}H_{44}O_{14}N_6P_2$ requires C, 46.5; H, 5.7; N, 10.9%).

Preparation of the Diphosphonium Derivatives from Chloroallyl Chloride.—(a) (i) A solution of 3-chloroallyl chloride (30 g.) in ethanol (20 c.c.) was added with cooling to a solution of tri-n-propylphosphine (40 g.) in the same solvent (150 c.c.). The reaction was completed under reflux. The colourless syrupy chloride which was precipitated by the addition of dry ether (800 c.c.) was purified by redissolving it in ethanol and reprecipitating it. Further quantities were obtained by extraction of the ethereal layers with water and evaporation of the combined extracts. The crude chloride (63 g., 93%) furnished 3-chloroallyltri-n-propylphosphonium picrate as prisms, m. p. 60—61°, from ethanol (Found: C, 46.2; H, 5.5; N, 9.3. $C_{18}H_{27}O_7N_3ClP$ requires C, 46.6; H, 5.8; N, 9.1%).

(ii) The above chloride, boiled for 16 hr. under reflux with an amyl alcoholic solution of tripropylphosphine (15 g. in 40 c.c.), afforded hexa-n-propylpropenylenediphosphonium picrate which had a somewhat lower m. p. (153—154°) than that previously obtained but was otherwise identical with it (mixed m. p. and solubilities) (Found: C, 48.3; H, 6.1; N, 10.1%).

(iii) Triethylphosphine was condensed with chloroallyltri-propylphosphonium chloride in the same way as before. Addition of sodium picrate solution to an aqueous solution of the product afforded first a picrate which separated from ethanol in small prisms, m. p. 164—165° raised to 177—179° by crystallisation from ethanol-acetone (Found: C, 46.5; H, 6.0; N, 11.3. Calc. for $C_{30}H_{44}O_{14}N_6P_3$: C, 46.5; H, 5.7; N, 10.9%). Two more crystallisations from acetone raised the m. p. to 183°. The analytical figures were similar to those above. The mother-liquors deposited more picrate which crystallised from ethyl acetate in flakes, m. p. 154—155° (Found: C, 46.2; H, 5.7; N, 11.1%).

(b) (i) Ethanolic triethylphosphine with 3-chloroallyl chloride afforded 3-chloroallyltriethylphosphonium picrate which was recrystallised by dissolving it in ethanol at 25—30° and cooling the solution to -10° (Found: C, 42.6; H, 5.2; N, 9.8; Cl, 8.3. $C_{12}H_{16}O_7N_3P_3Cl$ requires C, 42.7; H, 5.0; N, 10.0; Cl, 8.4%). Higher temperatures caused precipitation of an oil which crystallised with difficulty. The chloroplatinate separated from dilute ethanol as a light orange powder, m. p. 235° (decomp.) (Found: C, 27.8; H, 5.1. $C_9H_{13}Cl_3P_2Pt$ requires C, 27.2; H, 4.8%).

(ii) Condensation with tri-n-propylphosphine was accomplished in amyl alcohol in the usual way. The picrate of the product was recrystallised first from ethanol and then from ethanol-acetone and had m. p. 176—177° (Found: C, 47.1; H, 5.9; N, 11.1%). Further recrystallisations from acetone furnished a picrate, m. p. 183° (Found: C, 47.1; H, 5.8%).

The solubilities of the diphosphonium picrates in acetone at 25° were measured in the same way as those of the corresponding ammonium salts. The mean figure for the picrates, m. p. 183° (six determinations), prepared by either of the above methods was 0.0109 g./c.c. and was unaltered by the addition of either sample to the saturated solution.

Attempted Alkylation of the Unsaturated Diphosphonium Salts.—(a) A methanolic solution of hexa-n-propylpropenylenediphosphonium chloride (2 g.) was warmed for a few minutes with sodium methoxide (3 equivs.), excess of methyl iodide added, the mixture boiled under reflux for 10 min., then filtered, and the filtrate diluted with water and evaporated to dryness. The residue furnished a picrate, isomeric with that of the starting material, which separated from acetone-ethanol in narrow prisms, m. p. 204—205°. There was a slight depression of the m. p. when it was mixed with the original diphosphonium picrate (Found: C, 48.6; H, 6.3; N, 10.3%). The same picrate (mixed m. p.), m. p. 203° in this case, was obtained when the hexa-n-propyl-diphosphonium chloride was gently warmed in acetone solution with a slight excess of piperidine (Found: C, 48.2; H, 5.7; N, 10.6; P, 7.5; M, 750. $C_{33}H_{50}O_{14}N_6P_2$ requires C, 48.5; H, 6.1; N, 10.3; P, 7.6%. M, 810).

(b) Similarly, the reaction of sodium methoxide with triethyltri-n-propylpropenylenediphosphonium chloride yielded an isomeric compound the picrate of which separated from acetone-ethanol in feathery needles, m. p. 181—182°. This picrate depressed the m. p. of that of the starting material by about 5° when a trace of it was added to the latter and was also much less soluble in acetone (Found: C, 46.5; H, 5.9; N, 11.4. $C_{30}H_{44}O_{14}N_6P_2$ requires C, 46.5; H, 5.7; N, 10.9%).

Reduction of Propenylenediphosphonium Salts.—The unsaturated picrate (2 g.) was converted into the chloride and a hot solution of the latter in amyl alcohol containing 5% of water was treated with 2% sodium amalgam until reduction was complete. Acidification and evaporation of the solvent yielded the impure chloride which was converted into the picrate in the usual way. P'P'P'P'-Hexa-n-propyltrimethylenediphosphonium picrate separated in clusters of needles, m. p. 128° (Found: C, 48.7; H, 6.5; N, 10.6. $C_{33}H_{52}O_{14}N_6P_2$ requires C, 48.4; H, 6.4; N, 10.3%). The chloride did not decolorise permanganate solution. Hydrogenation at 50 atm.

in glacial acetic acid in presence of platinum oxide was also possible but not in the case of the triethyltripropyl derivative. The trimethylenediphosphonium salt was also synthesised independently from trimethylene bromide (2.5 equivs. of tri-*n*-propylphosphine) or 3-bromo-*n*-propyltri-*n*-propylphosphonium bromide (one equiv. of the phosphine). The picrate of the product from the former condensation had m. p. 129—130° and was identical with the other two (mixed m. p.) (Found : C, 48.7; H, 6.4; N, 10.3%).

PPP-Triethyl-P'P'P'-tri-*n*-propyltrimethylenediphosphonium picrate was obtained from the unsaturated chloride by sodium-amalgam reduction. It separated from ethanol in prisms, m. p. 138° (Found : C, 46.8; H, 5.9; N, 10.8. C₃₀H₄₆O₁₄N₆P₂ requires C, 46.4; H, 5.9; N, 10.8%). It was identical (m. p. and mixed m. p.) with the saturated picrates obtained analogously to the hexapropyl derivatives.

Preparation of Butenylenediphosphonium Salts.—(a) The product obtained by boiling under reflux a mixture of 1 : 3-dichlorobut-2-ene (6.25 g.) with tri-*n*-propylphosphine (16 g.) and ethanol (20 c.c.) for 6 hr. was isolated by precipitation with dry ether. It yielded 3-chlorobut-2-enyl-1-tri-*n*-propylphosphonium picrate, separating from ethanol in glistening leaflets, m. p. 75—76° (Found : C, 47.9; H, 5.8; N, 8.6; Cl, 7.3. C₁₈H₂₈O₇N₃ClP requires C, 47.7; H, 6.1; N, 8.8; Cl, 7.4%).

(b) The chloride of the above chloro-phosphonium compound was condensed with tri-*n*-propylphosphine in amyl alcohol at 120—130° and precipitated with dry ether. From this was obtained PPPP'P'P'-hexa-*n*-propylbut-2-enylene-1 : 3-diphosphonium picrate, crystallising from ethanol, containing a few drops of acetone, in prisms, m. p. 156—157° (Found : C, 49.2; H, 6.2; N, 10.4. C₃₄H₅₈O₁₄N₆P₂ requires C, 49.2; H, 6.3; N, 10.1%). The four or five recrystallisations necessary to obtain a constant m. p. for the picrate suggested the presence of an isomeride. The picrate depressed the m. p. of the hexapropylpropene derivative.

(c) 1 : 3-Dichlorobut-1-ene, b. p. 69—70°/125 mm., was obtained by the spontaneous rearrangement of 1 : 1-dichlorobut-2-ene prepared from crotonaldehyde and phosphorus pentachloride (Andrews, *J. Amer. Chem. Soc.*, 1946, **68**, 2584). The phosphonium chloride obtained by condensing the rearranged dichloride with tri-*n*-propylphosphine yielded no crystalline picrate or styphnate. 1-Chlorobut-1-enyl-3-tri-*n*-propylphosphonium chloroplatinate separated from ethanol, in which it was very sparingly soluble, as a crystalline powder, m. p. 188—189° (Found : C, 34.4, 34.7; H, 6.4, 5.9. C₂₆H₅₄Cl₃P₂Pt requires C, 34.4; H, 6.0%).

(d) The chlorobutenylphosphonium chloride condensed with a further mol. of tripropylphosphine to yield the diphosphonium chloride which afforded PPPP'P'P'-hexa-*n*-propylbut-1-enylene-1 : 3-diphosphonium picrate, separating from acetone-alcohol as a bright yellow crystalline powder, m. p. 101—102.5° (Found : C, 49.2; H, 6.2; N, 10.4. C₂₄H₅₂O₁₄N₆P₂ requires C, 49.2; H, 6.3; N, 10.1%). A mixture of equal parts of the diphosphonium picrates from (b) and (d) had m. p. 104—105°. No mixture of the two having a lower m. p. than this was found.

Trialkylallylphosphonium Salts.—(a) Allyl bromide (13 g.) was added with cooling to a solution of tri-*n*-propylphosphine (16 g.) in ethanol (30 c.c.) under reflux. When the initial vigorous reaction had subsided, the solution was boiled for 20 min., and the extremely deliquescent bromide precipitated with dry ether (1 l.) and purified by redissolving it in dry ethanol and reprecipitating it. Thus was obtained allyltri-*n*-propylphosphonium picrate which was very soluble in ethanol and was deposited therefrom in narrow prisms, m. p. 60° (Found : C, 50.7, 50.6; H, 6.6, 6.7; N, 10.0, 9.9. C₁₈H₂₈O₇N₃P requires C, 50.3; H, 6.5; N, 9.8%). The styphnate separated from ethanol in prisms, m. p. 90° (Found : C, 48.6; H, 6.4; N, 9.2. C₁₈H₂₈O₈N₃P requires C, 48.5; H, 6.3; N, 9.4%). The chloroplatinate was only slightly soluble in the same solvent whence it separated in clusters of orange needles, m. p. 192—194° (dependent on the rate of heating) (Found : C, 35.4; H, 6.1. C₂₄H₅₂Cl₃P₂Pt requires C, 35.6; H, 6.4%).

Allyltriethylphosphonium picrate, obtained similarly, crystallised from alcohol in deep-yellow flakes, m. p. 141° (Found : C, 47.0; H, 5.5; N, 11.4. C₁₅H₂₂O₇N₃P requires C, 46.5; H, 5.7; N, 10.9%). It was much less soluble in alcohol than the *n*-propyl analogue.

(b) *Attempted preparation of tri-*n*-propylprop-1-enylphosphonium salts.* Tri-*n*-propylphosphine (20 g.) was heated under reflux with 3-chloro-2-hydroxypropane (13 g.) for 3 hr. at 120—130°. The cooled product was dissolved in dry ethanol and the hygroscopic chloride precipitated with excess of dry ether (yield, 25 g.). The 2-hydroxy-*n*-propyltri-*n*-propylphosphonium styphnate, obtained from the chloride, crystallised from aqueous ethanol in narrow prisms, m. p. 87—88° (Found : C, 46.4; H, 6.3; N, 8.6. C₁₈H₃₀O₉N₃P requires C, 46.7; H, 6.5; N, 9.0%).

The above hydroxy-derivative (20 g.) was converted into the 2-chloro-compound by addition of phosphorus pentachloride (25 g., 50% excess) to a chloroform (120 c.c.) solution cooled to 0°.

The oil obtained by adding excess of dry ether (1 l.) to the mixture furnished an ill-defined picrate, m. p. 95°, and also 2-chloro-*n*-propyltri-*n*-propylphosphonium styphnate which separated from ethanol in deep yellow prisms, m. p. 85–86° (Found: C, 45.8; H, 6.2; N, 8.4. Calc. for $C_{18}H_{29}O_8N_3ClP$: C, 44.9; H, 6.0; N, 8.7%). Admixture of this styphnate with that of the hydroxy-compound depressed the m. p.; the high carbon content may have been due to the presence of olefinic compound resulting from the elimination of hydrogen chloride.

(c) *Dehydrohalogenation*. The 2-chlorophosphonium chloride (11 g.) was slowly added to a solution of potassium hydroxide (2.26 g.) in ethanol (85 c.c.) and left for 1 hr. at room temperature. After filtration the solution was made just acid to Congo-red with dilute hydrochloric acid and then evaporated to dryness, yielding a thick viscous residue which decolorised alkaline permanganate solution. The styphnate (Found: C, 47.7; H, 6.2; N, 9.6. Calc. for $C_{18}H_{28}O_8N_3P$: C, 48.5; H, 6.3; N, 9.5%) and the picrate were both identical (m. p. and mixed m. p.) with the corresponding allyltri-*n*-propylphosphonium salts.

(d) Other attempts to prepare the 1-enylphosphonium salts were also unsuccessful. 1-Bromoprop-1-ene (prepared together with the 2-bromo-derivative from propylene dibromide and sodium ethoxide) failed to condense with tripropylphosphine in ethyl or amyl alcohol.

*Reaction between Tri-*n*-propylphosphine and Trimethylene Bromide*.—An ethanolic solution of the phosphine (10 g.) was boiled under reflux with a large excess of trimethylene bromide for 2 hr., and the resulting bromide isolated by repeated precipitation from ethanol by dry ether. Treatment with sodium picrate solution yielded 3-bromopropyltri-*n*-propylphosphonium picrate as needles, m. p. 81°, from ethanol (Found: C, 42.3; H, 5.8; N, 8.3. $C_{18}H_{29}O_7N_3BrP$ requires C, 42.4; H, 5.7; N, 8.2%). The styphnate crystallised from this solvent in deep-yellow plates, m. p. 81–82° (Found: C, 41.6; H, 5.6; N, 8.2. $C_{18}H_{29}O_8N_3BrP$ requires C, 41.1; H, 5.5; N, 8.0%).

The compound was also obtained by condensing 3-chloropropan-1-ol (9.5 g.) with tripropylphosphine (16.1 g.) in alcohol, precipitating the chloride with ether, drying it over concentrated sulphuric acid, then adding phosphorus pentabromide to its solution in chloroform at 0°. The product was again isolated by precipitation with dry ether, and reprecipitated from ethanol. More of the phosphonium salt was obtained by extraction of the ethereal layers with water and evaporation of the aqueous solution. The styphnate was identical (m. p. and mixed m. p.) with that last described (Found: C, 41.4; H, 5.6; N, 8.2%).

*Reaction of 3-Bromopropyltri-*n*-propylphosphonium Bromide with Alcoholic Potassium Hydroxide*.—Alcoholic potassium hydroxide (1.5 equivs.) was added to an alcoholic solution of the bromide. A precipitate of potassium bromide was formed and a faint odour of phosphine became apparent after the addition of approx. one equiv. of alkali. After 10 min., the liquid was filtered, the filtrate made slightly acid by dilute hydrochloric acid, filtered again, and evaporated to dryness. The residue furnished *PPPP'P'*-hexa-*n*-propyltrimethylenediphosphonium picrate, m. p. 128–129°, identical (mixed m. p.) with that prepared from trimethylene bromide (Found: C, 49.0, 48.9; H, 6.5, 6.6; N, 10.3, 10.8%). The distyphnate, prisms (from ethanol-acetone), had m. p. 138–139° (Found: C, 46.5; H, 6.2; N, 9.4. $C_{33}H_{52}O_{16}N_6P_2$ requires C, 46.6; H, 6.1; N, 9.9%). The diphosphonium salt was also obtained when the 3-bromophosphonium bromide was heated with a little more than two equivs. of silver acetate. In this case neither the picrate nor the styphnate could be isolated crystalline. The chloroplatinate, m. p. 226–228°, which was nearly insoluble in most organic solvents, was obtained in orange flakes from a large volume of ethanol or water (Found: C, 32.7; H, 6.1; Pt, 25.3. $C_{21}H_{48}Cl_6P_2Pt$ requires C, 32.7; H, 6.2; Pt, 25.3%).

*Reactions of Allyltri-*n*-propylphosphonium Salts*.—(a) *Reduction*. With sodium amalgam these compounds are reduced to tetra-*n*-propylphosphonium derivatives identical with those obtained from tripropylphosphine and *n*-propyl bromide.

(b) *Ozonolysis*. A solution of the bromide in chloroform was ozonised for 3 days, the solvent being replenished from time to time. The liquid became yellow at the commencement of the reaction but the colour vanished after a short time and reappeared after 2 days, then being permanent. After removal of the solvent, the residue was shaken with saturated sodium styphnate solution, affording the somewhat oily 2:2-dibromoethyltri-*n*-propylphosphonium styphnate, separating from alcohol in prisms, m. p. 98° (Found: C, 34.4; H, 4.3; N, 7.4; Br, 24.2. $C_{17}H_{26}O_8N_3Br_2P$ requires C, 34.5; H, 4.4; N, 7.1; Br, 27.1%).

Ozonolysis in chloroform or acetic acid solutions over prolonged periods afforded somewhat more reliable results. Distillation of the aqueous liquid by shaking the ozonide with water afforded formaldehyde, identified by its 2:4-dinitrophenylhydrazone (Found: C, 40.3; H, 3.0. Calc. for $C_7H_8O_4N_4$: C, 40.0; H, 2.9%). The residual liquid afforded the 2:2-dibromo-

picrate, crystallising from ethanol in thick needles, m. p. 91°. Analyses were rather variable (Found: C, 34.9, 35.3; H, 4.3, 4.5; N, 8.2, 7.8; Br, 29.0, 28.1. $C_{17}H_{26}O_7N_3PBr_2$ requires C, 35.5; H, 4.5; N, 7.3; Br, 27.8%).

A similar fission of allyltri-*n*-propylphosphonium chloride furnished what appeared to be essentially 2 : 2-dichloroethyltri-*n*-propylphosphonium picrate as deep-yellow prisms, m. p. 78—79° (from ethanol). From analyses it appears that some trisubstitution had occurred (Found: C, 41.2, 42.9; H, 5.2, 5.5; N, —, 9.2; Cl, 15.7, 15.7. Calc. for $C_{17}H_{26}O_7N_3Cl_2P$: C, 42.0; H, 5.4; N, 8.6; Cl, 14.6%), but it is also possible that the analytical methods employed were unsuitable for this type of substance.

(c) *Reaction of allyltri-*n*-propylphosphonium bromide with diazomethane.* An ethereal solution of diazomethane (2.8 g.) was added to a suspension of the phosphonium bromide in the same solvent, and sufficient chloroform added to make the liquid homogeneous. After several hours the volatile constituents were distilled, leaving a residue which furnished *tri-*n*-propylpyrazolylphosphonium picrate*, prisms (from ethanol), m. p. 79—89.5° (Found: C, 47.9, 48.5; H, 6.4, 6.9; N, 15.4, 15.6. $C_{19}H_{30}O_7N_5P$ requires C, 48.4; H, 6.4; N, 14.8%).

(d) *Reaction with sodium alkoxides.* Sodium carbonate had no action but when a solution of allyltri-*n*-propylphosphonium bromide was mixed with ethyl-alcoholic potassium hydroxide (2.5 equivs.) addition occurred. The product was isolated by acidification with hydrochloric acid, followed by evaporation to dryness and extraction of the residue with ethanol. From the residue obtained by evaporation resulted *2-ethoxy-*n*-propyltri-*n*-propylphosphonium picrate* which was isolated in a crystalline condition with some difficulty but was then deposited from ethanol in prisms, m. p. 40—41° (Found: C, 50.6; H, 6.9; N, 9.0; P, 7.1. $C_{20}H_{34}O_8N_3P$ requires C, 50.5; H, 7.2; N, 8.6; P, 6.6%). The *styphnate*, prisms from ethanol, had m. p. 67° (Found: C, 48.6; H, 6.7; N, 8.8; P, 6.6. $C_{20}H_{34}O_9N_3P$ requires C, 48.9; H, 6.9; N, 8.6; P, 6.6%). The *chloroplatinate* slowly separated from ethanol as an orange powder, m. p. 117° (Found: C, 37.1; H, 7.3. $C_{28}H_{64}O_2Cl_6P_2Pt$ requires C, 37.3; H, 7.1%).

*2-Methoxy-*n*-propyltri-*n*-propylphosphonium styphnate* was similarly prepared from the product of the reaction between phosphonium chloride (5 g.), sodium methoxide (1.14 g.), and methanol (30 c.c.). It was very soluble in ethanol whence it crystallised in prisms, m. p. 50° (Found: C, 47.8; H, 6.9; N, 8.7. $C_{19}H_{32}O_9N_3P$ requires C, 47.8; H, 6.7; N, 8.8%).

*Independent Synthesis of 2-Alkoxypropyltri-*n*-propylphosphonium Salts.*—1-Chloro-2-methoxy- and -2-ethoxy-propane were obtained by alkylating 1-chloropropan-2-ol with the appropriate alkyl sulphate (Dewael, *Bull. Soc. chim. Belg.*, 1930, 39, 395) and had b. p. 103—104° and 117—118° respectively. The methoxy-derivative did not condense with tri-*n*-propylphosphine. To effect condensation of the ethoxy-compound, it was necessary to boil it (6 g.) for 2 days under reflux with the phosphine in amyl alcohol (15 c.c.), a stream of carbon dioxide being passed through the mixture. Addition of dry ether to the resinous product precipitated a clear oil. At this stage it was not possible to obtain a styphnate or a chloroplatinate, but addition of saturated sodium picrate solution precipitated an oil which eventually crystallised and was recrystallised for ethanol-acetone, whence it separated in shining plates, m. p. 154—155°, which depressed the m. p. of hexamethylpropenylene-1 : 3-diphosphonium picrate and appeared to be *2-ethoxy-PPPP'P'-hexa-*n*-propyltrimethylenediphosphonium picrate* (Found: C, 48.8; H, 6.9; N, 10.5. $C_{35}H_{56}O_{15}N_6P_2$ requires C, 48.7; H, 6.5; N, 9.7%). After this picrate had been removed, the remainder of the oil was reconverted into the chloride by addition of hydrochloric acid and repeatedly extracted with benzene. The aqueous layer was evaporated to dryness, and the residue extracted with ethanol, and after filtration the extract evaporated to dryness again. The residual oil yielded a styphnate, m. p. 63°, which was however identical (mixed m. p.) with the ethoxypropyltripropylphosphonium styphnate described above (Found: C, 48.9; H, 7.0; N, 9.0%).

*Fission by Ozone of 3-Chloroallyltri-*n*-propylphosphonium Chloride.*—Ozonised oxygen was passed through a solution of the chloride (~4 g.) in chloroform (20 c.c.) for 3 days, with periodic replacement of the solvent. The latter was distilled off, the residue boiled with water, and the solution concentrated. The syrup furnished *carboxymethyltri-*n*-propylphosphonium picrate*, prisms (from ethanol), m. p. 104—105° (Found: C, 46.0; H, 5.9; N, 9.1. $C_{17}H_{26}O_8N_3P$ requires C, 45.6; H, 5.8; N, 9.4%). The vapour evolved during the decomposition of the ozonide contained hydrogen chloride, did not give a precipitate with 2 : 4-dinitrophenylhydrazine, and probably contained carbon monoxide (blue flame).

Carboxymethyltri-*n*-propylphosphonium picrate was also prepared from chloroacetic acid by boiling it with alcoholic tri-*n*-propylphosphine for 1.5 hr. It was identical (mixed m. p.) with that obtained from the above ozonolysis product (Found: C, 46.1; H, 6.3; N, 9.1%).

Carboxymethyltriethylphosphonium picrate was similarly prepared by using triethylphosphine. It separated from ethanol in glistening leaflets, m. p. 122—123° (softening at 109°). An impurity was evidently present which could not be removed by repeated fractional crystallisation (Found: C, 41.6, 41.7; H, 5.1, 5.2; N, 11.6, 11.9. Calc. for $C_{14}H_{20}O_9N_3P$: C, 41.5; H, 4.8; N, 10.4%).

Reaction of 3-Chloroallyltri-n-propylphosphonium Chloride with Alcoholic Potassium Hydroxide.—Ethanolic potassium hydroxide (3 equivs.) was mixed with a solution of the chlorophosphonium chloride in the same solvent. A bright green colour was developed, but there was no odour of phosphine or evolution of heat. The colour gradually changed to yellow and potassium chloride was deposited. The solution was slightly acidified with dilute hydrochloric acid, filtered, and evaporated to dryness, yielding a residue which afforded an oil when mixed with saturated sodium picrate solution. After being kept for several days over concentrated sulphuric acid 3-chloro-2-ethoxypropyltri-n-propylphosphonium picrate crystallised; it recrystallised from ethanol in lemon-yellow prisms, m. p. 62—63 (Found: C, 47.5; H, 6.6; N, 8.5; Cl, 7.5; OEt, 8.5. $C_{20}H_{33}O_8N_3ClP$ requires C, 47.1; H, 6.5; N, 8.3; Cl, 7.0; OEt, 8.8%).

We are indebted to the Department of Scientific and Industrial Research for a Maintenance Award (to R. W. S.).

THE UNIVERSITY, LEEDS.

[Received, May 19th, 1953.]
