

191. *The Reactions of Organic Derivatives of Elements Capable of Valency-shell Expansion. Part VII.* Further Experiments with Quaternary Phosphonium Salts.*

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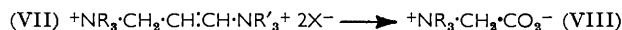
Unlike the corresponding quaternary ammonium salts, propen-1,3-ylenebistri-n-propylphosphonium salts, $X^{-+}PPr_3 \cdot CH:CH \cdot CH_2 \cdot PPr_3^{+} X^{-}$, react with dilute aqueous sodium permanganate, to give a dihydroxy-derivative in neutral solution and 2-hydroxypropen-1,3-ylenebistri-n-propylphosphonium hydroxide in alkaline solution. Alkali alone does not react but, if one of the phosphonium groups is replaced by a quaternary ammonium group, then hydroxylation occurs without the intervention of permanganate.

The two isomeric butenylene analogues mentioned in Part II are rather inert, but the lower-melting compound reacts with cold alkali, eliminating tri-n-propylphosphine. The product is a monophosphonium derivative, whose structure is discussed in the light of synthetic experiments and proton magnetic resonance spectra.

THE virtual identity of all samples of PPP-triethyl-P'P'P'-tri-n-propyl-1,3-propenylene-diphosphonium salts (I and II) was attributed by Rothstein, Saville, and Horn¹ to the rapidity with which equilibrium mixtures were formed, although direct evidence of this was unobtainable. On the other hand, the analogous butenylene derivatives (V and VI), obtained by the routes indicated below, were isolated as the separate isomers which could not be interconverted. There was no direct experimental evidence for the structures of (V) and (VI).



The propenylene derivatives (I and II) were resistant to ozone, but their failure to yield recognisable products on oxidation by permanganate was a little surprising in view of the ease with which the analogous diammonium salts (VII) afford² the corresponding betaines (VIII):



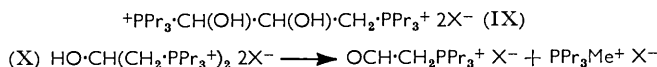
In case this had resulted from the instability of the phosphorus analogue of the betaine (VIII), *i.e.*, the carboxymethyltri-n-propylphosphonium salts, preliminary observations on the effect of pH on these compounds were made so that oxidation could be carried out under the appropriate conditions. It was found that carboxymethyltripropylphosphonium hydroxide was stable in cold alkaline solution, and at 100° at pH < 5.0 (*i.e.*, acid to Congo Red). At a somewhat higher pH (*e.g.*, acid to litmus but alkaline to Congo Red) decarboxylation to methyltri-n-propylphosphonium hydroxide occurred. However, in the subsequent experiments none of the above acid was isolated. Oxidation in neutral solution of propen-1,3-ylenebistri-n-propylphosphonium chloride gave a product which analysis suggested was a 1,2-dihydroxytrimethylene derivative (IX). In alkaline solution, sodium permanganate reacted with the propenylene salt to yield the known 2-hydroxy-derivative (X). Unlike the ammonium-phosphonium salts (XVI), the diphosphonium compound did not react with alkali alone, but it does not appear probable that the

* Part VI, preceding paper.

¹ Rothstein, Saville, and Horn, *J.*, 1953, 3994.

² Ingold and Rothstein, *J.*, 1931, 1666.

dihydroxy-compound (IX) is a necessary intermediate in the formation of the mono-hydroxy-derivative (X).

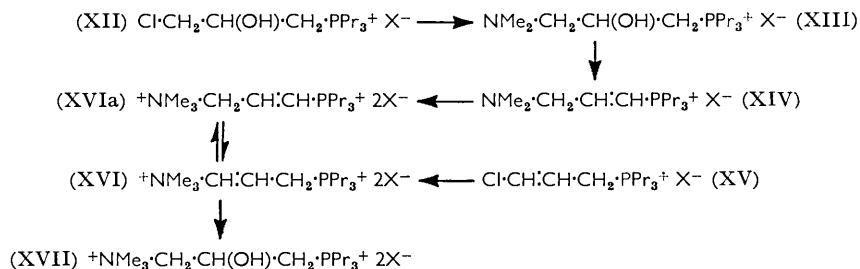


Since, by a reverse aldol reaction, the hydroxy-compound (X) could furnish the aldehyde and thence the betaine acid, it was clear that this hydroxylation would nullify structure determination by oxidation. Before proceeding further it is desirable to recall certain reactions concerning prop-1-enyl and prop-2-enyl derivatives of quaternary ammonium and phosphonium salts and of sulphones. Both 2-chloropropylammonium derivatives, $\text{Me}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{NR}_3^+\text{X}^-$, and 1-alkylsulphonyl-2-chloropropane, $\text{Me}\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{SO}_2\cdot\text{R}$, react with alkali to yield, mainly, the corresponding prop-1-enyl derivatives, $\text{Me}\cdot\text{CH}\cdot\text{CHY}$,^{3,4} but trialkyl-2-chloropropylphosphonium salts afford only the allyl compounds, $\text{CH}_2\cdot\text{CH}\cdot\text{CH}_2\cdot\text{PPr}_3^+\text{X}^-$.¹ Further, whilst 1,3-propenylenebis-trialkylammonium salts can be obtained by dehydration or dehydrohalogenation of the corresponding saturated 2-hydroxy- or 2-chloro-compounds, respectively, it is not possible to prepare a propen-1,3-ylenebis-dialkylamine in this way. There is, however, no difficulty in removing hydrogen chloride from 3-dialkylamino-2-chloropropyl-trialkylammonium salts, the products being 3-dialkylaminoprop-1-en-1-yl-trialkylammonium salts (XI):²



This is probably the case also with 1-alkylsulphonyl-3-alkylthio-2-chloropropane, $\text{R}\cdot\text{SO}_2\cdot\text{CH}_2\cdot\text{CHCl}\cdot\text{CH}_2\cdot\text{SR}$, though the evidence for this is inconclusive.⁵

Preparation of a phosphorus derivative similar to the nitrogen analogue (XI) and having a known structure proved impossible; instead 3-chloro-2-hydroxypropyl-PPP-tri-n-propylphosphonium chloride (XII) was condensed with dimethylamine, and the resulting dimethylamino-phosphonium salt (XIII) was dehydrated with phosphorus pentachloride. The expected structure of the olefinic compound so formed would be (XIV), but on methylation it yielded an ammonium-phosphonium salt identical with that obtained by condensation of 3-chloroallyltri-n-propylphosphonium chloride (XV) with trimethylamine. This should have had the structure (XVI) but the failure to obtain its tautomeride (XVIa) by condensing 3-chloroallyltrimethylammonium chloride with tri-n-propylamine (a recognisable product was not isolated) precluded direct comparisons of the isomers. The compound (XVI or XVIa) was also formed when the product obtained by condensing the chloro-derivative (XII) with trimethylamine was dehydrated with phosphorus pentachloride. The structure was confirmed by reduction to the saturated trimethylene derivative which was synthesized independently.



The non-formation, referred to above, of prop-1-enylphosphonium salts and the preparation of the ammonium-phosphonium salt (XVI) from the chloro-compound (XV) suggests that the double bond was in the β -position relative to phosphorus and that this may

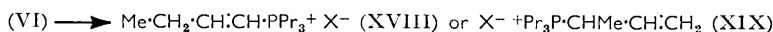
³ Rothstein, *J.*, 1940, 1560.

⁴ Rothstein, *J.*, 1934, 684.

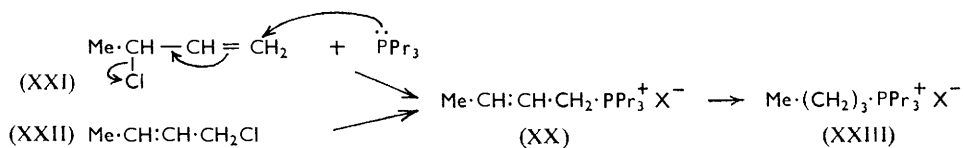
⁵ Rothstein, *J.*, 1937, 309.

have been the case even for the dimethylamino-derivative (XIV). It is true that the isomeric change (XVI) \rightarrow (XVIa) could occur, but with the bisammonium compounds (VII), at any rate, solution in aqueous alkali is necessary. Oxidation of compounds (XVI) followed the phosphonium rather than the ammonium pattern, and dilute sodium permanganate afforded the 2-hydroxy-compound (XVII) and not the betaine (VIII). Aqueous sodium hydroxide, alone, gave the same product.

Neither of the butene derivative (V) and (VI) could be reduced and their attempted interconversion in the presence of various basic catalysts was likewise unsuccessful. The structure of the chloro-phosphonium salt (III) was confirmed by ozonolysis. It was not interconvertible with its isomer (IV), and if absence of prototropic change is assumed, the bisphosphonium derivatives (V) and (VI) must have the structures assigned. The former was stable to cold sodium hydroxide but compound (VI) slowly eliminated tripropylphosphine, presumably by a paraffinic mechanism,⁶ to give a monophosphonium derivative of structure (XVIII) or (XIX):



If it were formed, however, the but-1-enyl compound (XVIII) might be expected to be transformed by a prototropic change into the more stable but-2-enylphosphonium structure (XX). The monophosphonium picrate exhibited an infrared absorption at 3080 cm^{-1} , characteristic of a vinyl-methylene stretching frequency and not shown by the picrate of the original material. This would be in accordance with structure (XIX), but in that case the resistance to catalytic reduction which was encountered was unexpected. The substance was not a but-2-enyltri-n-propylphosphonium salt (XX) because it was different from the product obtained by condensing either 3-chlorobut-1-ene (XXI) or 1-chlorobut-2-ene (XXII) with tri-n-propylphosphine.



The structure of the but-2-enyl compound (XX) was proved by its reduction to the n-butyl derivative (XXIII) which was synthesised independently from n-butyl bromide. On the other hand, a different product was obtained when s-butyl bromide was condensed with tri-n-propylphosphine. It will be noted that the suggested structure (XIX), unlike the allyl and but-2-enyl compounds discussed below, has no methylene adjacent to phosphorus in the olefinic chain.

Examination of the proton resonance spectra of allyl- and but-2-enyl-tri-n-propylphosphonium salts shows that such methylene groups are responsible for more or less symmetrical quartets centred between 5.9 and 6.7 p.p.m. (τ values). The same quartet is observed in the spectrum of the propenylenebisphosphonium salts (cf. I and II) but not in that of the butenylene compounds (V) and (VI) because, owing to their limited solubility, spectra in which the height of the low-field peaks could be distinguished from the general noise level were not obtainable. The quartet referred to above is absent from the spectrum of the substance (XIX), but a partially resolved band at very low fields makes it reasonable to infer that this absence is in fact due to a different structure and not to experimental conditions.

The intractable nature of the quaternary phosphonium salts led to some exploratory work on the synthesis of trialkylphosphine oxides by reaction of alkylmagnesium halides with di-n-butylphosphinic chloride. Tri-n-butyl- and di-n-butyl-n-propylphosphine oxide were obtained in good yield but allyldi-n-butylphosphine oxide could not be isolated in a pure condition.

⁶ Fenton and Ingold, *J.*, 1929, 2342.

EXPERIMENTAL

Preparation of Phosphines.—(a) *Tri-n-propylphosphine.* The method previously described¹ gave improved yields (66%) when the Grignard complex was decomposed with aqueous ammonium chloride, the ether layer distilled in nitrogen, and the remaining aqueous layer extracted with benzene in the vapour phase (the vapour-phase extraction apparatus was manufactured by L. V. D. Scoriah, M.Sc.). The dried (Na_2SO_4) benzene solution was distilled and the residual phosphine freed from small amounts of insoluble material by rapid filtration before the final distillation.

(b) *Diethylphosphine.* This has been reported to result from the reaction between an excess of ethylmagnesium bromide and tetraphosphorus trisulphide.⁷ In our hands a small amount of triethylphosphine only was isolated.

(c) An ethereal solution (1.5 l.) of n-propylmagnesium bromide (~4.5 moles) was slowly added to a stirred suspension of tetraphosphorus trisulphide (0.5 mole) in ether (350 c.c.) under nitrogen. The product of the vigorous reaction was boiled under reflux, with stirring, for a further 16 hr. and then decomposed by aqueous ammonium chloride. After the ethereal layer had been siphoned off, the aqueous layer was distilled in steam, and the distillate was extracted with ether. The combined dried (KOH) distillates yielded ~5% each of di-n-propylphosphine, b. p. 43—46°/24 mm., and tri-n-propylphosphine.

Preparation and Experiments with Alkylphosphine Oxides.—(a) *Di-n-butylphosphine oxide (di-n-butylphosphinous acid).*⁸ The yield (89%) of this substance, prepared from n-butylmagnesium bromide and diethyl hydrogen phosphite,⁹ was improved by decomposing the Grignard complex with aqueous ammonium chloride and extracting the aqueous layer in the vapour phase with benzene. The combined benzene and ethereal extracts were dried (Na_2SO_4) and the solvents removed in a vacuum and finally for 30 min. at 80°/20 mm. The residual di-n-butylphosphine oxide, which crystallised, could be distilled under reduced pressure without decomposition but this proved impracticable owing to the rapid crystallisation of the distillate. It reacted neither with ethylene oxide nor with boiling ethyl bromide.

A mixture of phosphorus pentachloride (20.8 g.) and benzene (100 c.c.) was slowly added to a stirred suspension of the above di-n-butylphosphine oxide (16 g.) in benzene (35 c.c.). There was a slight exothermic reaction and, when this had subsided, the liquid was boiled under reflux for a further 30 min. during which there was a slight evolution of hydrogen chloride. The mixture was kept overnight and then filtered through "Hyflo Supercel" on a sintered-glass filter with nitrogen pressure above and a partial vacuum below. Fractionation of the filtrate yielded as the only product di-n-butylphosphinic chloride (81.5%), identified by the b. p., 144—146°/15 mm., which agrees with that reported by Kosolapoff and Watson⁹ and differed from that recorded by Plets¹⁰ who considered the substance to be di-n-butylphosphinous chloride (di-n-butylchlorophosphine), b. p. 132—134°/15 mm. Hydrolysis with water yielded di-n-butylphosphinic acid, m. p. 70—71°, which agrees with that found for the substance by Kosolapoff.¹¹

(b) *Trialkylphosphine oxides.* (i) Tri-n-butylphosphine oxide was obtained by adding a solution of di-n-butylphosphinic chloride (10 g.) in ether (50 c.c.) to stirred ethereal n-butylmagnesium bromide (magnesium 1.85 g. and n-butyl bromide 12 g.) and boiling the mixture under reflux for 2 hr. The oxide, b. p. 120—123°/0.08 mm. (yield, 7.6 g., 68%), crystallised in needles and gave an infrared spectrum identical with that obtained from a specimen prepared by the reaction of n-butylmagnesium bromide with phosphorus oxychloride.¹²

(ii) In a similar way, ethereal di-n-butylphosphinic chloride with n-propylmagnesium bromide yielded di-n-butyl-n-propylphosphine oxide, b. p. 108—110°/0.09 mm. (76%), which crystallised in deliquescent needles.

(iii) Pure allyldi-n-butylphosphine oxide could not be isolated from the reaction product of allylmagnesium bromide¹³ and di-n-butylphosphinic chloride. The unsaturated oil obtained

⁷ Malatesta, *Gazzetta*, 1947, **77**, 518.

⁸ Hamilton and Williams, *J. Amer. Chem. Soc.*, 1952, **74**, 5418.

⁹ Kosolapoff and Watson, *J. Amer. Chem. Soc.*, 1951, **73**, 4101.

¹⁰ Plets, Dissertation, Kazan, 1938.

¹¹ G. M. Kosolapoff, "Organophosphorus Compounds," John Wiley & Sons, Inc., New York, 1950, p. 167.

¹² Davies and Jones, *J.*, 1929, 33.

¹³ Henze, Allen, and Leslie, *J. Org. Chem.*, 1942, **7**, 326.

decomposed when distilled at 0.01 mm., as did the substance produced by interaction of allyl-potassium and the phosphinic chloride. The latter was recovered unchanged after it had been boiled under reflux with a suspension of sodium powder in benzene containing allyl bromide and a crystal of antimony trichloride.¹⁴

Experiments with Derivatives of Bis-n-propylphosphonium Salts.—(a) *Oxidation of 1,3-propenylenebistri-n-propylphosphonium salts.* (i) In neutral solution. A 3.6% aqueous solution of sodium permanganate (20 c.c.) was added during 3 hr., with stirring, to a solution of the chloride (from 1.0 g. of picrate) in water (50 c.c.) containing magnesium sulphate (1.5 g.). After being stirred for a further hour the liquid was filtered, acidified to Congo Red, and evaporated to dryness. The residue was extracted with alcohol and the extract was evaporated, leaving a residuc which afforded a *picrate* separating from aqueous ethanol in needles, m. p. 131—132° (Found: C, 47.0; H, 5.8; N, 9.9. $C_{17}H_{28}N_3O_8P$ requires C, 46.6; H, 6.1; N, 9.9%). A mixture with 2-hydroxytrimethylenebistri-n-propylphosphonium dipicrate (m. p. 135°) had m. p. 127—129°. Aqueous sodium metaperiodate partially decomposed the chloride obtained from the picrate, m. p. 131—132°, but only a small quantity of unchanged material was recovered from the reaction mixture.

(ii) In alkaline solution. The bisphosphonium chloride (from 2 g. of picrate) and sodium carbonate (2 g.), each dissolved in water (100 c.c.), were mixed and to the solution was added aqueous sodium permanganate (0.02 g.) during 2 hr. After a further 30 min. the liquid was filtered and evaporated. The residue yielded 2-hydroxytrimethylenebistri-n-propylphosphonium picrate (1.2 g.) identified (m. p. and mixed m. p.) by comparison with an authentic specimen. It was thus different from that obtained by oxidation in neutral solution. Neither 5% sodium carbonate solution nor 2N-sodium hydroxide reacted with the unsaturated bisphosphonium salt and in both cases the unchanged material was isolated as the picrate in good yield.

Carboxymethyl-tri-n-propylphosphonium salts are evidently not formed. The corresponding chloride was unchanged by mixing it with either neutral or alkaline sodium permanganate or by passing ozonised oxygen through its solution in chloroform. A solution in aqueous sodium carbonate which was then neutralised to Congo Red by dilute mineral acid and evaporated to dryness afforded the unchanged material. Decarboxylation occurred if the evaporation followed neutralisation to litmus, and in this case the residue yielded *methyltri-n-propylphosphonium picrate* which crystallised from aqueous ethanol in needles, m. p. 81—81.5°. It was identical with the picrate (m. p. 81.5—82°) obtained from methyltri-n-propylphosphonium iodide prepared by mixing tri-n-propylphosphine with methyl iodide under nitrogen (Found: C, 47.4; H, 6.2; N, 10.5. $C_{11}H_{26}N_3O_7P$ requires C, 47.6; H, 6.4; N, 10.4%).

Experiments with Propenylene-1-ammonium-3-phosphonium Salts.—(a) A solution of 3-chloroallyltri-n-propylphosphonium chloride (8 g.) in pentanol (25 c.c.) was heated with trimethylamine (2 g.) in an autoclave at 136°. After 18 hr. the resulting dark brown liquid was dissolved in water, the solution extracted with ether, and the aqueous layer evaporated. The dark brown residue crystallised after being washed with ethanol and yielded *propenylene-1-trimethylammonium-3-tri-n-propylphosphonium picrate* separating from ethanol-acetone-light petroleum (b. p. 60—80°) in prisms, m. p. 174.5—175° (Found: C, 45.3; H, 5.5; N, 13.6. $C_{27}H_{38}N_7O_{14}P$ requires C, 45.1; H, 5.6; N, 13.9%). The greater part of the product, obtained by evaporating the alcoholic washings, was a dark brown syrup.

(b) *Condensation of tri-n-propylphosphine with 3-chloroallyltrimethylammonium chloride.*¹⁵ A solution of the phosphine (8 g.) in pentanol (25 c.c.) was boiled under reflux for 12 hr. with 3-chloroallyltrimethylammonium chloride (6 g.). Addition of an excess of dry ether precipitated a dark oil to which, after separation from the ether, was added an aqueous extract of the latter. Evaporation of the combined products gave a viscous residue from which two *picrates* were obtained. Neither of these was identified. The first separated from aqueous ethanol in large plates, m. p. 80.5—81.5° (Found: C, 46.2; H, 6.6; N, 10.7; P, 3.1%). The less soluble *picrate* crystallised from acetone and light petroleum (b. p. 60—80°) as a pale yellow powder, m. p. 201—203° (Found: C, 47.4; H, 6.2; N, 11.0%). There seemed the possibility that partial replacement of nitrogen by phosphorus had occurred, but if so it probably preceded the formation of the ammonium phosphonium salt. In order to test this, the corresponding saturated derivatives were prepared and heated with tri-n-propylphosphine.

(c) *Preparation of trimethylene-1-trimethylammonium-3-tri-n-propylphosphonium salts.* A

¹⁴ Cf. Michaelis, *Annalen*, 1901, **315**, 43; Worrall, *J. Amer. Chem. Soc.*, 1932, **52**, 2733.

¹⁵ Ingold and Rothstein, *J.*, 1929, 8.

33% ethanolic solution of trimethylamine (7.5 c.c.) was slowly added to a slight excess of 3-chloropropyl iodide (10 g.), little heat being evolved. Next morning the mixture was added to an excess of dry ether, yielding a crystalline precipitate of 3-chloropropyltrimethylammonium iodide (5.5 g., 39.5%). The picrate¹⁶ separated from chloroform-ethanol-light petroleum (b. p. 60–80°) in pale needles, m. p. 132.5–133.5° (Found: C, 39.4; H, 4.4; N, 15.2. Calc. for C₁₂H₁₇ClN₄O₇: C, 39.5; H, 4.7; N, 15.4%). A solution of the above chloro-iodide (5 g.) in ethanol (10 c.c.) was boiled under reflux for 6.5 hr. with tri-n-propylphosphine (4 g.) under nitrogen. A nearly quantitative yield of the crystalline condensation product was obtained when the cooled mixture was added to dry ether (300 c.c.). Addition of aqueous sodium picrate afforded *trimethylene-1-trimethylammonium-3-tri-n-propylphosphonium dipicrate* which separated from acetone-ethanol-light petroleum in pale yellow plates, m. p. 186–187° (Found: C, 45.2; H, 5.6; N, 13.1. C₂₇H₄₀N₇O₁₄P requires C, 45.1; H, 5.7; N, 13.1%). A suspension of the ammonium-phosphonium chloride iodide (5.3 g.) in pentanol (35 c.c.) was boiled under reflux for 19 hr. with tri-n-propylphosphine. Over 86% of the original salt was recovered unchanged and the picrate prepared from it was identical (m. p. and mixed m. p.) with that described above (Found: C, 45.2; H, 5.6; N, 12.6%).

(d) *Preparation of 3-dimethylamino-2-hydroxypropyltri-n-propylphosphonium salts.* An ethanolic solution (30 c.c.) of 3-chloro-2-hydroxypropyltri-n-propylphosphonium iodide¹ (19 g.) was heated at 70° for 1 hr. with dimethylamine (2.4 g.) under a reflux condenser cooled by acetone-solid carbon dioxide. When cooled, the reaction mixture deposited a light-brown solid (15 g.), which was washed with dry ether and dried over phosphorus pentoxide. Addition of aqueous sodium picrate to the compound afforded *2-hydroxytrimethylene-1-dimethylammonium-3-tri-n-propylphosphonium picrate* which crystallised in needles, m. p. 185–186°, from ethanol-acetone-light petroleum (b. p. 60–80°) (Found: C, 43.6; H, 5.1; N, 14.5. C₂₆H₃₈N₇O₁₅P requires C, 43.4; H, 5.3; N, 13.6%).

(e) *Preparation of Propenylene-1-dimethylammonium-3-tri-n-propylphosphonium derivatives.* 2-Hydroxytrimethylene-1-dimethylammonium-3-tri-n-propylphosphonium picrate (2 g.) was converted into the corresponding hydroxy-chloride, and the latter was dried (P₂O₅) and dissolved in chloroform (25 c.c.). When phosphorus pentachloride (1 g.) was added to the cooled (0°) solution there was no apparent reaction until the liquid was heated to the b. p.; then a vigorous reaction set in. After 30 min. the mixture was decomposed with ice-water, the chloroform layer removed, and the product isolated in the usual way as the picrate. *Propenylene-1-dimethylammonium-3-tri-n-propylphosphonium picrate* separated from ethanol-acetone-light petroleum (b. p. 60–80°) in plates, m. p. 204–204.5° (decomp.) (Found: C, 44.7; H, 5.2; N, 13.7. C₂₆H₃₈N₇O₁₄P requires C, 44.5; H, 5.1; N, 13.8%).

Methylation: Propenylene-1-dimethylammonium-3-tri-n-propylphosphonium chloride obtained from the above picrate (1 g.) was dissolved in nitromethane (20 c.c.), shaken for 12 hr. with an excess of silver acetate, filtered, and boiled under reflux with methyl iodide (5 g.) for 1.5 hr., then extracted with water. After separation of the organic layer, the aqueous extract was evaporated, yielding propenylene-1-trimethylammonium-3-tri-n-propylphosphonium picrate, m. p. 174.5°, identical (mixed m. p.) with the specimens obtained by other routes (Found: C, 45.7; H, 5.2; N, 14.0. Calc. for C₂₇H₃₈N₇O₁₄P: C, 45.2; H, 5.6; N, 13.9%).

(f) *Preparation and dehydration of 2-hydroxytrimethylene-1-trimethylammonium-3-tri-n-propylphosphonium salts.* An ethanolic solution of 3-chloro-2-hydroxypropyltri-n-propylphosphonium iodide (3.8 g. in 10 c.c.) was mixed with 31% ethanolic trimethylamine (2 c.c.) and boiled under an acetone-solid carbon dioxide condenser for 1 hr. The resulting product afforded *2-hydroxytrimethylene-1-trimethylammonium-3-tri-n-propylphosphonium picrate* which separated from ethanol-acetone-light petroleum (b. p. 60–80°) in pale yellow leaflets, m. p. 193.5–194.5° (Found: C, 44.1; H, 5.5; N, 13.6. C₂₇H₄₀N₇O₁₅P requires C, 44.2; H, 5.5; N, 13.4%). Phosphorus pentachloride converted the corresponding dihalide into propenylene-1-trimethyl-3-tri-n-propylphosphonium chloride identified (m. p. and mixed m. p.) as the picrate (Found: C, 45.2; H, 5.6; N, 13.8%). The hydroxytrimethylene derivative was also obtained by methylation of 3-dimethylamino-2-hydroxypropyltri-n-propylphosphonium chloride.

(g) *Reduction of propenylene-1-trimethylammonium-3-tri-n-propylphosphonium chloride.* A solution of the dried (P₂O₅) chloride (prepared from 2 g. of picrate) in ethanol (25 c.c.) was hydrogenated at 10.3 atm. in the presence of platinum oxide. The product yielded trimethylene-1-trimethylammonium-3-tri-n-propylphosphonium picrate identical (m. p. and

¹⁶ Rothstein, J., 1940, 1558.

mixed m. p.) with that previously obtained (Found: C, 45.2; H, 5.6. Calc. for $C_{27}H_{40}N_7O_{14}P$: C, 45.2; H, 4.1%).

(b) *Reaction of the propenyleneammonium-phosphonium chloride with sodium hydroxide.* A solution of the chloride (from 1 g. of picrate) in water (20 c.c.) was mixed with 2N-sodium hydroxide (20 c.c.) and kept overnight. It was then neutralised to Congo Red with hydrochloric acid and the product isolated in the usual way as the picrate, which was identical (m. p. and mixed m. p.) with 2-hydroxytrimethylene-1-trimethylammonium-3-tri-n-propylphosphonium picrate previously prepared (Found: C, 44.4; H, 5.6. Calc. for $C_{27}H_{40}N_7O_{15}P$: C, 44.2; H, 5.6%). The same picrate was obtained when the above chloride was oxidised by sodium permanganate in neutral solution. On the other hand, the propenylene derivative was recovered unchanged when treated with benzaldehyde and piperidine or with bromine in chloroform solution.

Experiments with Derivatives of Butenephosphonium Salts.—(a) *Ozonolysis of 3-chlorobut-2-enyl-1-tri-n-propylphosphonium chloride.* The phosphonium chloride¹ was ozonised for 37 hr. in alcohol-free chloroform, the solvent being replenished as necessary. After removal of the solvent the ozonide was decomposed by boiling water, and the product was converted into the picrate, m. p. 77—78°, which appeared to be identical (mixed m. p.) with that obtained by the ozonolysis of allyltri-n-propylphosphonium chloride,¹ namely, 2,2-dichloroethyltri-n-propylphosphonium picrate (Found: C, 42.3; H, 5.1. Calc. for $C_{17}H_{26}Cl_2N_3O_7P$: C, 42.0; H, 5.4%). A mixture of the picrate with that of the starting material (m. p. 75—76°) had m. p. 65—68°.

(b) *Ozonolysis of 1-chloro-1-methylallyltri-n-propylphosphonium chloride.* The reaction was carried out as above, but there was no recognisable product.

(c) *Preparation of 2-hydroxy-1-methyltrimethylenebis-tri-n-propylphosphonium salts.* Ethanolic tri-n-propylphosphine condensed with 1,3-dibromobutan-2-ol to give a product in 84% yield. This afforded the named *picrate* which separated from acetone-ethanol in rods, m. p. 146—147° (Found: C, 47.6; H, 6.4; N, 9.7. $C_{34}H_{54}N_6O_{15}P_2$ requires C, 48.1; H, 6.4; N, 9.7%).

This picrate was converted into the bromide (28 g.) which was treated in chloroform at 0° with phosphorus pentachloride (15.7 g.) in small portions. There was no visible reaction until the temperature was raised. After 45 min., the mixture was cooled and decomposed by ice-water, and the aqueous and the chloroform layer were separated. The aqueous layer was neutralised to Congo Red and evaporated, the residue being taken up in the usual way. The product was an oil from which a *picrate* crystallising from acetone-ethanol in rods, m. p. 190—191°, was obtained. The substance was not identified. The analysis corresponded to the replacement of hydroxyl by chlorine but only traces of the latter element were detected (Found: C, 47.4, 46.6; H, 6.2, 6.1; Cl, <1; N, 9.5, 9.8. $C_{34}H_{53}ClN_6O_{14}P_2$: requires C, 47.0; H, 6.1; Cl, 4.1; N, 9.7%).

(c) *Reactions of 3- and 1-methylpropen-1,3-ylenebis-tri-n-propylphosphonium chlorides.*

(i) *Hydrogenation.* Neither of these salts could be reduced in ethanol at 5 atm. Catalysts tried were platinic oxide, 5% rhodium on alumina, and Raney nickel. In each case the catalyst remained effective for other reductions.

(ii) *Reaction with sodium hydroxide.* The 3-methyl salt, $PPr_3 \cdot CHMe \cdot CH:CH \cdot PPr_3^{2+} Cl_2^{2-}$, prepared from the picrate, m. p. 104° (1 g.), was dissolved in water, 2N-sodium hydroxide (5 c.c.) was added, and the solution was kept for 22 hr. after which an odour of phosphine was perceptible. The acidified (Congo Red) liquid was then evaporated to dryness, the residue affording a *methylpropen-1,3-yltri-n-propylphosphonium picrate* which separated from ethanol in plates, m. p. 73.5° (Found: C, 51.5; H, 6.8; N, 9.2. $C_{19}H_{30}N_3O_7P$ requires C, 51.4; H, 6.5; N, 9.5%). Under the same conditions the 1-methyl isomer was stable to sodium hydroxide and there was a 94% recovery of the starting material.

(d) *Preparation of but-2-enyltri-n-propylphosphonium salts and their reduction products.*

(i) Tri-n-propylphosphine (20 g.), 3-chlorobut-1-ene,¹⁷ and ethanol (50 c.c.) were boiled together under reflux for 2.5 hr., nitrogen being passed through the liquid. The whole was mixed with ether and repeatedly extracted with water. The aqueous solution was evaporated on the steam-bath, and the residue dried over phosphorus pentoxide. The white deliquescent solid (25 g., 74.3%) afforded a picrate which was crystalline only below room temperature. Addition

¹⁷ Curtin and Gerber, *J. Amer. Chem. Soc.*, 1952, **74**, 4052.

of chloroplatinic acid yielded *but-2-enyltri-n-propylphosphonium chloroplatinate* which separated from ethanol in orange needles, m. p. 192° (Found: C, 37.3; H, 6.8. $C_{26}H_{36}Cl_6P_2Pt$ requires C, 37.2; H, 6.7%). The identical product was obtained when the condensation was repeated in dry acetone solution.

(ii) Reduction of the above phosphonium salt. The phosphonium chloride (1.07 g.) was shaken in ethanol (50 c.c.) for 14 hr. with Raney nickel in hydrogen at 5 atm., yielding a semi-solid which was converted into the picrate. *n-Butyltri-n-propylphosphonium picrate* separated from ethanol in pale yellow needles, m. p. 72—73° (Found: C, 52.0; H, 7.6; N, 9.3. $C_{19}H_{32}N_3O_7P$ requires C, 51.2; H, 7.2; N, 9.4%). The *chloroplatinate* separated from alcohol in needles, m. p. 216.5—217° (Found: C, 37.7; H, 7.6. $C_{26}H_{60}Cl_6P_2Pt$ requires C, 37.1; H, 7.1%).

(iii) Condensation of tri-n-propylphosphine with n-butyl bromide. Ethanolic tri-n-propylphosphine (4 g.) and n-butyl bromide (6.8 g.) yielded 6.1 g. (82%) of n-butyltri-n-propylphosphonium bromide. The picrate, separating from ethanol at -40°, had m. p. 73.5° and was identical (mixed m. p.) with that obtained by the above hydrogenation (Found: C, 51.4; H, 7.0%). The chloroplatinate, m. p. 216.5°, was also similar to the one described above.

(iv) Condensation of tri-n-propylphosphine with s-butyl bromide. This reaction was carried out as that with n-butyl bromide. s-Butyltri-n-propylphosphonium bromide (3 g., 40.5%) was obtained as deliquescent needles. A crystalline picrate could not be isolated, but the chloroplatinate was formed and separated from ethanol in deep-orange needles, m. p. 216—220° (extensive decomp.).

(v) Condensation of tri-n-propylphosphine with 1-chlorobut-2-ene. There was no reaction at room temperature when the phosphine (8 g.) was mixed with 1-chlorobut-2-ene (4.5 g.) in ethanol (25 c.c.). Raising the temperature of the liquid initiated a very vigorous reaction which was completed by boiling the mixture under reflux for a further 2 hr. The product (10.1 g., 81%) afforded the chloroplatinate, m. p. 192—192.5° (Found: C, 37.3; H, 6.8%). Hydrogenation at 5 atm. (Raney nickel) yielded the n-butyltri-n-propylphosphonium salt which was identified by comparing its picrate with the specimens previously obtained.

The condensation gave the same result in acetone. *But-2-enyltri-n-propylphosphonium bromide* was recovered unchanged when it was kept in an excess of 0.5N-potassium hydroxide for 1 hr., and the solution was then acidified. Though reaction occurred, no recognisable product was obtained when a solution of bromine in chloroform was mixed with the phosphonium chloride and, after 1 hr., the solvent removed in a vacuum. The residue was boiled with aqueous silver chloride and a *picrate* prepared in the usual way. It crystallised at a low temperature from ethanol as a powder, m. p. 60—61°, containing halogen (Found: C, 46.8; H, 6.2; N, 8.3, 8.4%).

But-2-enyltri-propylphosphonium chloride reacted neither with potassium hydroxide nor with sodium ethoxide but with 2 mol. of methanolic sodium methoxide addition occurred and what was presumably *2-methoxybutyltri-n-propylphosphonium chloroplatinate* was prepared from the product. This crystallised from ethanol in deep orange-brown needles, m. p. 194—196° (Found: C, 37.4; H, 7.1. $C_{28}H_{64}Cl_6O_2P_2Pt$ requires C, 37.3; H, 7.1%). The picrate was prepared but could not be obtained crystalline.

Proton Resonance Spectra.—These were measured on a Varian A-60 nuclear magnetic resonance spectrometer for deuteriochloroform solutions. Assignments of chemical shifts, in τ values, based on observations made on model compounds are only approximate and in the case of complex bands refer to their "centres of gravity." In many cases, low solubilities limited the deductions that could be made from the spectra, which were usually measured on the picrates. The following features were noted:

(i) All the compounds studied were mono- or bis-tri-n-propylphosphonium derivatives with 21 or 42 protons, respectively having correspondingly intense absorptions. There were three main bands corresponding to the protons on the γ -, β -, and α -carbon atoms, and located at 8.8, 8.3, and 7.31 p.p.m., respectively. The methyl group gave the expected triplet and the β -methylene a more or less symmetrical quartet further split by the α -methylene protons. The latter was a symmetrical band showing splittings due to spin-spin interactions with phosphorus as well as with the protons of the β -methylene group. The latter separations were approximately 7 c./sec.

(ii) *P-Methyl* gave an easily distinguishable doublet with separations of 14 c./sec. In the case of methyltri-n-propylphosphonium picrate it was located at 8.02 p.p.m. and at 7.80 p.p.m.

for the iodide. The absorption of the α -methylene of the propyl group was about 0.5 p.p.m. higher than usual.

(iii) The absorptions of propene methylenic protons adjacent to phosphorus were obtained from allyl- and but-2-enyl-tri-n-propylphosphonium picrate. These were centred at 6.70 and 6.62 p.p.m., respectively, and consisted of doublets separated by 15 c./sec. and were due no doubt to splitting by phosphorus. Each of the peaks was further split (separation 6 c./sec.), presumably by the single adjacent olefinic proton. There were also unresolved absorptions near 3 p.p.m. which could be attributed to the olefinic protons themselves.

(iv) Propen-1,3-ylenebistri-n-propylphosphonium picrate also gave the methylenic quartet at a somewhat lower field (5.90 p.p.m.), as well as less intense absorptions between 2.2 and 2.7 p.p.m. For the methylpropenylenebisphosphonium salts only the absorptions due to the six propyl groups could be identified. The lack of low-field absorption was probably due to the very low solubility of these derivatives.

(v) There was no absorption between 5 and 6 p.p.m. by the butenylphosphonium salt, although in this case olefinic absorptions between 3.0 and 3.7 p.p.m. were observed. The chemical shift for the methyl of the butenyl chain could not be measured directly, though as judged from the integrated areas it was in the neighbourhood of 7.5 p.p.m. The terminal methyl of but-2-enyltripropylphosphonium picrate similarly was judged to give absorptions at about 8.25 p.p.m.

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