# Quasiphosphonium Intermediates. Part 7.[1] The Preparation of Trinorborn-1-yl Phosphite and its Reactions with Halogeno Compounds: Stable Intermediates of the Arbuzov and Perkow Reactions and their Structural Characterization by X-Ray Diffraction, NMR Spectroscopy, and Fast Atom Bombardment Mass Spectrometry

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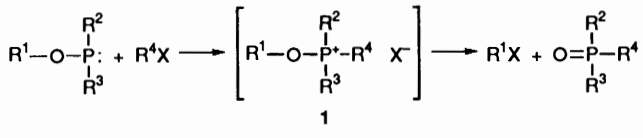
Trinorborn-1-yl phosphite has been prepared and has been shown to give highly stable phosphonium salts in its reactions with iodomethane and with a number of α-halogenoketones. Phenacyl bromide and *p*-bromophenacyl bromide underwent reaction at room temperature to give the corresponding ketophosphonium halides (Arbuzov intermediates) as the exclusive products, whilst *p*-nitrophenacyl chloride gave the corresponding vinyloxyphosphonium chloride (Perkow intermediate) as the first example of a stable intermediate of this type. The structures of these two types of intermediate in the solid state were confirmed by X-ray diffraction measurements which revealed distorted tetrahedral arrangements around phosphorus, with $P^+ \cdots Br^-$ and $P^+ \cdots Cl^-$ interionic distances of 4.58 and 4.71 Å for the phenacyl bromide and *p*-nitrophenacyl chloride adducts respectively. Phenacyl chloride, chloroacetone, and *p*-nitrophenacyl bromide gave mixed products, amongst which trinorborn-1-yl phosphate was always present. Possible reaction mechanisms are discussed. Thermal decomposition of the Arbuzov intermediates (149 °C) gave the expected phosphonates but the Perkow intermediate underwent elimination of alkyne under these conditions to give trinorborn-1-yl phosphate. $^{31}P$ NMR and fast atom bombardment mass spectra of the quasiphosphonium salts are reported and discussed.

One of the best known reactions of classical organophosphorus chemistry is the Arbuzov (or Michaelis–Arbuzov) reaction, in which a phosphorus(III) ester interacts with a halogenoalkane to give the corresponding phosphonate, phosphinate, or phosphine oxide (Scheme 1).[2,3] The reaction involves nucleophilic



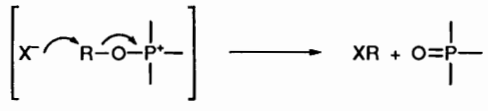
**1**

**Scheme 1**

displacement of halogen by phosphorus to give an alkoxyphosphonium intermediate **1**, followed by dealkylation and formation of the P=O bond.[4] Although the intermediate generally undergoes rapid dealkylation and is not therefore detectable, examples of stabilized intermediates have been isolated as crystalline solids in the reactions of halogenomethanes with sterically hindered neopentyl esters, *viz.* trineopentyl phosphite ($R^1 = Bu^tCH_2$, $R^2 = R^3 = Bu^tCH_2O$),[5] dineopentyl phenylphosphonite ($R^1 = Bu^tCH_2$, $R^2 = Bu^tCH_2O$, $R^3 = Ph$), or neopentyl diphenylphosphinite ($R^1 = Bu^tCH_2$, $R^2 = R^3 = Ph$).[6] Intermediates have also been obtained at 0 °C in reactions with certain alkyl dialkylphosphinites ($R^2 = R^3$ = alkyl),[7–10] dialkyl allylphosphonites ($R^2 = R^1O$, $R^3$ = allyl or 3-methylallyl,[11–14] and dialkyl alkylphosphonites ($R^2 = R^1O$, $R^3$ = alkyl)[15,16] but only the neopentyloxy derivatives are stable at room temperature.[11,12,16]

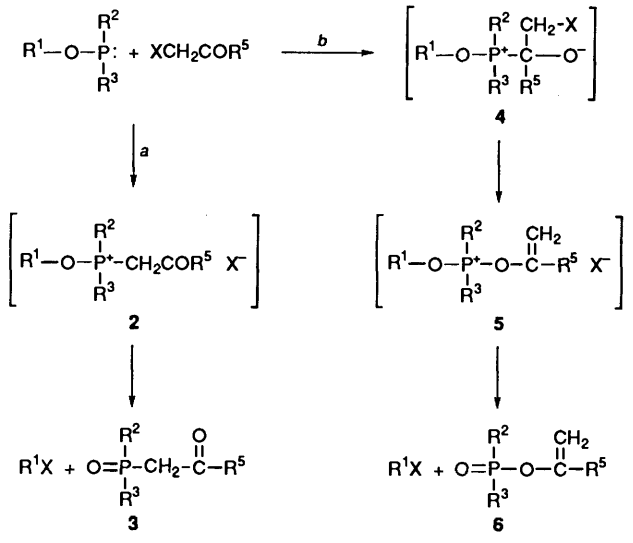
The structures of Arbuzov intermediates were for many years uncertain but it is now clear from $^{31}P$ NMR studies that in most cases they exist as phosphonium salts rather than pentacoordinate phosphoranes.[17] The presence of a small equilibrium level of the pentacoordinate structure in solution cannot, however, be totally excluded.[18] Pentacoordinate intermediates have been clearly identified in the reactions of alkyl *ortho*-phenylene phosphites with halogens at low temperatures.[19,20]

The intermediates obtained in the reactions of bromomethane with neopentyl diphenylphosphinite **1** ($R^1 = Bu^tCH_2$, $R^2 = R^3 = Ph$, $R^4 = Me$, X = Br) and dineopentyl phenylphosphonite **1** ($R^1 = Bu^tCH_2$, $R^2 = Bu^tCH_2O$, $R^3 = Ph$, $R^4 = Me$, X = Br), were suitable for characterization by X-ray diffraction and the tetracoordinate phosphonium structure in the solid state was demonstrated for these types of intermediate for the first time.[6] Structure determination was not however possible for the trineopentyl phosphite–methyl halide adducts **1** ($R^1 = Bu^tCH_2$, $R^2 = R^3 = Bu^tCH_2O$, $R^4 = Me$, X = Br or I),[5] as only twinned crystals were obtainable. In solution ($CDCl_3$), intermediates of these types decompose by a first order process, in which collapse of the alkoxyphosphonium–halide ion-pair occurs with $S_N2$-type cleavage of the alkyl–oxygen bond to give neopentyl halide and the corresponding Arbuzov product (Scheme 2).[21]



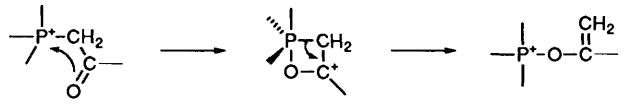
**Scheme 2**

The reactions of phosphorus(III) esters with α-halogenoketones are of particular interest in that more than one reaction pathway is possible.[22] In addition to the Arbuzov reaction (Scheme 3, route *a*), which yields a β-keto-phosphonate, -phosphinate, or -phosphine oxide **3**, an alternative process (the Perkow reaction) (Scheme 3, route *b*) can give rise to the formation of the isomeric vinyl ester **6**. The proportion of each product that is formed depends on the nature of the halogen, the medium, and reaction temperature.[23,24] α-Chloroketones tend to enter preferentially into the Perkow reaction, which is generally thought to proceed by initial attack of phosphorus at

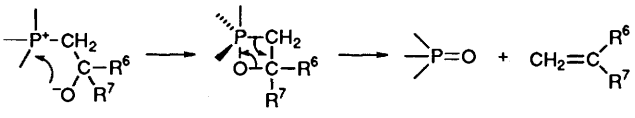


Scheme 3

the carbonyl carbon atom to give a betaine **4**, followed by rapid migration of phosphorus from carbon to oxygen to give a vinyloxyphosphonium species **5**, and finally dealkylation (Scheme 3).[4,22] It has also been suggested[25] that the vinyloxyphosphonium halide **5** could be formed by rearrangement of the first formed Arbuzov intermediate **2** *via* a four-membered cyclic intermediate or transition state (Scheme 4), similar to that which occurs in the Wittig reaction (Scheme 5).[26]



Scheme 4

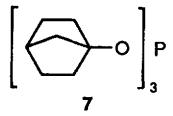


Scheme 5

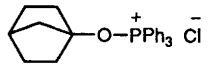
In our earlier investigations of the reactions of phosphorus(III) esters with α-halogenoketones,[27] we found that ketophosphonium (Arbuzov) intermediates **2** could be isolated in the reactions of trineopentyl phosphite, dineopentyl phenylphosphonite, or neopentyl diphenylphosphinite with α-bromoacetophenone and similar α-bromoketones,[27] but that they did not rearrange as proposed.[25] In all cases they decomposed to give the Arbuzov products **3** exclusively. The thermal stabilities of these intermediates increase as the number of alkoxy groups attached to phosphorus decreases; that obtained from neopentyl diphenylphosphinite and α-bromoacetophenone **2** ($R^1$ = $Bu^tCH_2$, $R^2$ = $R^3$ = $R^4$ = Ph, X = Br) was the first example of a ketophosphonium intermediate sufficiently stable for structural investigation by X-ray diffraction.[1] Although the trineopentyl phosphite derivative **2** ($R^1$ = $Bu^tCH_2$, $R^2$ = $R^3$ = $Bu^tCH_2O$, $R^4$ = Ph, X = Br) was also obtainable as crystals which could be stored under anhydrous ether for several days,[27] it was noticeably less stable than the bromomethane adduct, due perhaps to the electron-attracting effect of the β-carbonyl group.

Perkow intermediates **5** are very much less stable than the corresponding Arbuzov intermediates **2**, a fact that may be attributed to the inductive influence of the additional electron-attracting oxygen atom that is attached directly to phosphorus. In the reactions of trineopentyl phosphite with α-chloroacetophenone[27] or chloroacetone[28] at room temperature, only the final products **6** ($R^2$ = $R^3$ = $Bu^tCH_2O$, $R^4$ = Ph or Me) were detectable. A short-lived Perkow intermediate **5** ($R^1$ = $Bu^tCH_2$, $R^2$ = $R^3$ = Ph, X = Cl) was nevertheless obtained in the reaction of neopentyl diphenylphosphinite with α-chloroacetophenone at −5 to 0 °C and was shown to decompose in chloroform at 33 °C with a half-life of about 40 min.[27] It is generally found that the replacement of alkoxy groups by phenyl increases the nucleophilic reactivity of the phosphorus(III) ester and hence the rate of the initial reaction and also has a stabilising effect on the quasiphosphonium intermediates that are involved.[21,27] No intermediate could be detected, however, in the reaction of dineopentyl phenylphosphonite, $PhP(OCH_2Bu^t)_2$, with α-chloroacetophenone.[27]

In order to obtain intermediates of higher stability for further structural investigation, we have now prepared trinorborn-1-yl phosphite **7**, a new compound, and studied its reactions with



**7**



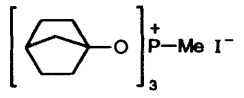
**8**

halogeno-compounds.[29] In these reactions, the cage structure of the norbornyl group precludes $S_N2$ dealkylation of the quasiphosphonium intermediate and leads to high thermal stability, as shown previously for triphenyl(norborn-1-yloxy)-phosphonium chloride **8**.[30] We have thus been able to obtain the first example of a stable Perkow intermediate and to carry out the first X-ray structural characterisations of Arbuzov and Perkow intermediates that occur in the reactions of α-halogenoketones with trialkyl phosphites.

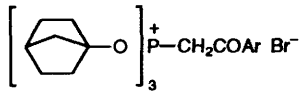
## Results and Discussion

Norborn-1-yl alcohol was prepared by a described sequence of reactions starting from norborn-2-ene-5-*endo*-carboxylic acid and involving finally the oxidation of norbornane-1-carboxylic acid by hydrogen peroxide and concentrated sulfuric acid.[31-34] The oxidation step[34] was only successful, however, when a modified procedure was used, involving a smaller excess of hydrogen peroxide (as reported elsewhere for peracid formation)[35] and a substantially longer period of reaction below 0 °C before decomposition of the so-formed norbornane-1-carboxylic peracid in iced-water. Trinorborn-1-yl phosphite was prepared by a standard procedure for phosphite esters[36] from the alcohol, phosphorus trichloride, and *N*,*N*-dimethylaniline in light petroleum and was obtained as a white crystalline solid. Oxidation by *tert*-butyl hydroperoxide gave the corresponding phosphate.

*Reaction of Trinorborn-1-yl Phosphite with Iodomethane.*—As observed previously with trineopentyl phosphite,[5] trinorborn-1-yl phosphite reacted with iodomethane at room temperature to give a stable phosphonium iodide **9**. Reaction was essentially



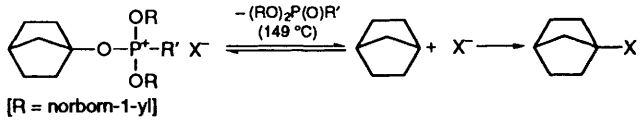
**9** $\delta_P$ 36.9



**10** (Ar = Ph) $\delta_P$ 26.7
**11** (Ar = *p*-$BrC_6H_4$) $\delta_P$ 26.3

complete after 24 h in deuterochloroform and the crystalline compound was separated by treatment with anhydrous ether. The compound was also obtained over a longer period of time by allowing it to crystallise from a solution of the reactants in ether. However, whilst the neopentyl analogue decomposed at 33 °C in $CDCl_3$, with a half-life of 105 min,[5] trinorborn-1-

yloxy(methyl)phosphonium iodide did not decompose at a measurable rate until heated to about 150 °C. Under these conditions, in deuterochloroform (sealed tube), the rate of conversion to products was still extremely slow with a half-life in excess of 100 h; 41% of the phosphonium iodide was recovered by addition of anhydrous ether to the mixture after 144 h of heating. It is assumed that the mechanism of the carbon–oxygen fission is $S_N1$ (Scheme 6; R′ = Me, X = I). As

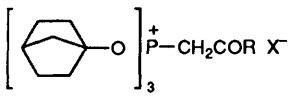



**Scheme 6**

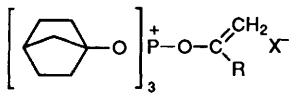
mentioned above, the $S_N2$ mode of reaction is impossible and the inability of the bridgehead carbon atom to assume a planar configuration makes carbonium ion formation energetically unfavourable. At the same time, there was no evidence for the formation of products that might have been associated with homolytic fission of the carbon–oxygen bond.

*Reaction of Trinorborn-1-yl Phosphite with α-Bromoketones.*—With α-bromoketones (phenacyl bromide and *p*-bromophenacyl bromide), the Arbuzov intermediates **10** and **11** were also obtained. Decomposition to the corresponding ketophosphonates (presumably *via* an $S_N1$ route, Scheme 6; R′ = $PhCOCH_2$ or *p*-$BrC_6H_4COCH_2$, X = Br) occurred more readily than for the methyl iodide adduct ($t_{\frac{1}{2}}$ for the phenacylphosphonium bromide, *ca.* 4–5 h at 149 °C), a result that may be attributed to the electron-attracting effect of the phenacyl substituent at phosphorus. There was no evidence of rearrangement to the isomeric vinyloxyphosphonium intermediate. This result confirms our earlier view[27] that Perkow intermediates are formed by a parallel reaction between the phosphorus(III) ester and the halogenoketone and not by rearrangement of the Arbuzov intermediate through a four-membered cyclic intermediate or transition state (Scheme 4) as has been suggested.[25] The estimated minimum interatomic distance between the carbonyl oxygen atom and phosphorus in the Arbuzov intermediates derived from phenacyl bromide and neopentyl diphenylphosphinite **2** ($R^1$ = Bu$^t$$CH_2$, $R^2$ = $R^3$ = $R^4$ = Ph, X = Br)[1] or phenacyl bromide and trinorborn-1-yl phosphite **10** (calculated from the relevant bond lengths and bond angles) is in the region of 2.9 Å and indicates that considerable strain would be involved in the formation of a phosphorus–oxygen bond. The fact that the Wittig reaction proceeds so readily *via* a formally similar cyclic process (Scheme 5) suggests that the formal negative charge on the carbonyl oxygen atom of the intermediate betaine provides an additional driving force in this reaction.

*Reactions of Trinorborn-1-yl Phosphite with α-Chloroketones.*—Trinorborn-1-yl phosphite was significantly less reactive than acyclic phosphites towards α-chloroketones. No detectable reaction occurred at room temperature with either α-chloroacetophenone or α-chloroacetone, although trineopentyl phosphite undergoes relatively quick reaction with these ketones to give almost complete conversion to the corresponding vinyl phosphates (Perkow products) within a few hours under similar conditions.[27,28] Whether the effect is steric or electronic is not certain, although it is possible that the bridgehead position of C-1 in the norborn-1-yl group may inhibit the relay of inductive electron release from this tertiary centre[37] and thereby reduce the nucleophilicity of phosphorus. Reaction of trinorborn-1-yl phosphite with these α-chloroketones occurred only on heating to 70 °C and in neither case was the Perkow route favoured. α-Chloroacetophenone gave only the unexpected[22] ketophosphonium (Arbuzov) intermediate **12**, together with some trinorbornyl phosphate, a little



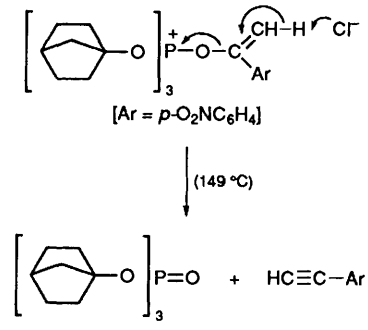

**12** (R = Ph; X = Cl) $\delta_P$ 26.7
**13** (R = Me; X = Cl) $\delta_P$ 26.4
**17** (R = *p*-$O_2NC_6H_4$; X = Br) $\delta_P$ 25.2




**14** (R = Me; X = Cl) $\delta_P$ –16.9
**15** (R = *p*-$O_2NC_6H_4$; X = Cl) $\delta_P$ –17.1
**16** (R = *p*-$O_2NC_6H_4$; X = Br) $\delta_P$ –16.9

dinorbornyl phosphite, and two unidentified products. α-Chloroacetone gave both ketophosphonium **13** and vinyloxyphosphonium **14** intermediates, although in minor quantities, again accompanied by trinorbornyl phosphate, dinorbornyl phosphite, and several unidentified products. However, α-chloro-*p*-nitroacetophenone, in which the carbonyl group is more electrophilic, reacted readily with trinorborn-1-yl phosphite at room temperature to give a virtually quantitative yield of the vinyloxyphosphonium (Perkow) intermediate **15** within 24 h. No other phosphorus-containing products were detectable. The vinyloxyphosphonium chloride was separated as a light yellow crystalline solid after evaporation of the solvent and the addition of anhydrous ether. The corresponding bromide **16** was formed by interaction of trinorborn-1-yl phosphite with α-bromo-*p*-nitroacetophenone but was accompanied by the Arbuzov intermediate **17** and other by-products.

Thermal decomposition of the vinyloxyphosphonium chloride **15** did not give the normal Perkow product because of the resistance of the norborn-1-yl group to nucleophilic attack. Preferential cleavage of the vinyl–oxygen bond occurred at 149 °C with the formation of *p*-nitrophenylacetylene and trinorborn-1-yl phosphate (Scheme 7), decomposition being




**Scheme 7**

complete within 1.4 h. Alkyne elimination has similarly been observed in the thermal decomposition of certain triphenylvinyloxyphosphonium salts.[38] It is possible that the formation of trinorborn-1-yl phosphate in reactions of the phosphite with α-chloroacetone or phenacyl chloride at 70 °C, as mentioned above, may be accounted for by elimination from a vinyloxyphosphonium intermediate, although the latter was not detectable in either case.

*Thermal and Hydrolytic Stability of Arbuzov and Perkow Intermediates.*—The relative stabilities of quasiphosphonium intermediates towards thermal decomposition (involving R–O fission) and towards nucleophilic attack at phosphorus (involving P–O fission) have generally been found to decrease as the number of oxygen ligands attached to phosphorus increases, showing that reactivity is determined more by the inductive influence of oxygen than by its mesomeric interaction with phosphorus.[17] In the present studies, however, the Arbuzov

**Table 1** Bond angles (°) at phosphorus and at oxygen in trinorborn-1-yloxy(phenacyl)phosphonium bromide **10** and trinorborn-1-yloxy[(1-*p*-nitrophenyl)vinyloxy]phosphonium chloride **15**

| **10** | | **15** | |
|---|---|---|---|
| O(2)–P–O(1) | 113.3(8) | O(2)–P–O(1) | 107.2(7) |
| O(3)–P–O(2) | 107.9(7) | O(3)–P–O(2) | 109.7(6) |
| C(1)–P–O(2) | 106.4(9) | O(4)–P–O(2) | 113.0(6) |
| O(3)–P–O(1) | 103.0(7) | O(3)–P–O(1) | 114.5(6) |
| C(1)–P–O(1) | 111.8(8) | O(4)–P–O(1) | 106.4(6) |
| C(1)–P–O(3) | 114.6(8) | O(4)–P–O(3) | 106.2(6) |
| P–O(1)–C(11) | 134(1) | P–O(1)–C(11) | 129.4(10) |
| P–O(2)–C(21) | 127(1) | P–O(2)–C(21) | 128.2(10) |
| P–O(3)–C(31) | 133(1) | P–O(3)–C(31) | 133.0(9) |
| | | P–O(4)–C (41) | 128.3(10) |

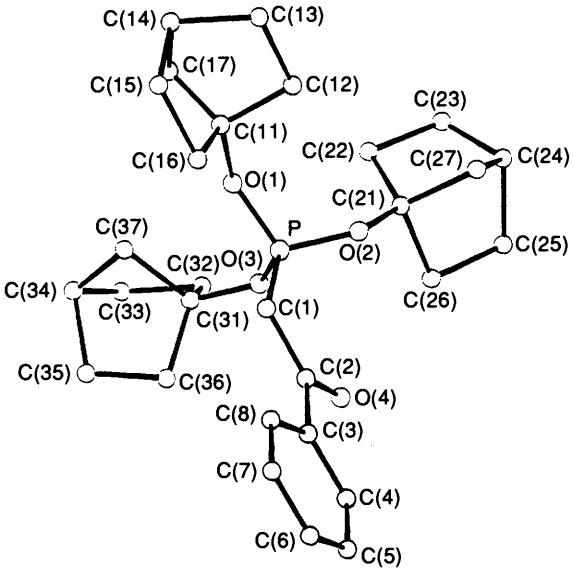



**Fig. 1** Structure of the phosphonium ion in trinorborn-1-yloxy(phenacyl)phosphonium bromide **10**

intermediates **9**–**11** and the Perkow intermediate **15** were found to be extremely resistant to hydrolysis and could be stored indefinitely without the need for a dry atmosphere. (The Perkow intermediate was also shown to undergo no change in methanolic solution over a period of two months.) It is possible that nucleophilic attack at phosphorus is hindered in these structures by the presence of the three bulky norborn-1-yloxy substituents. X-ray structural studies could therefore be carried out in the open laboratory atmosphere without the need for exclusion of moisture.

*Structural Characterization of Arbuzov and Perkow Intermediates by X-Ray Diffraction.*—Choice of suitable crystals of the Arbuzov **10** and Perkow **15** intermediates for X-ray structure determination was limited by the small amounts of final products available. For the bromide **10**, the crystals obtained from the reaction mixture over a period of 11 weeks were apparently well formed but did not diffract well. For the chloride **15**, a few plate-like crystals were obtained from reaction in the NMR tube. Despite relatively poor diffraction by both crystals, X-ray structure analysis clearly established that the two intermediates **10** and **15** were phosphonium salts with $P^+ \cdots Br^-$ and $P^+ \cdots Cl^-$ interatomic distances of 4.58 and 4.71 Å respectively (Figs. 1 and 2). Bond angles at phosphorus (Table 1) reveal a distorted tetrahedral structure in each case, with variations of between 103.0 and 114.6(8)° for **10** and between 106.2 and 114.5(6)° for **15**. The phosphorus–oxygen bond lengths for both cations [Table 2, range from 1.490 to 1.563 Å, mean 1.517(12) Å] are very much shorter than the

**Table 2** Bond lengths (Å) to phosphorus in trinorborn-1-yloxy(phenacyl)phosphonium bromide **10** and trinorborn-1-yloxy-[1-*p*-nitrophenyl)vinyloxy]phosphonium chloride **15**

| **10** | | **15** | |
|---|---|---|---|
| P–O(1) | 1.510(13) | P–O(1) | 1.505(12) |
| P–O(3) | 1.563(13) | P–O(3) | 1.495(11) |
| P–O(2) | 1.508(14) | P–O(2) | 1.490(11) |
| P–C(1) | 1.737(20) | P–O(4) | 1.548(11) |

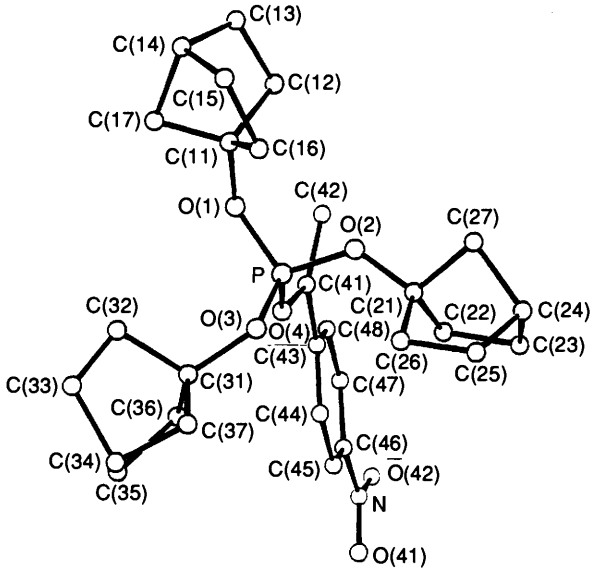


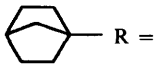

**Fig. 2** Structure of the phosphonium ion in trinorborn-1-yloxy[1-(*p*-nitrophenyl)vinyloxy]phosphonium chloride **15**

calculated length of a phosphorus–oxygen single bond (1.76 Å, based on the sum of the covalent radii of phosphorus and oxygen).[39] These lengths, together with the mean P–O–C angles of 131(1) for **10** and 130(1)° for **15**, are consistent with a significant degree of double bond character, with $p_\pi$–$d_\pi$ back-donation from oxygen to phosphorus. Similar observations were made in the structure analysis of methyltri(*p*-nitrophenoxy)phosphonium chloride where the mean P–O length was 1.552(2) Å and the mean P–O–C angle was 128.6(2)°.[40]

$^{31}P$ *NMR Spectroscopy.*—An interesting feature of the $^{31}P$ NMR chemical shifts of the norborn-1-yl derivatives is that values for the four-coordinate compounds (trinorborn-1-yl phosphate, dinorborn-1-yl phosphonate, and the trinorborn-1-yloxyphosphonium salts) are all at higher field by 5–15 ppm than those for their neopentyl analogues (Table 3).[5,27,41,42] The chemical shift of trinorborn-1-yl phosphite ($\delta$ 139.7) is not, however, significantly different from that of other trialkyl phosphites.[43] (The *tert*-alkyl esters, tri-*tert*-butyl phosphate and di-*tert*-butyl phosphonate also have relatively high field chemical shifts, at $\delta_P$ −13.3 and −3.9 respectively,[44] although tri-*tert*-butyl phosphite has a normal value of $\delta_P$ 138.2).[45] It is likely that the steric bulk of the α-branched (tertiary) norborn-1-yl and *tert*-butyl groups causes distortion from tetrahedral geometry in the tetracoordinate phosphorus derivatives (as noted above in the structures of the Arbuzov and Perkow intermediates) and that this factor influences the $^{31}P$ chemical shifts of these compounds.

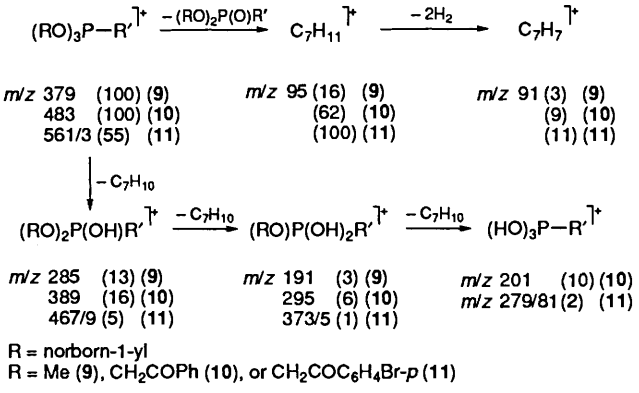
*Fast Atom Bombardment Mass Spectrometry.*—In the fast atom bombardment mass spectra of the quasiphosphonium salts,[46] the relative stabilities of the two types of intermediate are reflected in the relative abundances of the parent phosphonium ions (55–100% for the Arbuzov types but only *ca.* 10%

**Table 3** $^{31}P$ NMR chemical shifts for some four-coordinate norborn-1-yloxy phosphorus compounds and their neopentyloxy analogues

| Compound | R =  | R = Bu$^t$CH$_2$ | Ref. |
|---|---|---|---|
| $(RO)_3PO$ | −10.2 | −0.6 | 41[a] |
| $(RO)_2PHO$ | −0.4 ($J_{PH}$ 685) | 7.7 ($J_{PH}$ 695) | 42[a] |
| $(RO)_2P(O)CH_2COPh$ | 13.4 | 19.0 | 27 |
| $(RO)_3\overset{+}{P}(O)CH_2COPh\ Br^-$ | 26.7 | 41.0 | 27 |
| $(RO)_3\overset{+}{P}(O)CH_3\ I^-$ | 36.9 | 54 | 5 |

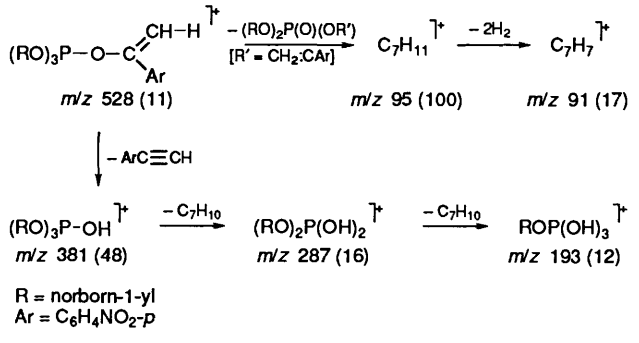
[a] Other acyclic analogues have similar $^{31}P$ chemical shifts, except the *tert*-alkyl types (*cf.* ref. 43, pp. 241, 289–90).

for the Perkow intermediate). Fragmentation of the methyl iodide adduct **9** and of the ketophosphonium salts **10**, **11** occurs by cleavage of the norbornyl–oxygen bond in one of two ways (Scheme 8), to give either the norbornyl cation (*m/z* 95) with loss




**Scheme 8**

of the corresponding phosphonate as a neutral species, or to give the protonated phosphonate, with hydrogen transfer and elimination of a neutral fragment, $C_7H_{10}$. The latter is presumed to be norbornene, formed as the result of an intramolecular hydride shift to position 1. In the case of the Perkow intermediate, alkyne elimination was observed (as in thermal decomposition) with formation of the protonated phosphate by hydrogen transfer (Scheme 9). In all cases, the protonated




**Scheme 9**

phosphonate or protonated phosphate underwent further stepwise loss of what were presumed to be neutral norbornene fragments. In addition, all compounds exhibited weak ions at *m/z* 253 and 91. The former is assigned the structure $(RO)_2P^+$, an ion which is commonly detected in the mass spectra of organophosphorus esters.[47] The peak at *m/z* 91 is indicative of the relatively stable tropylium ion, which may be formed from the norborn-1-yl cation by elimination of two molecules of hydrogen and ring expansion.

## Experimental

$^{31}P$ and $^{13}C$ NMR spectra were recorded on a Bruker WP-80 instrument operating at 32.4 and 20.12 MHz respectively. $^1H$ NMR spectra were recorded on a Perkin-Elmer R12B instrument at 60 MHz. Chemical shifts (ppm, downfield positive) are relative to 85% $H_3PO_4$ ($^{31}P$) or to $SiMe_4$ ($^1H$ and $^{13}C$), *J*-values in Hz. EI mass spectra were obtained by direct insertion on a Kratos Profile mass spectrometer and FAB spectra (using a glycerol matrix) on a VG analytical ZAB-1F instrument with a primary beam of xenon atoms at 7 kV.

*Starting Materials.*—Iodoacetone,[48] α-bromo-*p*-nitroacetophenone[49] and α-chloro-*p*-nitroacetophenone,[50] were prepared as described. Other α-halogenoketones and starting materials were obtained commercially.

*Norborn-1-yl Alcohol.*—Diels–Alder addition of acrylic acid to cyclopentadiene as described[31] gave norborn-2-ene-5-*endo*-carboxylic acid, which was converted by a stepwise series of reactions to norbornane-2-*endo*-carboxylic acid,[31] 2-*exo*-bromonorbornane-1-carboxylic acid,[32] 2-*exo*-bromonorbornane-1-carbonyl chloride,[33] 2-*exo*-bromonorbornane-1-carboxamide,[33] norbornane-1-carboxamide,[33] and norbornane-1-carboxylic acid.[33] Oxidative cleavage[34] of the latter (5 g, 0.04 mol) by hydrogen peroxide and conc. sulfuric acid[35] gave norborn-1-yl alcohol which was recrystallized from hexane as colourless plates (2.2 g, 55%), m.p. 150 °C (lit.,[30] 152–154 °C); $\delta_H(CCl_4)$ 3.1 (s, 1 H, OH) and 1.38–2.0 (br m, ring H); $\delta_C(CDCl_3)$ 83.0 (C-1), 43.9 (C-7), 35.4 (C-2, 6), 34.8 (C-4) and 30.3 (C-3, 5).

*Trinorborn-1-yl Phosphite* **7**.—Phosphorus trichloride (2.04 g, 0.15 mol) in light petroleum (b.p. 30–40 °C) (50 cm$^3$) was added dropwise to a stirred solution, under nitrogen, of norborn-1-yl alcohol (5.27 g, 0.047 mol) and *N*,*N*-dimethylaniline (5.41 g, 0.045 mol) in light petroleum at 0 °C.[36] The mixture was stirred at room temperature (60 h) and then filtered to remove amine hydrochloride which was washed with further quantities of light petroleum. Evaporation of the combined filtrate and washings gave a solid residue which was recrystallized from acetonitrile to give the white crystalline phosphite **7** (3.5 g, 64.8%) (Found: C, 69.5; H, 9.2. $C_{21}H_{33}O_3P$ requires C, 69.2; H, 9.1%), m.p. (sealed tube) 183–184 °C; *m/z* (%) 364 (M$^+$, 4.4), 253 (51.6) and 95 (100); $\delta_P(CDCl_3)$ 141.4; $\delta_H(CDCl_3)$ 0.96–2.45 (m); $\delta_C(CDCl_3)$ 86.1 (d, C-1, $^2J_{PC}$ 6.1), 43.0 (d, C-7, $^3J_{PC}$ 7.9), 35.1 (d, C-2, 6, $^3J_{PC}$ 6.7), 33.6 (s, C-4) and 30.0 (s, C-3, 5); $\nu_{max}$/cm$^{-1}$ 2960, 2880, 1455, 1310 and 1085.

*Trinorborn-1-yl Phosphate.*—*tert*-Butyl hydroperoxide (70%) (0.12 cm$^3$) was added to a stirred solution of trinorborn-1-yl phosphite (0.254 g, 0.7 mmol) in anhydrous 1,4-dioxane and the mixture was stirred for 1.5 h. The solvent was evaporated under reduced pressure to give trinorborn-1-yl phosphate (0.26 g, 98%) (Found: M$^+$, 380.2115. $C_{21}H_{33}O_4P$ requires *M*, 380.2116) as a white solid, m.p. (sealed tube) 220–221 °C; *m/z* (%) 380

($M^+$, 16.9), 351 (100), 287 (16.3), 257 (38.5), 159 (10.9), 95 (64.9), 67 (43.2) and 54 (31.7); $\delta_P(CDCl_3)$ −10.2; $\delta_H(CDCl_3)$ 1.7–2.0 (m); $\delta_C(CDCl_3)$ 89.2 (d, C-1, $^2J_{PC}$ 7.3), 42.1 (d, C-7, $^3J_{PH}$ 4.9), 33.6 (d, C-2, 6, $^3J_{PC}$ 7.9), 33.6 (C-4) and 29.8 (C-3, 5); $\nu_{max}/cm^{-1}$ 2980, 2880, 1455, 1310, 1280, 1085, 1015, 990 and 940.

*Reactions of Trinorborn-1-yl Phosphite with α-Halogenoketones.*—The α-halogenoacetophenone dissolved in $CDCl_3$ was added to trinorborn-1-yl phosphite (1 mol equiv.) in $CDCl_3$ in an NMR tube in such quantity that the initial concentration of phosphite was *ca.* 20% w/v. The tubes were sealed and the reactions monitored by $^{31}P$ or $^1H$ NMR. At room temperature, α-bromoacetophenone gave only the ketophosphonium bromide **10** ($\delta_P$ 27.1), as follows (% conversion, time/h): 33, 1.0; 50, 1.9; 59, 2.9; 94, 21.0. α-Chloroacetophenone showed no reaction at room temperature but at 69 °C (65 h) gave the ketophosphonium chloride **12** ($\delta_P$ 26.7, 31%), trinorborn-1-yl phosphate ($\delta_P$ −10.4, 31%), dinorborn-1-yl phosphite ($\delta_P$ −0.2, d, $^1J_{PH}$ 684) (5%), and two unidentified products ($\delta_P$ 41.9, 30% and $\delta_P$ −14.3, 3%). α-Bromo-*p*-bromoacetophenone at room temperature (24 h) gave only the ketophosphonium bromide **11** ($\delta_P$ 26.3). α-Chloro-*p*-nitroacetophenone at room temperature gave only the vinyloxyphosphonium chloride **15** ($\delta_P$ −17.0), as follows (% conversion, time/h): 20, 0.6; 45, 1.3; 92, 23.2. α-Bromo-*p*-nitroacetophenone at room temperature (24 h) gave the ketophosphonium bromide **17** ($\delta_P$ 25.2, 12%), the vinyloxyphosphonium bromide **16** ($\delta_P$ −16.9, 16%), trinorborn-1-yl phosphate ($\delta_P$ −10.3, 28%), and two unidentified products ($\delta_P$ 11.2, 29% and $\delta_P$ −10.7, 15%). Chloroacetone showed no reaction at room temperature but at 69 °C (71.5 h) gave the ketophosphonium chloride **13** ($\delta_P$ 26.4, 12%), the vinyloxyphosphonium chloride **14** ($\delta_P$ −16.9, 8%), trinorborn-1-yl phosphate ($\delta_P$ −10.4, 15%), dinorborn-1-yl phosphite ($\delta_P$ −0.4, d, $^1J_{PH}$ 685) (11%), and four unidentified products ($\delta_P$ 116.0, 21%; $\delta_P$ 29.2, 15%; $\delta_P$ 23.5, 14%; $\delta_P$ −4.4, 4%).

*Isolation of Quasiphosphonium Salts in the Reactions of Trinorborn-1-yl Phosphite with Halogeno Compounds.*—(a) *Reaction with iodomethane.* Trinorborn-1-yl phosphite (1.23 g, 3.4 mmol) and iodomethane (0.576 g, 4.0 mmol) were mixed in anhydrous ether at room temperature. Crystals, which separated over a period of four weeks, were washed with ether and dried *in vacuo* to afford trinorborn-1-yloxy(methyl)phosphonium iodide **9** (1.39 g, 81.3%) as white plates, m.p. 145–147 °C (Found: C, 52.3; H, 7.4. $C_{22}H_{36}O_3PI$ requires: C, 52.2; H, 7.1%); $\delta_P(CDCl_3)$ 36.9 (q, $^2J_{PH}$ 16.4); $\delta_C(CDCl_3)$ 97.3 (d, norbornyl C-1, $^2J_{PC}$ 11), 42.8 (d, norbornyl C-7, $^3J_{PC}$ 3.7), 34.2 (d, norbornyl C-2, 6, $^3J_{PC}$ 3.0), 33.0 (norbornyl C-4), 29.8 (norbornyl C-3, 5) and 16.1 (d, $CH_3$, $^1J_{PC}$ 130); $\delta_H(CDCl_3)$ 2.51 (d, $CH_3$, $^2J_{PH}$ 16.2) and 1.54–2.25 (m, norbornyl); FAB MS: *m/z* (%) 379 ($P^+$ ion, 100), 285 (13), 253 (4), 191 (3), 95 (16) and 91 (3); $\nu_{max}/cm^{-1}$ 2985, 2880, 1320, 1085 and 1060.

(b) *Reaction with α-bromoacetophenone.* By a similar procedure to the above, α-bromoacetophenone (0.58 g, 1.2 mmol) and trinorborn-1-yl phosphite (0.91 g, 2.5 mmol) in anhydrous ether (11 weeks) gave trinorborn-1-yloxy(phenacyl)phosphonium bromide **10** (0.95 g, 67.1%), m.p. 177–178 °C (Found: C, 62.2; H, 7.2. $C_{29}H_{40}BrO_4P$ requires: C, 61.8; H, 7.1%). The reaction of α-bromoacetophenone (0.24 g, 1.2 mmol) and the phosphite (0.437 g, 1.2 mmol) in $CDCl_3$ (2.5 $cm^3$) (sealed NMR tube) was monitored by $^{31}P$ NMR; after 24 h at ambient temperature, the solvent was evaporated and the residue was triturated with anhydrous ether to give the phosphonium bromide **10** (0.275 g, 40.6%), m.p. 170–172 °C; $\delta_P(CDCl_3)$ 26.7; $\delta_C(CDCl_3)$ 190.2 (d, C=O, $^2J_{PC}$ 7.9), 135.7 (d, ArC-1, $^3J_{PC}$ 7.3), 134.6 (ArC-4), 130.1 (ArC-2, 6), 129.1 (ArC-3, 5), 98.0 (d, norbornyl C-1, $^2J_{PC}$ 12.2), 42.4 (d, norbornyl C-7, $^3J_{PC}$ 3.7), 40.6 (d, $PCH_2$, $^1J_{PC}$ 134.9), 33.8 (d, norbornyl C-2, 6, $^3J_{PC}$ 3.1), 32.8 (norbornyl C-4) and 29.6 (norbornyl C-3, 5); $\delta_H(CDCl_3)$ 1.38–2.2 (m, 33 H, norbornyl), 5.22 (d, 2 H, $PCH_2$, $^2J_{PH}$ 18.1), 7.58 (m, 3 H, Ar) and 8.4 (m, 2 H, Ar); FAB MS: *m/z* (%) 483 ($P^+$ ion, 100), 389 (16), 295 (6), 253 (9), 201 (10), 95 (62) and 91 (9); $\nu_{max}/cm^{-1}$ 2960, 1680, 1595, 1450 and 1090–1070br.

(c) *Reaction with α-bromo-p-bromoacetophenone.* The acetophenone (0.10 g, 0.36 mmol) and phosphite (0.13 g, 0.36 mmol) were allowed to react in $CDCl_3$ (0.6 $cm^3$) in a sealed NMR tube at room temperature. After 24 h, work up as above gave trinorborn-1-yloxy(*p*-bromophenacyl)phosphonium bromide **11** (0.13 g, 57.3%), m.p. 172–173 °C; $\delta_P(CDCl_3)$ 26.3 (t, $^2J_{PH}$ 18); $\delta_C(CDCl_3)$ 134.3 (d, ArC-1, $^3J_{PC}$ 8.5), 132.4 (ArC-3, 5), 131.8 (ArC-2, 6), 130.3 (ArC-4), 98.0 (d, norbornyl C-1, $^2J_{PC}$ 12.2), 42.4 (d, norbornyl C-7, $^3J_{PC}$ 3.7), 40.7 (d, $PCH_2$, $^1J_{PC}$ 136.1), 33.8 (d, norbornyl C-2, 6, $^3J_{PC}$ 3.0) and 32.8 (norbornyl C-4), 29.6 (norbornyl C-3, 5); $\delta_H(CDCl_3)$ 1.2–2.2 (m, norbornyl) and 5.15 (d, $PCH_2$, $^2J_{PH}$ 18.6); FAB MS: *m/z* (%) 563/561 ($P^+$ ion, 55), 469/467 (5), 375/373 (1), 281/279 (2), 253 (6), 95 (100) and 91 (11); $\nu_{max}/cm^{-1}$ 2985, 2880, 1685, 1580, 1315 and 1080.

(d) *Reaction with α-chloro-p-nitroacetophenone.* Reaction of the acetophenone (0.273 g, 1.4 mmol) and the phosphite (0.482 g, 1.3 mmol) in $CDCl_3$ (2.5 $cm^3$) in an NMR tube at room temperature (24 h), followed by work-up as above, gave trinorborn-1-yloxy[1-(*p*-nitrophenyl)vinyloxy]phosphonium chloride **15** (0.53 g, 71%), m.p. 120–123 °C; $\delta_P(CDCl_3)$ −17.1; $\delta_C(CDCl_3)$ 150.4 (d, POC=C, $^2J_{PC}$ 9.8), 148.8 ($CNO_2$), 137.5 (d, ArC-1, $^3J_{PC}$ 7.9), 127.0 (ArC-2, 6), 124.5 (ArC-3, 5), 105.4 (C=$CH_2$), 100.5 (d, norbornyl C-1, $^2J_{PC}$ 11.6), 42.3 (d, norbornyl C-7, $^3J_{PC}$ 4.3), 33.5 (d, norbornyl C-2, 6, $^3J_{PC}$ 3.1), 32.7 (norbornyl C-4) and 29.5 (norbornyl C-3, 5); $\delta_H(CDCl_3)$ 5.48 (1 H, dd, POC=$CH^A$, $^1J_{H^AH^B}$ 5.6, $^4J_{PH^A}$ 1.7), 6.37 (1 H, dd, POC=$CH^B$, $^1J_{H^AH^B}$ 5.6, $^4J_{PH^B}$ 2.6) and 7.86–8.4 (4 H, m, Ar); FAB MS: *m/z* (%) 528 ($P^+$ ion, 11), 381 (48), 287 (16), 253 (2), 193 (12), 95 (100) and 91 (17); $\nu_{max}/cm^{-1}$ 2985, 1640, 1610, 1525, 1460, 1355, 1100, 1045 and 1005.

*Thermal Decomposition of Quasiphosphonium Salts.*—Each salt was dissolved in $CDCl_3$ (3 $cm^3$) and the solution divided between six sealed NMR tubes which were heated in a thermostatted oil bath (149 °C). Reaction was monitored by removing the tubes after various intervals of time, rapid cooling to room temperature, and recording the $^1H$ NMR spectrum as follows.

(a) *Tri-1-norbornyloxy(phenacyl)phosphonium bromide* **10**. The bromide (0.64 g, 1.1 mmol) [$\delta_H$ 5.20 ($PCH_2$, d, $^2J_{PCH}$ 19)] decomposed to give dinorborn-1-yl phenacylphosphonate [$\delta_H$ 3.6 ($PCH_2$, d, $^2J_{PCH}$ 22.8)] with $t_{\frac{1}{2}}$ *ca.* 4–5 h. After 6 h the solution contained unchanged phosphonium bromide ($\delta_P$ 26.6, 33%), dinorborn-1-yl phenacylphosphonate ($\delta_P$ 13.5, 40%), trinorborn-1-yl phosphate ($\delta_P$ −10.5, 1%) and three unidentified compounds ($\delta_P$ 18.2, d, $J_{PH}$ 8.9, 16%; $\delta_P$ 12.3, 11%; $\delta_P$ −14.2, 1%). After a further 24 h heating, $CDCl_3$ was removed under reduced pressure; the solid residue was dissolved in acetone and the solution triturated with hexane to yield a solid which was washed with hexane to give dinorborn-1-yl phenacylphosphonate (0.183 g, 49.8%), m.p. 101–103 °C (Found: C, 67.3; H, 7.6. $C_{22}H_{29}O_4P$ requires: C, 68.0; H, 7.5%); *m/z* (%) 388 ($M^+$, 3.3), 351 (24), 277 (23.6), 105 (18.1), 103 (14.7), 95 (26.5), 85 (83.5), 83 (100), 77 (18.6), 70 (22.3) and 67 (19.4); $\delta_P(CDCl_3)$ 13.4; $\delta_C(CDCl_3)$ 192.4 (d, C=O, $^2J_{PC}$ 7.3), 137.1 (ArC-1), 133.3 (ArC-4), 129.3 (ArC-2, 6), 128.5 (ArC-3, 5), 89.9 (d, norbornyl C-1, $^2J_{PC}$ 7.9), 42.2 (d, norbornyl C-7, $^3J_{PC}$ 4.3), 41.5 (d, $PCH_2$, $^1J_{PC}$ 130), 34.0 (d, norbornyl C-2, 6, $^3J_{PC}$ 2.4), 33.3 (norbornyl C-4) and 29.7 (norbornyl C-3, 5); $\delta_H(CDCl_3)$ 1.34–2.1 (br m, norbornyl), 3.57 (2 H, d, $PCH_2$, $^2J_{PH}$ 22.2), 7.54 (3 H, m, Ar) and

8.0 (2 H, m, Ar); $\nu_{max}$(KBr disc)/cm$^{-1}$ 2980, 2880, 1680, 1605, 1585, 1455, 1425, 1325, 1280, 1080, 1025, 1015, 945 and 900.

(b) *Trinorborn-1-yloxy-*[1-(p-*nitrophenyl*)*vinyl*]*oxyphosphonium chloride* **15**. The chloride (0.43 g, 0.75 mmol) [$\delta_H$ 5.4 (dd, C=CH$^A$) and 6.30 (dd, C=CH$^B$)] underwent complete decomposition within 1.4 h. The product contained no vinyl protons but showed singlets at $\delta_H$ 3.3 (acetylenic H) and 2.6 ($CH_3$ of *p*-nitroacetophenone) (trace). $^{31}$P and $^{13}$C NMR showed the major products to be trinorborn-1-yl phosphate, $\delta_P$ −10.2; $\delta_C$ 29.7 (C-3, 5), 33.4 (C-2, 6, d, $^3J_{PC}$ 4.0), 33.7 (C-4), 42.0 (C-7, d, $^3J_{PC}$ 4.1) and 89.1 (C-1, d, $^2J_{PC}$ 7.5), and *p*-nitrophenylacetylene, $\delta_C$ [with 0.9 mg Cr(acac)$_3$ added] 147.6 (ArC-4), 133.2 ArC-2, 6), 129.0 (ArC-1), 123.7 (ArC-3, 5), 82.9 (=CH), 81.7 (–C=) (in agreement with lit. values),[50] together with an unidentified phosphorus-containing compound, $\delta_P$ −13.4 (*ca.* 4 mol%).

(c) *Trinorborn-1-yloxy*(*methyl*)*phosphonium iodide* **9**. The iodide (0.92 g, 0.0018 mol) [$\delta_H$ 2.40 (Me, d, $^2J_{PH}$ 16.2)] decomposed with $t_{\frac{1}{2}}$ > 100 h, as measured against benzene (0.1 cm$^3$) ($\delta_H$ 7.4), as internal standard. After 24.6 h the solution contained unchanged phosphonium iodide ($\delta_P$ 36.5, 71%) and dinorborn-1-yl methylphosphonate ($\delta_P$ 24.6). After a further 120 h heating the solvent was removed and the residue was triturated with anhydrous ether to give the phosphonium iodide (0.38 g, 41%) [$\delta_P$($CDCl_3$) 35.5]; evaporation of the filtrate and washings yielded an oily product identified as dinorborn-1-yl methylphosphonate (0.13 g, 25%); *m/z* (%) 284 (M$^+$, 32.2), 256 (17.1), 255 (100), 191 (15.9), 161 (12.1), 97 (15.8) and 95 (54); $\delta_P$($CDCl_3$) 24.4 (q, $^2J_{PH}$ 17.6); $\delta_C$($CDCl_3$) 97.4 (norbornyl C-1, d, $^2J_{PC}$ 11.0), 42.9 (norbornyl C-7, d, $^3J_{PC}$ 4.3), 34.1 (norbornyl C-2, 6, d, $^3J_{PH}$ 3.1), 32.8 (norbornyl C-4), 29.8 (norbornyl C-3, 5) and 15.4 (Me, d, $^1J_{PC}$ 130); $\delta_H$($CDCl_3$) 1.4–2.1 (norbornyl, br m), 1.46 ($CH_3$, d, $^2J_{PH}$ 16.8); $\nu_{max}$/cm$^{-1}$ 2970, 2880, 1460, 1330, 1275, 1180, 1090, 1030, 1000, 950 and 760.

*Attempted Solvolysis of Trinorborn-1-yloxy*[1-(p-*nitrophenyl*)*vinyloxy*]*phosphonium Chloride* **15**.—The chloride **15** (0.05 g) was dissolved in anhydrous methanol (0.5 cm$^3$, containing 10% [$^2H_4$]-methanol) and the mixture was monitored by $^{31}$P NMR at room temperature. Only the original signal ($\delta_P$ −17.5) was detectable after a period of two months.

*X-Ray Crystallography.*—X-Ray diffraction data for the Arbuzov intermediate **10** and the Perkow intermediate **15** were measured on a Phillips PW1100 4-circle diffractometer with Mo-Kα radiation ($\lambda$ = 0.710 69 Å) using crystals of dimensions 0.56 × 0.51 × 0.16 (**10**) and 0.40 × 0.19 × 0.08 mm (**15**). Crystals for both compounds diffracted very weakly at high angle, so data were collected in the slightly limited $\theta$-range 3–22°. Both structures were solved by direct methods.[51] In compound **15** the presence of a molecule of solvent was deduced from examination of several regions of extended electron density observed in a difference-Fourier synthesis after initial refinement. The most satisfactory refinement was obtained when seven local maxima were interpreted as chlorine atom sites of partial occupancy, corresponding to a disordered molecule of $CDCl_3$. The vinyl hydrogen atoms of compound **15** were located in a difference-Fourier synthesis calculated with low angle data ($\sin\theta$ < 0.35) and were included in structure factor calculations but were not refined; the remaining hydrogen atoms of both compounds were included in the refinement at calculated positions 'riding' on the relevant carbon atoms. Despite evidence in difference-Fourier maps of some anisotropy for the atoms of the neopentyl groups, the limited number of data obtained from the crystals precluded assignment of anisotropic thermal parameters to any but the phosphorus, bromine, and phenacyl oxygen atoms of compound **10** and to the phosphorus, oxygen, and chlorine atoms of compound **15** (apart from those of 0.25 site occupancy). Final refinement was carried out by full-matrix least squares procedures using 1484 and 1652 reflections with $I/\sigma(I)$ > 3.0 for compounds **10** and **15** respectively and converged at $R$ = 0.0985 and $R_w$ = 0.0952 (for compound **10**) and $R$ = 0.1084 (for compound **15**), and final difference-Fourier syntheses showed no residual electron density greater than 1 e Å$^{-3}$. The relatively high final $R$ values are a consequence of the poor quality of the only crystals that could be obtained; the main structural features of these novel compounds are nevertheless unambiguously established.

*Crystal data.* **10**, $C_{29}H_{40}BrO_4P$, $M_r$ = 563.51, monoclinic, space group $P2_1/c$, $a$ = 14.413(4), $b$ = 9.996(3), $c$ = 19.215(5) Å, $\beta$ = 90.73(3)°, $V$ = 2768.13 Å$^3$, $Z$ = 4, $F$(000) = 1184, $\mu$ = 15.12 mm$^{-1}$, $D_c$ = 1.35 g cm$^{-3}$.

*Crystal data.* **15**, $C_{29}H_{39}ClNO_6P$•$CDCl_3$, $M_r$ = 684.44, monoclinic, space group $P2_1/c$, $a$ = 9.288(3), $b$ = 30.074(6), $c$ = 11.894(3) Å, $\beta$ = 98.69(3)°, $V$ = 3284.12 Å$^3$, $Z$ = 4, $F$(000) = 1432, $\mu$ = 0.45 mm$^{-1}$, $D_c$ = 1.38 g cm$^{-3}$.

*Supplementary data.* Atomic coordinates, and complete lists of bond angles, bond lengths, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.†

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