Alkyl Di-t-butylphosphinites.   Exceptionally Halogenophilic Phosphinites in Arbuzov Reactions
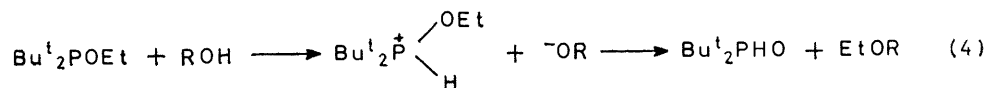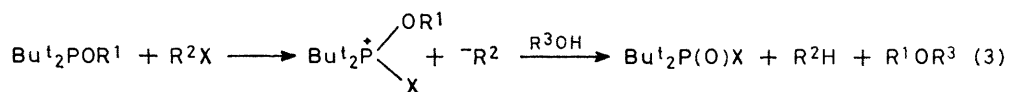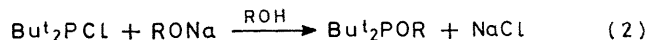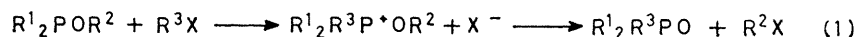
By **Otto Dahl**, Department of General and Organic Chemistry, University of Copenhagen, the H. C. Ørsted Institute, DK–2100 Copenhagen, Denmark

Methyl and ethyl di-t-butylphosphinite have been prepared and reactions of the latter with a number of alkyl halides investigated. Normal Arbuzov products, Bu^t_2RPO, are the predominant or sole products for RX = MeI, EtI, $PhCH_2Br$, $Br(CH_2)_3Br$, $BrCH_2CH_2OPh$, $ClCH_2COOEt$, and $ClCH_2CONH_2$. For RX = $ClCH_2CN$, CH_2I_2, and $BrCH_2CH_2Br$ the main products are $Bu^t_2P(O)X$, and for RX = $ClCH_2COCH_3$ and $ClCH_2P(O)Ph_2$ both products are formed. The reaction mixtures have been analysed mostly by ^1H n.m.r. spectroscopy, and major products have been isolated and characterized and plausible reaction pathways outlined. It is shown that $Bu^t_2P(O)X$ arises from attack of Bu^t_2POEt on the halogen of RX, the pronounced halogenophilicity of Bu^t_2POEt being ascribed to steric hindrance from the t-butyl groups.

ALKYL PHOSPHINITES, like other tricovalent alkoxy-phosphorus compounds, usually undergo the Arbuzov reaction when heated with alkyl halides [equation (1)]. The reaction has been widely used for generating new carbon–phosphorus bonds [1] and is an attractive synthetic pathway to tertiary phosphine oxides with a functional group in one of the substituents (R^3).[2-7]

The Arbuzov reaction is normally clean and gives a

$X = Br$ a mixture of the Perkow product, the Arbuzov product $[Ph_2P(O)CH_2COR]$, and the dehalogenated ketone is obtained. (ii) $(EtO)_3P$ and hexachlorocyclopentadiene,[9] $ClC(Ph)_2CN$,[10] or $BrCH(COPh)_2$,[11] in which cases the products may be regarded as being derived from attack of $(EtO)_3P$ on halogen.

This paper describes the reactions of alkyl di-t-butylphosphinites with a number of alkyl halides. It is

$$R^1_2POR^2 + R^3X \longrightarrow R^1_2R^3P^+OR^2 + X^- \longrightarrow R^1_2R^3PO + R^2X \quad (1)$$

$$Bu^t_2PCl + RONa \xrightarrow{ROH} Bu^t_2POR + NaCl \quad (2)$$

$$Bu^t_2POR^1 + R^2X \longrightarrow Bu^t_2\overset{+}{P}\overset{\displaystyle OR^1}{\underset{\displaystyle X}{\big<}} + {}^-R^2 \xrightarrow{R^3OH} Bu^t_2P(O)X + R^2H + R^1OR^3 \quad (3)$$

$$Bu^t_2POEt + ROH \longrightarrow Bu^t_2\overset{+}{P}\overset{\displaystyle OEt}{\underset{\displaystyle H}{\big<}} + {}^-OR \longrightarrow Bu^t_2PHO + EtOR \quad (4)$$

$$Bu^t_2\overset{+}{P}\overset{\displaystyle OEt}{\underset{\displaystyle Cl}{\big<}} + {}^-R \xrightarrow{\text{no solvent}} Bu^t_2\overset{+}{P}\overset{\displaystyle OEt}{\underset{\displaystyle R}{\big<}} + Cl^- \quad (5)$$

high yield of tertiary phosphine oxide. However, when the alkyl halide RX is an α-halogeno-ketone or is substituted in such a way that ^-R becomes strongly stabilized, the reaction may take another course. Examples are provided by the reactions between (i) Ph_2POEt and XCH_2COR.[8] For $X = Cl$ the product is largely $Ph_2P(O)OC(R)=CH_2$ (the Perkow reaction), whereas for

shown that Bu^t_2POR reacts anomalously with several substituted alkyl halides and in some cases gives unexpected products. A comparative study of the reaction of a phosphinite with a broad selection of alkyl halides has, to the author's knowledge, not been published before. The system $Bu^t_2POR + RX$ is well-suited to analysis for two reasons. (i) The phosphorus products resulting from halogen attack, $Bu^t_2P(O)X$, are very resistant to hydrolysis [12] in contrast to most other

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[12] P. Haake and P. S. Ossip, *J. Amer. Chem. Soc.*, 1971, **93**, 6924.

ABP(O)X compounds. This facilitates the determination of the degree of halogen attack. (ii) Mixtures of $Bu^t_2P(O)$ compounds are comparatively easy to analyse by ^1H n.m.r. spectroscopy due to the presence of strong Bu^t-doublets in their spectra.

Alkyl di-t-butylphosphinites have not been described previously. Only one di-t-butylphosphinite, viz. Bu^t_2-POPh, is known,[13] but this, like other tricovalent aryloxyphosphorus compounds, is unable to undergo the S_N2 substitution which is the second step in the Arbuzov reaction.[14] Methyl and ethyl di-t-butylphosphinite were

product (ca. 80%), whilst Bu^t_2POEt was recovered unchanged ($>90\%$) after being heated under reflux with Bu^tBr for 24 h. $Bu^t_2P(O)X$ (2—3%) and traces of Bu^t_2PHO were detected in both reaction mixtures.

Reactions with Substituted Alkyl Halides.—Bu^t_2POEt was allowed to react with a series of substituted alkyl halides (Table) which, with the exception of CH_2I_2, $BrCH_2CH_2OPh$, and $Br(CH_2)_3Br$, are known to react with Ph_2POR to give high yields of the normal Arbuzov products [equation (1)].[2,8,17-19] The reactions were run either at 100—160 °C without solvent or in boiling EtOH,

Products from the reactions of Bu^t_2POEt with substituted RX. Numbers are mole-% of consumed Bu^t_2POEt.
Reaction conditions are 100—120 °C or reflux in EtOH for 2 h, unless otherwise stated

RX	Solvent	Bu^t_2RPO	$Bu^t_2P(O)X$	Other phosphorus-containing products	Other products
$ClCH_2CO_2Et$	None	94.5	0.5	Bu^t_2PHO, 2; $Bu^t_2P(O)OEt$, 3	
$ClCH_2CO_2Et$	EtOH	84	3	Bu^t_2PHO, 11; $Bu^t_2P(O)OEt$, 2	
$ClCH_2CONH_2$	None	93	1	Bu^t_2EtPO, 1; Bu^t_2PHO, 4; $Bu^t_2P(O)OEt$, 1	
$ClCH_2CONH_2$	EtOH	73	1	Bu^t_2EtPO, 5; Bu^t_2PHO, 18; $Bu^t_2P(O)OEt$, 3	
$ClCH_2CN$	None	11	48	$Bu^tP(OEt)CHCN$, 39; Bu^t_2EtPO, 0.5; Bu^t_2PHO, 0.5; $Bu^t_2P(O)OEt$, 1	CH_3CN, $(CH_2CN)_2$
$ClCH_2CN$	EtOH	0	70	$Bu^t_2P(OEt)CHCN$, 21; Bu^t_2PHO, 1; $Bu^t_2P(O)OEt$, 8	CH_3CN
CH_2I_2	None	0	39	Bu^t_2MePO, 18; Bu^t_2EtPO, 32; $Bu^t_2(CH_2=CH)PO$, 8; unid., 3	EtI
CH_2I_2	EtOH	0	40	Bu^t_2MePO, 40; Bu^t_2EtPO, 20	MeI, EtI, Et_2O
$BrCH_2CH_2Br$	None[a,b]	7,[c] 10[d]	37	Bu^t_2EtPO, 35; $Bu^t_2(CH_2=CH)PO$, 7; $Bu^t_2P(O)OEt$, 4	$CH_2=CH_2$
$Br(CH_2)_3Br$	None[a]	72[e]	0.5	Bu^t_2EtPO, 27; $Bu^t_2P(O)OEt$, 0.5	
$BrCH_2CH_2OPh$	None[f]	65	0	Bu^t_2EtPO, 35	
$ClCH_2COCH_3$	None	83	3	Bu^tEtPO, 2; Bu^t_2PHO, 2; $Bu^t_2P(O)OEt$, 5; unid., 5	
$ClCH_2COCH_3$	EtOH[g]	73	13	Bu^t_2EtPO, 3; Bu^t_2PHO, 6; $Bu^t_2P(O)OEt$, 2; unid., 2; unid., 1	CH_3COCH_3
$ClCH_2P(O)Ph_2$	None[h]	34	17	Bu^t_2EtPO, 49; Ph_2MePO	

[a] $Bu^t_2POEt : Br[CH_2]_nBr$, 1 : 1. [b] 110 °C for 20 h. [c] $Bu^t_2P(O)CH_2CH_2Br$. [d] $Bu^t_2P(O)CH_2CH_2P(O)Bu^t_2$. [e] $Bu^t_2P(O)(CH_2)_3Br$
and $Bu^t_2P(O)(CH_2)_3P(O)Bu^t_2$ (superimposed signals). [f] 160 °C for 2 h. [g] Reflux for 4 h. [h] 150 °C for 50 h.

prepared from di-t-butylphosphinous chloride and the corresponding sodium alkoxides in alcohol [equation (2)]. The reaction of phosphinous chlorides with alkoxides to produce phosphinites is usually inferior to that with alcohol and an excess of a tertiary amine,[15] but the reverse holds for Bu^t_2PCl. In contrast to a report in the literature,[13] good yields were obtained by the alkoxide method, whereas no reaction took place between Bu^t_2PCl and MeOH in pyridine (20 °C, 24 h).

Reactions with Simple Halides.—The phosphinites Bu^t_2POMe and Bu^t_2POEt are reactive compounds despite their bulky t-butyl groups. They fume in contact with air and react vigorously with halogens to give $Bu^t_2P(O)X$. Arbuzov reactions with MeI, EtI, and $PhCH_2Br$ proceed readily to give Bu^t_2RPO, no $Bu^t_2P(O)X$ being detected (^1H n.m.r.) even when the reactions were run in a protic solvent (MeOH). The absence of $Bu^t_2P(O)X$ shows [16] that attack of Bu^t_2POR on the halogen of RX [equation (3)] does not occur with these simple alkyl halides. The slow reaction of Bu^t_2POEt with Pr^iI gave Bu^t_2EtPO as the main

and the reaction mixtures analysed by ^1H n.m.r., ^{31}P n.m.r., and g.l.c.–mass spectrometry, usually after removal of low-boiling components by evaporation. Reaction products were identified by isolation and characterization for the more abundant products, and by comparison of n.m.r., g.l.c., and m.s. data with those of authentic samples for the minor products. The formation of small amounts of $Bu^t_2P(O)OEt$ due to inadvertent oxidation of Bu^t_2POEt during the reactions was detected in most cases. Bu^t_2PHO was also formed, in small amounts when no solvent was used and in appreciable quantities when the reactions were run in EtOH. Control experiments showed that Bu^t_2PHO is formed by attack of H_2O or EtOH on Bu^t_2POEt [equation (4)]. The third product found in most cases was Bu^t_2EtPO, formed by alkylation of Bu^t_2POEt by the reaction product EtX (cf. the reaction with Pr^iI above).

$ClCH_2CO_2Et$, $ClCH_2CONH_2$, and $ClCH_2CN$. These alkyl chlorides reacted with Bu^t_2POEt to give the normal Arbuzov products together with $Bu^t_2P(O)Cl$ which is the product expected from attack of Bu^t_2POEt on Cl [equation (3)]. $Bu^t_2P(O)Cl$ is a major product

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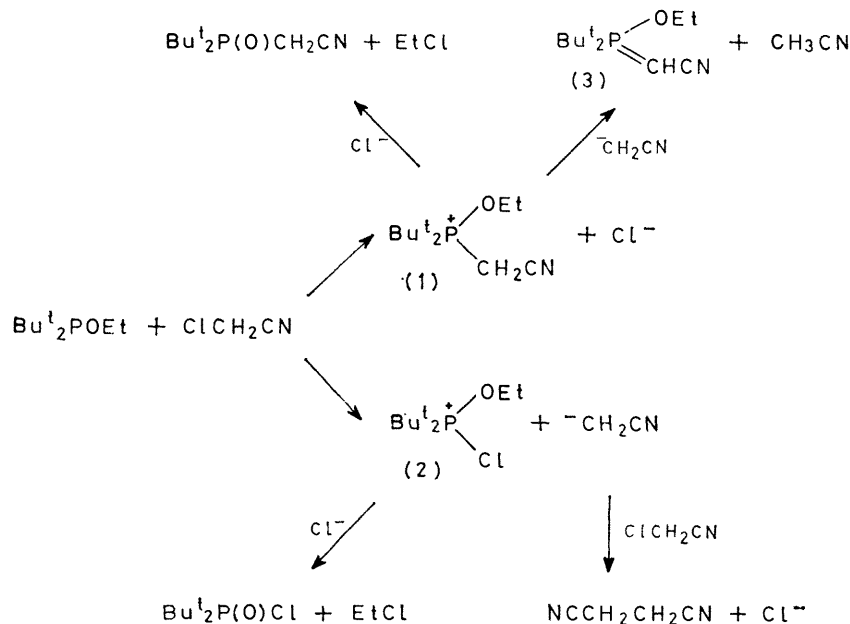[16] H. Hoffmann and H. J. Diehr, *Angew. Chem.*, 1964, **76**, 944.
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[19] M. I. Kabachnik, T. Ya. Medved, Yu. M. Polikarpov, and K. S. Yudina, *Izvest. Akad. Nauk S.S.S.R., Ser. Khim.*, 1967, 591 (*Chem. Abs.*, 1968, **68**, 39743y).

only in the case of ClCH₂CN in which case CH₃CN and an ylide, Buᵗ₂P(OEt)CHCN, were identified as the other major products. The formation of these products with ClCH₂CN may be rationalized as follows (Scheme 1). Buᵗ₂POEt gives the normal Arbuzov intermediate (1) as well as the intermediate formed by attack on halogen (2). The carbanion ⁻CH₂CN formed in the latter reaction reacts with (1) essentially before the latter has time to be dealkylated, giving CH₃CN and the ylide (3).

suggest that this base abstracts a proton from Buᵗ₂P⁺-(OEt)CH₂CN much faster than the latter is dealkylated by Cl⁻.

In conclusion, the results show that Buᵗ₂POEt attacks ClCH₂CO₂Et and ClCH₂CONH₂ nearly exclusively at carbon whereas attack on ClCH₂CN takes place at both carbon and chlorine with preference for the latter.

CH₂I₂, BrCH₂CH₂Br, and Br(CH₂)₃Br. The vigorous reaction of Buᵗ₂POEt with CH₂I₂ at 120 °C gave five

SCHEME 1

The other phosphorus products are formed from dealkylation of (1) and (2) by Cl⁻. The ylide (3) was isolated and found to be stable towards water, although it reacts with HCl to give Buᵗ₂P(O)CH₂CN. Small amounts of butanedinitrile were identified in the reaction mixture in accord with the postulated carbanion mechanism.

The normal Arbuzov intermediates, Buᵗ₂RP⁺OEt, may be formed either directly [equation (1)] or via the products of Cl-attack [equation (5)].[20] In hydroxylic solvents the latter mode of formation is highly improbable since ⁻R is scavenged by protonation. The reactions were therefore also run in EtOH in order to examine to what extent Buᵗ₂RP⁺OEt was formed via Buᵗ₂P⁺(OEt)Cl. The product composition in EtOH (Table) differed significantly from that obtained without solvent only in the case of ClCH₂CN, the proportion of Buᵗ₂P(O)Cl being increased relative to that of Buᵗ₂P(O)-CH₂CN and Buᵗ₂P(OEt)CHCN. This indicates that a substantial fraction of the Buᵗ₂P⁺(OEt)CH₂CN obtained without solvent is formed via Buᵗ₂P⁺(OEt)Cl. It is perhaps surprising that the ylide is formed in 21% yield and the phosphine oxide is not observed when the reaction with ClCH₂CN is run in EtOH. However, EtO⁻ (from ⁻CH₂CN + EtOH) is in abundance relative to Cl⁻ in the reaction mixture, and it is reasonable to

products, four of which were identified as Buᵗ₂P(O)I, Buᵗ₂MePO, Buᵗ₂EtPO, and Buᵗ₂(CH₂=CH)PO (Table). The unidentified product (δ_P 52 p.p.m., 3%) could be Buᵗ₂P(O)CH₂I, although no ¹H n.m.r. signal around δ_H 3.6 [where Ph₂P(O)CH₂I [21] absorbs] was observed. A reaction sequence initiated by attack of Buᵗ₂POEt on iodine rationalizes the formation of these products (Scheme 2). The postulated formation of ICH₂CH₂I from ⁻CH₂I and CH₂I₂ followed by deprotonation of the Arbuzov intermediate formed by reaction of Buᵗ₂POEt with ICH₂CH₂I is a plausible pathway to the unexpected product, Buᵗ₂(CH₂=CH)PO, although other possibilities exist. The fact that more Buᵗ₂MePO than Buᵗ₂-(CH₂=CH)PO is formed may be explained by formation of additional MeI from ⁻CH₂I and traces of water or other proton donors present as impurities. Neither CH₂=CH₂ nor Buᵗ₂P(O)CH₂CH₂I could be detected (cf. the following discussion). When the reaction was run in EtOH, Buᵗ₂P(O)I and Buᵗ₂MePO were the main products, and in accord with the postulated mechanism no Buᵗ₂(CH₂=CH)PO was detected.

The reaction of Buᵗ₂POEt with CH₂Br₂ proceeded similarly to that with CH₂I₂, although more slowly. No reaction with CH₂Cl₂ was observed after reflux for 48 h.

The slow reaction of Buᵗ₂POEt with BrCH₂CH₂Br

[20] Ref. 14, p. 111.

[21] W. Wegener and P. Scholz, Z. Chem., 1971, **11**, 20.

gave $Bu^t_2P(O)Br$ and Bu^t_2EtPO as the main products, and substantial amounts of $CH_2=CH_2$ could be detected (^1H n.m.r. and Br_2 addition). Small amounts of $Bu^t_2P(O)CH_2CH_2Br$, $Bu^t_2P(O)CH_2CH_2P(O)Bu^t_2$, and $Bu^t_2(CH_2=CH)PO$ were also observed, in accordance with the reaction sequence outlined in Scheme 3. Bu^t_2-$(CH_2=CH)PO$ may be formed from either $Bu^t_2P(O)$-CH_2CH_2Br or the intermediate, $Bu^t_2P^+(OEt)CH_2CH_2Br$,

normal Arbuzov product, $Bu^t_2P(O)CH_2CH_2OPh$, without detectable amounts of $Bu^t_2P(O)Br$ or the elimination product, $Bu^t_2(CH_2=CH)PO$.

$ClCH_2COCH_3$ *and* $ClCH_2P(O)Ph_2$. The reaction of Bu^t_2POEt with $ClCH_2COCH_3$ gave the normal Arbuzov product, $Bu^t_2P(O)CH_2COCH_3$, and only a small amount of the dehalogenation product, $Bu^t_2P(O)Cl$. The latter was more abundant when the reaction was run in EtOH,
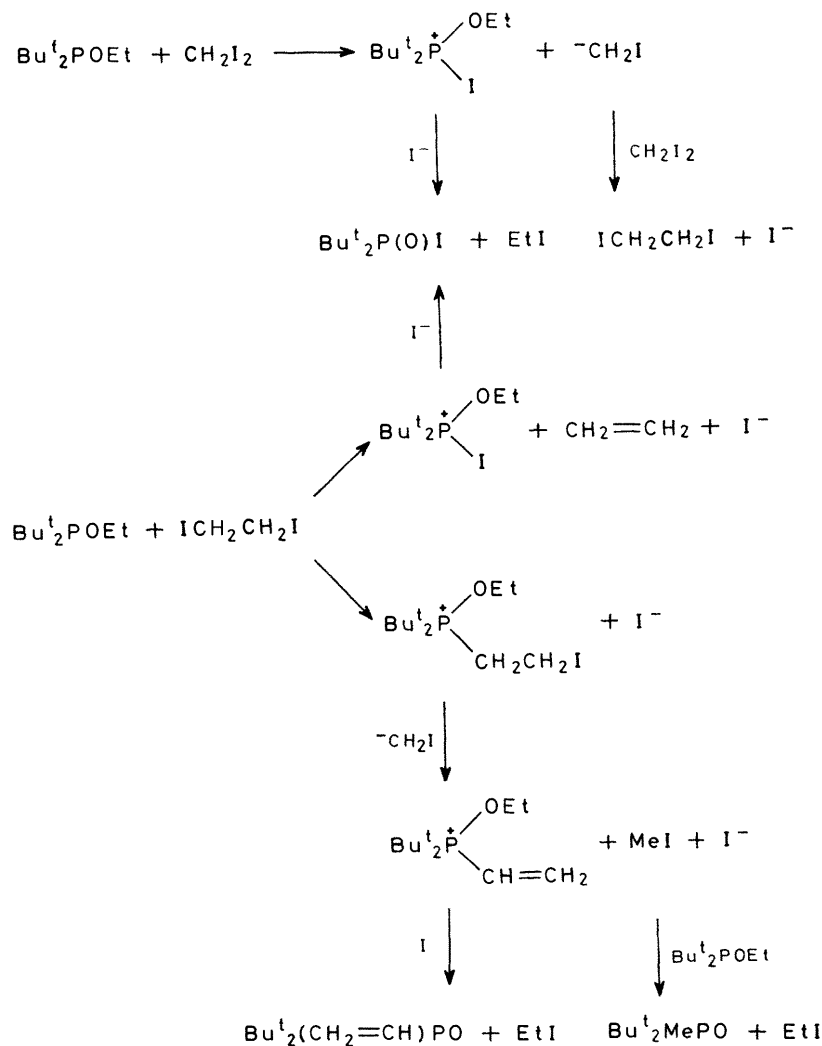
SCHEME 2

by elimination of HBr thermally or by the action of Br on Bu^t_2POEt. However, no Bu^t_2PHO was detected.

The reaction of Bu^t_2POEt with $Br(CH_2)_3Br$ gave the normal Arbuzov products, $Bu^t_2P(O)CH_2CH_2CH_2Br$ and $Bu^t_2P(O)CH_2CH_2CH_2P(O)Bu^t_2$ together with barely detectable amounts of $Bu^t_2P(O)Br$.

The observed reactions of $X[CH_2]_nX$ with Bu^t_2POEt show that Bu^t_2POEt attacks CH_2X_2 and XCH_2CH_2X predominantly at X, whereas $X(CH_2)_3X$ and presumably also higher dihalides are attacked predominantly at carbon.

$BrCH_2CH_2OPh$ reacted with Bu^t_2POEt to give the

and CH_3COCH_3 was then observed in the reaction mixture. However, the still large amount of Arbuzov product obtained in EtOH indicates that attack at carbon is dominant. A Perkow product, $Bu^t_2P(O)OC$-$(CH_3)=CH_2$, was not detected in either case [no ^1H n.m.r. signals in the δ 4.2—4.6 vinylic region where $Ph_2P(O)OC(CH_3)=CH_2$ absorbs [8]]. The absence of a Perkow product in EtOH is remarkable since Ph_2POEt and $ClCH_2COCH_3$ give 80% of Perkow product under the same conditions.[8]

The slow reaction between Bu^t_2POEt and $ClCH_2$-$P(O)Ph_2$ gave a 2 : 1 mixture of the normal Arbuzov

product and $Bu^t_2P(O)Cl$. The identification of Ph_2MePO in the reaction mixture provides further evidence that some dehalogenation had occurred in this case.

DISCUSSION

In the preceding sections it was shown that although Bu^t_2POEt reacts in the typical Arbuzov mode with many alkyl halides, it reacts anomalously in several cases, notably with $ClCH_2CN$, CH_2I_2 (and CH_2Br_2), and $BrCH_2CH_2Br$, and that the product formation with these halides can be rationalized by assuming that Bu^t_2POEt attacks at the halogen atom. Attack at the halogen of $ClCH_2CN$ does not occur with phosphinites

The pronounced halogenophilicity of Bu^t_2POEt is most probably a consequence of the steric requirements of the Bu^t-groups. Any steric hindrance to nucleophilic attack on an alkyl halide (except MeX) must be greater at carbon than at the face of the halogen atom. There are reports which suggest that the presence of two Bu^t-groups on phosphorus results in severe steric hindrance to reactions at the phosphorus atom, both in tricovalent compounds (e.g. Bu^t_2PCl failed to react with Et_2NH [13] or Bu^tMgCl [31]) and phosphoryl compounds [e.g. hydrolysis of $Bu^t_2P(O)Cl$ [12] and addition reactions of Bu^t_2-PHO [32]]. The increasing extent of attack at the halogen of $ClCH_2CN$ observed for the series Et_2POEt,

$$Bu^t_2P(O)CH_2CH_2P(O)Bu^t_2 + EtBr$$
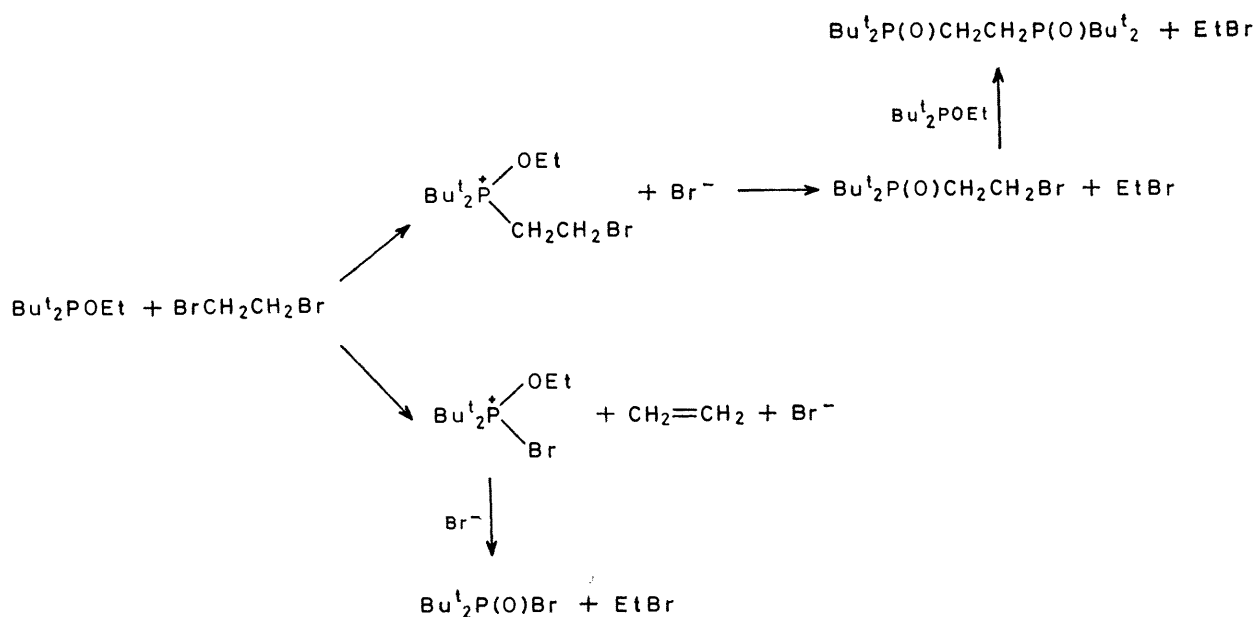
SCHEME 3

such as Ph_2POEt [2,22] or Et_2POEt,[22,23] although it does occur to a slight extent with Pr^i_2POEt.[7] $PhP(OEt)_2$ [22] and $(EtO)_3P$ [24] also give the normal Arbuzov products in high yields, and even Ph_3P reacts with $BrCH_2CN$ in benzene to give the phosphonium salt, although attack at bromine is inferred from the behaviour when MeOH is added.[25] Thus Bu^t_2POEt is unique in its behaviour towards $ClCH_2CN$. Although less studied, CH_2I_2 is known to react normally with $(EtO)_3P$ [26] and Ph_3P.[27] $BrCH_2CH_2Br$ reacts with Ph_2POEt to give $Ph_2P(O)-CH_2CH_2Br$ and $Ph_2P(O)CH_2CH_2P(O)Ph_2$ in high yields,[18] and Ph_3P [28] and $(EtO)_3P$ [29] react similarly. However, ethylene is formed when $BrCH_2CH_2Br$ reacts with $(EtO)_2PO^-$.[30]

Pr^i_2POEt, and Bu^t_2POEt is also indicative of a steric effect. However, the balance between carbon and halogen attack is delicate, as illustrated by the reactions of Bu^t_2POEt with $BrCH_2CH_2Br$ and $BrCH_2CH_2OPh$, respectively. The former reaction proceeds largely by attack at halogen to give ethylene, whereas the latter reaction proceeds exclusively by attack at carbon. The first reaction is presumably a concerted β-elimination process, the difference in behaviour of the two halides presumably reflecting the much better leaving group ability of Br^- than of PhO^-. For the α-substituted alkyl halides it is tempting to try to correlate the extent of attack at halogen with steric hindrance and carbanion stability. Steric hindrance from an α-substituent would

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[32] P. C. Crofts and D. M. Parker, *J. Chem. Soc.* (C), 1970, 332.

be expected to shift the reactions towards attack at halogen, and the same holds for reactions where attack at halogen gives rise to a strongly stabilized carbanion (*cf.* the examples given in the first section of this paper). However, for the α-substituted alkyl halides studied here the observed extent of attack at halogen does not correlate with either steric hindrance or carbanion stability. Steric hindrance towards attack at carbon must be smaller in $ClCH_2CN$ than in $ClCH_2CO_2Et$ or $ClCH_2COCH_3$, but the halogen attack/carbon attack product ratio is nevertheless larger in the former case. Carbanion stability decreases in the series $^-CH_2COR >$ $^-CH_2CO_2R > {}^-CH_2CN \sim {}^-CH_2CONH_2 > {}^-CH_2X$ (estimated from the rates of dissociation of the corresponding C–H acids [33]), whereas the halogen attack/carbon attack product ratio decreases in the series $CH_2I_2 > ClCH_2CN >$ $ClCH_2COCH_3 > ClCH_2CONH_2 \sim ClCH_2CO_2Et$ (Table). The softness of the iodine atom may be responsible for the large extent of halogen attack in the case of CH_2I_2, but $ClCH_2CN$ is clearly an exceptional case. Further studies are necessary to elucidate additional factors which may determine the site of attack of soft nucleophiles, such as Bu^t_2POEt, on substituted alkyl halides.

EXPERIMENTAL

All manipulations with Bu^t_2POR and with hygroscopic compounds were carried out under nitrogen. Analyses were performed by the microanalytical department of this laboratory. ^1H and ^{31}P n.m.r. spectra were recorded on a Bruker HX 90 E spectrometer (solvent $CDCl_3$, temperature *ca.* 30 °C unless otherwise specified). Chemical shifts (p.p.m.) are given relative to internal $SiMe_4$ for ^1H data (δ_H) and relative to external 85% H_3PO_4 for ^{31}P data (δ_P), and are positive for low-field shifts. The δ_P values were mostly obtained from the ^1H spectra by ^{31}P selective decoupling. G.l.c.–m.s. analyses were carried out on a Varian Aerograph 1700 gas chromatograph coupled to a Finnigan 1015 S/L mass spectrometer. The column was 3% SE 30 on Chromosorb W 80/100, 1/8 in × 2 m.

Methyl Di-t-butylphosphinite.—Bu^t_2PCl [34] (36.1 g, 0.20 mol) was added dropwise to a stirred solution of MeONa in MeOH [from Na (4.7 g, 0.20 mol) and MeOH (60 ml)]. During the addition the temperature rose from 20 to 45 °C. The reaction mixture was heated under reflux for 1 h and the flask was then attached to a distillation apparatus with a 15-cm Vigreux column. After removal of MeOH and a small forerun Bu^t_2POMe was collected (22.9 g, 65%), b.p. 33—34 °C at 2.5 mmHg. No impurities were detectable from its ^1H n.m.r. spectrum. N.m.r.: δ_P 166.4; δ_H 1.09 (Bu^t, $^3J_{PH}$ 11.3 Hz) and 3.64 (OMe, $^3J_{PH}$ 12.4 Hz).

Ethyl Di-t-butylphosphinite.—This ester was prepared in the same way as Bu^t_2POMe, using absolute EtOH (75 ml) in place of MeOH. Distillation directly from the reaction mixture as above gave Bu^t_2POEt (33.5 g, 88%), b.p. 40—41 °C at 2 mmHg, 59—60 °C at 7 mmHg. No impurities were detectable from its ^1H n.m.r. spectrum. N.m.r.: δ_P 159.7; δ_H 1.09 (Bu^t, $^3J_{PH}$ 11.3 Hz), 1.24 (CH_2CH_3, $^3J_{HH}$ 7.0 Hz), and 3.81 (CH_2CH_3, $^3J_{PH}$ 7.8 Hz).

Di-t-butylphosphinic Halides.—Bu^t_2POEt was added

dropwise with stirring to an ice-cooled solution of an excess of the halogen in CH_2Cl_2. Evaporation gave the crude product which was recrystallized from hexane. $Bu^t_2P(O)Cl$, m.p. 82—83 °C (lit.,[32] m.p. 82.5 °C). N.m.r.: δ_P 94.7; δ_H 1.42 ($^3J_{PH}$ 17.1 Hz) (Found: C, 48.8; H, 9.35; Cl, 17.9. $C_8H_{18}ClOP$ requires C, 48.86; H, 9.22; Cl, 18.03%). $Bu^t_2P(O)Br$, m.p. 101—102 °C (lit.,[35] 98—99 °C). N.m.r.: δ_P 102.5; δ_H 1.42 ($^3J_{PH}$ 17.3 Hz) (Found: C, 39.85; H, 7.6; Br, 33.2. $C_8H_{18}BrOP$ requires C, 39.85; H, 7.52; Br, 33.15%). $Bu^t_2P(O)I$, m.p. 89.5—90.5 °C. N.m.r.: δ_P 104.9; δ_H 1.40 ($^3J_{PH}$ 17.8 Hz) (Found: C, 33.45; H, 6.6; I, 43.3. $C_8H_{18}IOP$ requires C, 33.35; H, 6.30; I, 44.05%).

Di-t-butylphosphine Oxide.—A mixture of Bu^t_2POEt (3.81 g, 20 mmol), EtOH (2 ml), and aqueous 4M-HCl (5.2 ml, 21 mmol) was heated under reflux for 1 h. The solvent was removed by rotary evaporation, and the residue dissolved in CH_2Cl_2. Traces of HCl and H_2O were removed by stirring with powdered KOH for 1 h followed by filtration. Evaporation of the solvent gave crude Bu^t_2PHO (3.07 g, 95%), m.p. 82—88 °C (hygroscopic). One recrystallization from hexane raised the m.p. to 90—91 °C (lit., 55—57 °C,[32] 65—68° [13]). N.m.r.: δ_P 65.7; δ_H 1.27 (Bu^t, $^3J_{PH}$ 14.9 Hz) and 6.06 (PH, $^1J_{PH}$ 426 Hz) (Found: C, 58.4; H, 11.6. $C_8H_{19}OP$ requires C, 59.23; H, 11.81%).

Ethyl Di-t-butylphosphinate.—Bu^t_2POEt (3.81 g, 20 mmol) was added dropwise with stirring to a mixture of aqueous 35% H_2O_2 (3 ml, 30 mmol H_2O_2) and acetone (25 ml), kept at 0—10 °C. Excess of H_2O_2 was then decomposed by addition of a small amount of MnO_2 and the solvent removed by rotary evaporation. The crude product was distilled *in vacuo* to give $Bu^t_2P(O)OEt$ (3.45 g, 83%), b.p. 41—43 °C at 0.1 mmHg. N.m.r.: δ_P 64.3; δ_H 1.24 (Bu^t, $^3J_{PH}$ 14.0 Hz), 1.30 (CH_2CH_3), and 4.12 (CH_2CH_3, $^3J_{PH}$ 7.0, $^3J_{HH}$ 7.0 Hz) (Found: C, 58.1; H, 11.55. $C_{10}H_{23}O_2P$ requires C, 58.23; H, 11.24%).

Di-t-butylvinylphosphine Oxide.—A mixture of Bu^t_2-$P(O)CH_2CH_2OPh$ (7.35 g, 26 mmol) and NaH (3.0 g, 55—60% suspension in oil, *ca.* 70 mmol) in benzene (20 ml) was stirred under reflux for 4 h. Excess of NaH was filtered off and the solvent evaporated. The residue was then dissolved in CH_2Cl_2 and the solution extracted with 2M-aqueous NaOH to remove PhO^-. The solution was dried (K_2CO_3) and the solvent evaporated to give a mixture of $Bu^t_2(CH_2=CH)PO$ and the oil originating from the NaH suspension. Vacuum distillation through a small Vigreux column without condenser gave $Bu^t_2(CH_2=CH)PO$ (3.20 g, 65%), b.p. 79—80 °C at 1.0 mmHg, m.p. 39—44 °C (strongly hygroscopic). One recrystallization from pentane gave an analytical sample, m.p. 44—46 °C. N.m.r.: δ_P 50.8; δ_H 1.24 (Bu^t, $^3J_{PH}$ 13.5 Hz) and 6.03—6.50 ($CH_2=CH$, 2nd order m) (Found: C, 64.2; H, 11.25. $C_{10}H_{21}OP$ requires C, 63.80; H, 11.25%).

Ethylenebis(di-t-butylphosphine oxide).—A solution of $Bu^t_2(CH_2=CH)PO$ (0.38 g, 2 mmol) and Bu^t_2PHO (0.33 g, 2 mmol) in toluene (20 ml) was evaporated at 1 atm to 15 ml in order to remove H_2O. A small amount of Bu^tOK in toluene was then added as a catalyst [36] and the mixture refluxed for 35 h under N_2. Evaporation of the solvent *in vacuo* and recrystallization of the residue from hexane gave $Bu^t_2P(O)CH_2CH_2P(O)Bu^t_2$ (0.46 g, 65%), m.p. 155—156 °C. N.m.r.: δ_P 59.9; δ_H 1.26 [Bu^t, $^3J_{PH}$ 13.1 Hz, d with a broad s in the middle, characteristic of $(Ar_tX_n)_2$

[33] R. G. Pearson and R. L. Dillon, *J. Amer. Chem. Soc.*, 1953, **75**, 2439.

[34] M. Fild, O. Stelzer, and R. Schmutzler, *Inorg. Synth.*, 1973, **14**, 6.

[35] H. P. Angstadt, *J. Amer. Chem. Soc.*, 1964, **86**, 5040.

[36] R. B. King, J. C. Cloyd, jun., and R. H. Reimann, *J. Org. Chem.*, 1976, **41**, 972.

systems [37]] and 2.02 (CH_2CH_2, broad s) (Found: C, 61.5; H, 11.7. $C_{18}H_{40}O_2P_2$ requires C, 61.69; H, 11.50%).

2-Bromoethyldi-t-butylphosphine Oxide.—To a stirred solution of $Bu^t_2P(O)CH_2CH_2OPh$ (2.82 g, 10 mmol) in benzene (10 ml) was added dropwise BBr_3 (0.5 ml, 5 mmol) in benzene (5 ml). The mixture was heated under reflux for 1 h, the solvent and excess of BBr_3 were removed on a rotary evaporator, and the residue was dissolved in CH_2Cl_2 and the solution extracted with 2M-aqueous NaOH to remove $(PhO)_3B$. The solution was then dried (K_2CO_3) and the solvent removed by evaporation *in vacuo* to give crude $Bu^t_2P(O)CH_2CH_2Br$ (2.45 g, 91%), m.p. 59—64 °C (hygroscopic). Two recrystallizations from pentane gave an analytical sample, m.p. 70—72 °C. N.m.r.: δ_P 59.8; δ_H 1.27 (Bu^t, $^3J_{PH}$ 13.5 Hz), 2.33 ($P-CH_2$, $^2J_{PH}$ 7.9 Hz), and 3.69 ($Br-CH_2$, $^3J_{PH}$ 3.8 Hz) (Found: C, 44.35; H, 8.15; Br, 29.0. $C_{10}H_{22}BrOP$ requires C, 44.62; H, 8.24; Br, 29.69%).

Small Scale Reactions for Product Analysis.—A stirred mixture of Bu^t_2POEt (2 mmol) and RX (2.2 mmol) was heated without solvent in an oil-bath (100—160 °C), or in absolute EtOH (1 ml) under reflux, until a withdrawn sample showed no ^1H n.m.r. signals due to Bu^t_2POEt (1—50 h). EtX and other gaseous products were allowed to escape through a trap filled with $CDCl_3$. This procedure permitted the subsequent identification of low-boiling products by ^1H n.m.r. spectroscopy and g.l.c. The reaction mixture was subjected to rotary evaporation (10 mmHg for 0.5 h) and the residue was dissolved in $CDCl_3$ and analysed by ^1H and ^1H-{^{31}P} n.m.r. The various signals due to a given compound [*e.g.* Bu^t and CH_3CN signals from $Bu^t_2P(O)CH_2CN$] were identified by ^{31}P selective decoupling (maximum decoupling effect at the same ^{31}P frequency). Compounds were identified by comparison of chemical shifts (δ_H and δ_P) and coupling constants with those for authentic samples, and in some cases also by comparison of g.l.c. retention times and mass spectra of the components of the reaction mixtures with those of authentic samples. The n.m.r. analysis was sometimes complicated by the presence of small amounts of water which altered the chemical shifts and coupling constants of many of the phosphine oxides as a result of hydrate formation. Addition of samples of the pure compounds aided identification in such cases. Relative amounts of products were estimated by measuring the heights of ^1H n.m.r. signals (mostly the intense Bu^t-doublets) and were reproducible to within $\pm5\%$ for the more abundant and $\pm20\%$ for the less abundant components. The results are given in the Table.

Preparative Scale Reactions.—Bu^t_2POMe *with* MeI. Bu^t_2POMe (3.52 g, 20 mmol) and MeI (0.28 g, 2 mmol) were mixed at 25 °C. Colourless crystals, presumably of $Bu^t_2MeP^+OMe$ I^-,[38] were formed immediately, but after 0.5—1 min the mixture became hot and boiled vigorously. Vacuum distillation through a small Claisen head gave Bu^t_2MePO (2.30 g, 65%), b.p. 67—67.5 °C at 0.5 mmHg, m.p. 35—38 °C (lit., b.p. 57 °C at 0.02 mmHg,[39] 74—75 °C at 1.5 mmHg [40]), hygroscopic. N.m.r.: δ_P 60.3; δ_H 1.28 (Bu^t, $^3J_{PH}$ 13.3 Hz) and 1.35 (Me, $^2J_{PH}$ 10.8 Hz) (Found: C, 61.05; H, 12.25. $C_9H_{21}OP$ requires C, 61.33; H, 12.01%).

Bu^t_2POEt *with* EtI. (*a*) Bu^t_2POEt (0.38 g, 2 mmol) and EtI (0.31 g, 2 mmol) were stirred at 25 °C for 24 h. The crystals formed were filtered off, washed with dry ether, and dried *in vacuo* at 25 °C for 0.5 h to give $Bu^t_2EtP^+OEt$ I^- (0.10 g, 15%), m.p. 84.5—85 °C (decomp.). N.m.r. ($CDCl_3$, 0 °C): δ_P 103.4; δ_H 1.53 (Bu^t, $^3J_{PH}$ 15.5 Hz), 3.01 (PCH_2CH_3, $^2J_{PH}$ 10.0, $^3J_{HH}$ 7.5 Hz), and 4.61 (OCH_2CH_3, $^3J_{PH}$ 4.9, $^3J_{HH}$ 6.9 Hz), CH_3 signals from both ethyl groups obscured by the Bu^t signals (Found: C, 41.3; H, 7.9; I, 36.25. $C_{12}H_{28}IOP$ requires C, 41.63; H, 8.15; I, 36.65%). The compound decomposed giving Bu^t_2EtPO and EtI with a $t_{\frac12}$ of 17 min at 30 °C in $CDCl_3$.

(*b*) Bu^t_2POEt (3.81 g, 20 mmol) and EtI (0.31 g, 2 mmol) were stirred and heated on an oil-bath (110 °C) for 1 h. Vacuum distillation through a small Claisen head gave Bu^t_2EtPO (3.25 g, 85%), b.p. 61—61.5 °C at 0.2 mmHg (lit.,[39] b.p. 73 °C at 0.1 mmHg), hygroscopic oil. N.m.r.: δ_P 59.8; δ_H 1.26 (Bu^t, $^3J_{PH}$ 12.9 Hz), 1.24 (CH_2CH_3, $^3J_{PH}$ 13.7 Hz), and 1.74 (CH_2CH_3, $^2J_{PH}$ *ca.* 8, $^3J_{HH}$ 7.7 Hz) (Found: C, 63.15; H, 12.35. $C_{10}H_{23}OP$ requires C, 63.12; H, 12.18%).

Bu^t_2POEt *with* $PhCH_2Br$. Bu^t_2POEt (1.90 g, 10 mmol) and $PhCH_2Br$ (1.71 g, 10 mmol) were heated and stirred on an oil-bath (110 °C) for 1 h. The solid reaction mixture was recrystallized from hexane to give $Bu^t_2(PhCH_2)PO$ (2.00 g, 80%), m.p. 121—121.5 °C (lit.,[13] 115—117 °C). N.m.r.: δ_P 57.7; δ_H 1.36 (Bu^t, $^3J_{PH}$ 13.2 Hz) and 3.18 (CH_2, $^2J_{PH}$ 10.6 Hz) (Found: C, 71.55; H, 10.15. $C_{15}H_{25}OP$ requires C, 71.39; H, 9.99%).

Bu^t_2POEt *with* $ClCH_2CO_2Et$. Bu^t_2POEt (3.81 g, 20 mmol) and $ClCH_2CO_2Et$ (2.70 g, 22 mmol) were heated and stirred on an oil-bath (110 °C) for 1 h. The reaction mixture was distilled *in vacuo* through a small Claisen head to give (after a small forerun) $Bu^t_2P(O)CH_2CO_2Et$ (4.40 g, 90%), b.p. 105—106 °C at 0.30 mmHg, m.p. 40—48 °C (hygroscopic). One recrystallization from hexane raised the m.p. to 49—49.5 °C. N.m.r.: δ_P 58.5; δ_H 1.33 (Bu^t, $^3J_{PH}$ 13.9 Hz), 2.92 ($P-CH_2$, $^2J_{PH}$ 11.6 Hz), and 4.19 and 1.29 (Et, $^3J_{HH}$ 7.1 Hz) (Found: C, 58.35; H, 10.3. $C_{12}H_{25}O_3P$ requires C, 58.04; H, 10.15%).

Bu^t_2POEt *with* $ClCH_2CONH_2$. Bu^t_2POEt (1.90 g, 10 mmol) and $ClCH_2CONH_2$ (0.93 g, 10 mmol) were heated and stirred on an oil-bath (110 °C) for 2 h. The reaction mixture solidified after cooling, and was ground to powder and extracted with hexane. The residue was dried *in vacuo* leaving $Bu^t_2P(O)CH_2CONH_2$ (2.01 g, 92%), m.p. 129—137 °C. One recrystallization from hexane–acetone (1 : 1) gave the pure compound, m.p. 139.5—140.5 °C. N.m.r.: δ_P 59.3; δ_H 1.31 (Bu^t, $^3J_{PH}$ 13.9 Hz), 2.72 (CH_2, $^2J_{PH}$ 8.7 Hz), and 5.9 and 8.0 (NH) (Found: C, 54.5; H, 9.9; N, 6.55. $C_{10}H_{22}NO_2P$ requires C, 54.77; H, 10.12; N, 6.39%).

Bu^t_2POEt *with* $ClCH_2CN$. (i) Bu^t_2POEt (19.0 g, 0.10 mol) was added in *ca.* 2-ml portions with stirring to $ClCH_2CN$ (8.3 g, 0.11 mol) preheated to 120 °C (bath temperature). The reaction was strongly exothermic and attachment of a reflux condenser was necessary. Vacuum distillation through a 15-cm Vigreux column without condenser gave $Bu^t_2P(O)Cl$ (8.4 g, 43%), b.p. 104—106 °C at 4.5 mmHg, m.p. 72—80 °C. Two recrystallizations from hexane raised the m.p. to 82—83 °C. The ^1H n.m.r. spectrum was identical with that of authentic $Bu^t_2P(O)Cl$.

[37] G. Hagele, R. K. Harris, and J. M. Nichols, *J.C.S. Dalton*, 1973, 79.
[38] *Cf.* A. I. Razumov and N. N. Bankovskaya, *Doklady Akad. Nauk S.S.S.R.*, 1957, **116**, 241 (*Chem. Abs.*, 1958, **52**, 6164).
[39] A. D. Brown, jun., and G. M. Kosolapoff, *J. Chem. Soc. (C)*, 1968, 839.
[40] N. J. De'ath, S. T. McNeilly, and J. A. Miller, *J.C.S. Perkin I*, 1976, 741.

Distillation of the residue gave $Bu^t_2P(OEt)CHCN$ (4.9 g, 21%), b.p. 144—146 °C at 1.1 mmHg, a yellow oil. N.m.r.: δ_P 91.8; δ_H 1.36 (Bu^t, $^3J_{PH}$ 14.9 Hz), 1.32 (CH_2CH_3), 1.45 (CHCN, $^2J_{PH}$ 4.5 Hz), and 4.14 (CH_2CH_3, $^3J_{PH}$ 9.1, $^3J_{HH}$ 7.0 Hz) (Found: C, 62.3; H, 10.05; N, 6.0. $C_{12}H_{24}NOP$ requires C, 62.85; H, 10.55; N, 6.11%).

(ii) *With addition of* HCl. To the cooled reaction mixture, prepared as above, was added dropwise 12M-aqueous HCl (4.2 ml) in order to convert $Bu^t_2P(OEt)CHCN$ into $Bu^t_2P(O)CH_2CN$ (exothermic). Vacuum distillation as above gave $Bu^t_2P(O)Cl$ (8.4 g, 43%), b.p. 104—106 °C at 4.5 mmHg, and $Bu^t_2P(O)CH_2CN$ (8.8 g, 44%), b.p. 132—134 °C at 0.9 mmHg, m.p. 79—82 °C. One recrystallization from hexane raised the m.p. to 86.5—87.5 °C. N.m.r.: δ_P 58.2; δ_H 1.41 (Bu^t, $^3J_{PH}$ 14.5 Hz) and 2.82 (CH_2CN, $^2J_{PH}$ 12.6 Hz) (Found: C, 59.75; H, 9.95; N, 6.95. $C_{10}H_{20}NOP$ requires C, 59.68; H, 10.02; N, 6.96%).

Bu^t_2POEt *with* $PhOCH_2CH_2Br$. Bu^t_2POEt (7.61 g, 40 mmol) and $PhOCH_2CH_2Br$ [41] (9.05 g, 45 mmol) were mixed in a flask fitted with a Claisen head with condenser. The mixture was stirred and heated on an oil-bath (160 °C) for 2 h. Bu^t_2EtPO and residual $PhOCH_2CH_2Br$ were removed by vacuum distillation (b.p. 56—57 °C at 0.1 mmHg) to give $Bu^t_2P(O)CH_2CH_2OPh$ (7.50 g, 66%), a yellow oil which crystallized upon cooling, m.p. 64—69 °C. Two recrystallizations from hexane gave an analytical sample, m.p. 72—73 °C. N.m.r.: δ_P 58.7; δ_H 1.28 (Bu^t, $^3J_{PH}$ 13.3 Hz), 2.24 (P–CH_2, $^2J_{PH}$ 8.4 Hz), 4.35 (O–CH_2, $^3J_{PH}$ 4.7, $^3J_{HH}$ 8.1 Hz), and 6.8—7.4 (Ph) (Found: C, 68.3; H, 9.55. $C_{16}H_{27}O_2P$ requires C, 68.05; H, 9.64%).

Bu^t_2POEt *with* $Br(CH_2)_3Br$. (i) Bu^tPOEt (5.70 g, 30 mmol) and $Br(CH_2)_3Br$ (3.03 g, 15 mmol) were mixed in a flask fitted with a Claisen head with condenser. The mixture was stirred and heated on an oil-bath (140 °C) until evolution of EtBr ceased (3 h). Vacuum distillation gave Bu^t_2EtPO (1.98 g, 35%), b.p. 56—59 °C at 0.1 mmHg, a middle fraction (0.37 g), b.p. 61—99 °C at 0.1 mmHg, and $Bu^t_2P(O)CH_2CH_2CH_2Br$ (0.65 g, 8%), b.p. 99—103 °C at 0.1 mmHg. The solid residue, consisting mainly of $Bu^t_2P(O)CH_2CH_2CH_2P(O)Bu^t_2$ (2.85 g, 50%), was recrystallized twice from hexane to give an analytical sample, m.p. 131.5—133 °C. N.m.r.: δ_P 59.8; δ_H 1.26 (Bu^t, $^3J_{PH}$ 13.1 Hz) and 1.7—2.3 ($CH_2CH_2CH_2$, m) (Found: C, 62.7; H, 11.65. $C_{19}H_{42}O_2P_2$ requires C, 62.61; H, 11.62%).

(ii) Bu^t_2POEt (5.70 g, 30 mmol) and $Br(CH_2)_3Br$ (60 g,

[41] C. S. Marvel and A. L. Tanenbaum, *Org. Synth.* Coll. Vol. I, 1958, 435.

0.3 mol) were mixed and heated as above for 2 h. Excess of $Br(CH_2)_3Br$ was removed by vacuum distillation (10 mmHg), and the residue washed with hexane leaving $Bu^t_2P(O)CH_2CH_2CH_2Br·HBr$ (8.80 g, 80%), m.p. *ca.* 220 °C (decomp.), δ_P 79.5. Allyl bromide was identified (n.m.r.) in the EtBr distillate, suggesting that $Bu^t_2P(O)CH_2CH_2$-CH_2Br had abstracted HBr from $Br(CH_2)_3Br$. The hydrobromide was dissolved in CH_2Cl_2, the solution extracted with 2M-aqueous NaOH, and the organic phase dried (K_2CO_3) and evaporated to give crude $Bu^t_2P(O)CH_2CH_2$-CH_2Br. Vacuum distillation through a 15-cm Vigreux column gave $Bu^t_2P(O)CH_2CH_2CH_2Br$ (4.20 g, 50%), b.p. 105—107 °C at 0.1 mmHg, m.p. 43—46.5 °C (hygroscopic). Two recrystallizations from pentane gave an analytical sample, m.p. 48—49 °C. N.m.r.: δ_P 59.1; δ_H 1.27 (Bu^t, $^3J_{PH}$ 13.2 Hz), 1.7—2.5 (P–CH_2CH_2, m), and 3.57 (Br–CH_2, $^3J_{HH}$ 6.0 Hz) (Found: C, 46.3; H, 8.6; Br, 27.9. $C_{11}H_{24}$-BrOP requires C, 46.55; H, 8.54; Br, 28.22%).

Bu^t_2POEt *with* $ClCH_2COCH_3$. Bu^t_2POEt (0.38 g, 2 mmol) and $ClCH_2COCH_3$ (0.21 g, 2.2 mmol) were heated and stirred on an oil-bath (110 °C) for 1 h. The reaction mixture solidified on cooling and was recrystallized once from hexane to give $Bu^t_2P(O)CH_2COCH_3$ (0.27 g, 62%), m.p. 68—70 °C. Two further recrystallizations gave an analytical sample, m.p. 70—71 °C. N.m.r.: δ_P 57.3; δ_H 1.29 (Bu^t, $^3J_{PH}$ 14.0 Hz), 2.41 (CH_3), and 2.98 (CH_2, $^2J_{PH}$ 11.0 Hz) (Found: C, 60.5; H, 10.55. $C_{11}H_{23}O_2P$ requires C, 60.53; H, 10.62%).

Bu^t_2POEt *with* $ClCH_2P(O)Ph_2$. Bu^t_2POEt (0.38 g, 2 mmol) and $ClCH_2P(O)Ph_2$ [42] (0.50 g, 2 mmol) were heated and stirred on an oil-bath (150 °C) for 50 h. The reaction mixture was extracted with hexane (10 ml) and filtered to give a solid residue (0.49 g) consisting of $Bu^t_2P(O)CH_2P(O)$-Ph_2, Ph_2MePO, and $ClCH_2P(O)Ph_2$. The residue was chromatographed [silica, Merck 0.06—0.2, eluted with $CHCl_3$–EtOH (19 : 1)] to give, as the final fraction, $Bu^t_2P(O)CH_2P(O)Ph_2$ (0.19 g, 25%), m.p. 172—173 °C (softening at 159 °C) [recrystallized from CH_2Cl_2–ether (1 : 6), gave a 1 : 1 CH_2Cl_2 solvate which decomposed at 100° *in vacuo*]. N.m.r.: δ_P 26.4 and 59.1; δ_H 1.23 (Bu^t, $^3J_{PH}$ 14.0 Hz), 2.78 (CH_2, $^2J_{PH}$ 9.8 and 16.3 Hz), and 7.4—8.2 (Ph, m) (Found: C, 66.95; H, 8.1. $C_{21}H_{30}O_2P_2$ requires C, 67.00; H, 8.03%).

[42] H. Hellmann and J. Bader, *Tetrahedron Letters*, 1961, 724.