Reactions of Tris(2,6-dimethoxyphenyl)phosphine with Epoxides

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Treatment of tris(2,6-dimethoxyphenyl)phosphine [abbr. $(2,6)_3P$] with a variety of epoxides $\overline{CH_2CR^1R^2O}$ in alcohol at room temperature readily gave the $[(2,6)_3P\text{-}CH_2CR^1R^2OH]^+$ species, which were isolated and characterized as the perchlorate salts. Thermolysis of these salts in the presence of the ethoxide anion gave the $[(2,6)_3P\text{-}Me]^+$ salt and ketone R^1R^2CO [R^1,R^2 = Me,Me; Me,Ph; Ph,Ph $(CH_2CH_2)_2CHBu^t$], the $[(2,6)_3PCH_2CHR^1OR]^+$ salt (R^1R^2 = Me,H; H,H), the $[(2,6)_3P\text{-}CH_2CH=CMeH]^+$ salt (R^1R^2 = Et,H), or the $[(2,6)_3P\text{-}CH=CPhH]^+$ salt (R^1R^2 = Ph,H), depending on the substituent of the starting epoxide; however, no phosphorus–carbon bond cleavage product was obtained. In isopropyl alcohol, demethylenation of 2-methyl-1,2-epoxypropane occurred even at room temperature.

We have recently reported that triphenylphosphines bearing methoxy substituents at the 2,6-positions of the phenyl groups, $(2,6)_3P$ and $(2,4,6)_3P$ [abbr. $(2,6)$ = $2,6\text{-}(MeO)_2C_6H_3$ and $(2,4,6)$ = $2,4,6\text{-}(MeO)_3C_6H_2$], are highly basic, and that they exhibit unusually high reactivity towards alkyl chlorides.[1] During further investigations on their highly nucleophilic behaviour mediated by the methoxy substituents, we have found high reactivity directed towards the ring-opening reaction of terminal epoxides in alcoholic solution at room temperature to give the 2-hydroxyalkylphosphonium species. Reactions of common triarylphosphines with epoxides have long been known to demand much more severe conditions.[2,3] Products of the latter reactions in protic solvent are complex mixtures of triarylphosphine oxide and alkene (*i.e.* the normal Wittig products) formed directly from betaine or oxaphosphetan intermediates and diarylalkylphosphine oxide or diarylvinylphosphine oxide formed from 2-hydroxyalkylphosphonium or vinylphosphonium intermediates by rearrangement or by loss of an aryl group.[2d,2e,3] In contrast, the quaternary phosphonium salts derived from $(2,6)_3P$ and $(2,4,6)_3P$ showed the phosphorus-carbon (P–C) bond to be highly stable and no P–C bond cleavage products were obtained, although various reactions on the 2-hydroxyalkyl groups were observed. Furthermore, no aryl-type cleavage products were isolated, *e.g.* $(2,6)_2P(O)CH_2CR^1Cl^2OH$.

Results and Discussion

Reactions investigated in the present work are summarized in the Scheme. Physical properties, analytical results, and ^1H and ^{13}C n.m.r. spectral data of the products are summarized in Tables 1—3, respectively.

Reaction of Tris(2,6-dimethoxyphenyl)phosphine with Epoxides to Form 2-Hydroxyalkyl Phosphonium Species.— When 2-methyl-1,2-epoxypropane (1a) was added to a suspension of $(2,6)_3P$ in ethanol, the mixture formed a clear solution in a few minutes. Treatment with 60% aqueous perchloric acid resulted in the formation of 2-hydroxy-2-methylpropylphosphonium perchlorate, $[(2,6)_3P\text{-}CH_2CMe_2OH]ClO_4$ (2a), in good yield. Using $(2,4,6)_3P$, we obtained an analogous salt, $[(2,4,6)_3P\text{-}CH_2CMe_2OH]ClO_4$ (3).

Triphenylphosphine was inert toward the epoxide (1a) under these conditions. On heating the mixture, (1a) was subject to alcoholysis, and some triphenylphosphine was recovered unchanged.
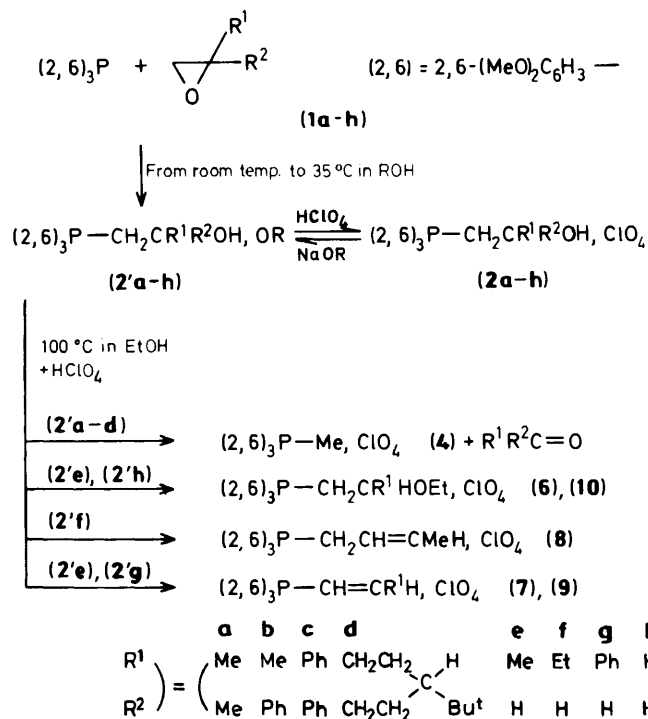
Scheme.

Treatment of $(2,6)_3P$ with the terminal epoxides (1b)—(1h) (see Scheme) in an analogous manner to that of (1a) gave the corresponding 2-hydroxyalkylphosphonium perchlorate salts (2b)—(2h) in good yields; although the reactions with α-methyl-α,β-epoxystyrene (1b) and α-phenyl-α,β-epoxystyrene (1c) were very slow at room temperature due probably to steric hindrance. 1,2-Epoxycyclohexene did not react under these conditions.

Tertiary phosphonium salts, $[(2,6)_3P\text{-}H]ClO_4$ and $[(2,4,6)_3P\text{-}H]ClO_4$, which do not react with epoxides in alcohol, gave quaternary phosphonium compounds (2a) and (3) when treated with (1a) in the presence of a catalytic amount (1/20) of $(2,6)_3P$ or $(2,4,6)_3P$ at room temperature. Other 2-hydroxyalkylphosphonium perchlorates (2e)—(2g) were also obtained using epoxides (1e)—(1g).

Characterization of 2-hydroxyalkylphosphonium perchlorates (1a)—(2h) and (3) were performed by elemental analyses (Table 1). The i.r. spectra (Table 1) showed a broad band due to $v(O-H)$, and a very strong band due to $v(ClO_4)$ at *ca.* 1 100 cm^{-1}. The ^1H n.m.r. spectra (Table 2) showed the

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Table 1. Analytical data[a] for tris(2,6-dimethoxyphenyl)phosphonium perchlorates, $[(2,6)_3P\text{-}R]ClO_4$

Compounds[b]	Method[c] (Yield %)	C%	H%	Cl%	I.r. (Nujol) (cm⁻¹)
$[(2,6)_3P\text{-}CH_2CMe_2OH]ClO_4$ (2a)	A(89)	54.6	6.0	5.7	3 520 (m, OH)
	B(85)	(54.7)	(5.9)	(5.8)	1 095 (vs, ClO_4)
$[(2,6)_3P\text{-}CH_2CMePhOH]ClO_4$ (2b)	A(76)	58.3	5.6	5.4	3 510 (m, OH)
		(58.5)	(5.7)	(5.2)	1 090 (vs, ClO_4)
$[(2,6)_3P\text{-}CH_2CPh_2OH]ClO_4$ (2c)	A(65)	61.6	5.5	4.5	3 460 (m, OH)
		(61.8)	(5.5)	(4.8)	1 100 (vs, ClO_4)
$[(2,6)_3P\text{-}CH_2C(OH)(C_2H_4)_2CHBu^i]ClO_4$ (2d)	A(94)	58.8	6.8	5.1	3 500 (m, OH)
		(59.1)	(6.8)	(5.0)	1 100 (vs, ClO_4)
$[(2,6)_3P\text{-}CH_2CMeHOH]ClO_4$ (2e)	A(92)	54.0	5.8	5.7	3 500 (m, br, OH)
	B(81)	(54.0)	(5.7)	(5.9)	1 100 (vs, ClO_4)
$[(2,6)_3P\text{-}CH_2CEtHOH]ClO_4$ (2f)	A(93)	54.6	5.9	5.8	3 500 (m, br, OH)
	B(91)	(54.7)	(5.9)	(5.8)	1 100 (vs, ClO_4)
$[(2,6)_3P\text{-}CH_2CPhHOH]ClO_4$ (2g)	A(91)	58.2	5.5	5.6	3 400 (w, br, OH)
	B(94)	(58.0)	(5.5)	(5.4)	1 095 (vs, ClO_4)
$[(2,6)_3P\text{-}CH_2CH_2OH]ClO_4$ (2h)	A(79)	53.3	5.5	6.3	3 520 (m, OH)
	C(94)	(53.2)	(5.5)	(6.0)	1 100 (vs, ClO_4)
$[(2,4,6)_3P\text{-}CH_2CMe_2OH]ClO_4$ (3)	A(95)	53.2	6.2	5.1	3 530 (m, OH)
	B(68)	(52.8)	(6.0)	(5.0)	1 095 (vs, ClO_4)
$[(2,6)_3P\text{-}Me]ClO_4$ (4)	D(90)[d]	54.2	5.6	6.5	1.095 (vs, ClO_4)
	E(87)[d,e]	(53.9)	(5.4)	(6.4)	
$[(2,4,6)_3P\text{-}Me]ClO_4$ (5)	D(92)	52.3	5.8	5.5	1 095 (vs, ClO_4)
	E(98)	(52.0)	(5.6)	(5.5)	
$[(2,6)_3P\text{-}CH_2CMeHOEt]ClO_4$ (6)	D	55.2	5.9	5.9	1 100 (vs, ClO_4)
	E	(55.4)	(6.1)	(5.6)	
$[(2,6)_3P\text{-}CH_2CH=CMeH]ClO_4$ (8)	D(52)	56.4	5.7	5.9	1 090 (vs, ClO_4
	E(54)	(56.3)	(5.7)	(5.9)	
	C(88)				
$[(2,6)_3P\text{-}CH=CPhH]ClO_4$ (9)	D(57)	59.2	5.2	5.6	1 090 (vs, ClO_4)
	E(68)	(59.6)	(5.3)	(5.5)	
$[(2,6)_3P\text{-}CH_2CH_2OEt]ClO_4$ (10)	D(76)	54.7	5.8	5.8	1 100 (vs, ClO_4)
	E(71)	(54.7)	(5.9)	(5.8)	

[a] Calculated values given in parentheses. [b] No melting point observed below 230 °C, except for (2d) 218—220 °C, (2g) 223—227 °C, (4) 200 °C decomp., and (5) 170—175 °C. [c] See Experimental section for the method. [d] From (2a). [e] 89, 89, and 86% from (2b), (2c), and (2d), respectively.

2,6-MeO proton signal as a sharp singlet, the 4-H signal as a triplet, and that of the 3,5-H as double doublets with a J_P value of 5—6 Hz. Resonance signals of the 2-hydroxyalkyl group were often very weak or broad, and characterization of all the proton resonances could not be satisfied. The ^{13}C n.m.r. spectra (Table 3) were fully consistent with the formulations, (2a)—(2h) and (3).

In order to characterize the stable species formed in solution, detailed investigations of the reaction of $(2,6)_3P$ with (1a) were performed. The ^1H n.m.r. spectrum of $(2,6)_3P$ in [$^2H_4$]methanol showed signals at δ 7.15 (t, J_H 8 Hz, 4-H), 6.47 (dd, J_H 8 Hz, J_P 3 Hz, 3,5-H), and 3.45 (s, 2,6-OMe), and those of (1a) were found at δ 2.59 (s, CH_2), and 1.29 (s, CMe_2). When these solutions were mixed in 1:1 mol ratio, the spectrum changed gradually to show new resonances at δ 7.55 (t, J_H 9 Hz), 6.71 (dd, J_H 9 Hz, J_P 5 Hz), 3.82 (d, J_P 17 Hz), 3.66 (s), and 1.18 (d, J_P 2 Hz, CMe_2). This spectrum is quite similar to that of (2a) Table 2. Thus, we believe that the stable species formed in solution is $[(2,6)_3P\text{-}CH_2CMe_2OH]OMe$ (2'a) rather than betaine or oxaphosphetan. Analogous spectral changes were observed for the mixture of $(2,4,6)_3P$ and (1a) in methanol.

Formation of the ionic species was further confirmed by conductivity measurements. Fresh methanolic $(2,6)_3P$ ($10^{-3}M$) showed a small conductivity of 6.8 Ω^{-1} cm² M^{-1} at 35 °C, probably due to the presence of an equilibrium with the tertiary phosphonium alkoxide, $[(2,6)_3P\text{-}H]OMe$. When an excess of (1a) ($10^{-1}M$) was added, the conductivity increased to ca. 74 Ω^{-1} cm² M^{-1} during 2 h. The perchlorate salt (2a) showed a molar conductivity of 95.2 Ω^{-1} cm² M^{-1} at $10^{-3}M$ at 25 °C. Analogous results were obtained for $(2,3,6)_3P$ of which the conductivity on addition of (1a) ($10^{-3}M$) varied from 20.6 Ω^{-1} cm² M^{-1} to ca. 70 Ω^{-1} cm² M^{-1} during 1 h at 35 °C, and compound (3) showed a molar conductivity of 86.1 Ω^{-1} cm² M^{-1}. The larger conductivity of $(2,4,6)_3P$ compared with that of $(2,6)_3P$ is consistent with the greater basicity of $(2,4,6)_3P$[1] and the increased formation of $[(2,4,6)_3P\text{-}H]OMe$ in equilibrium. Condutivity of ethanolic solutions of $(2,6)_3P$, and $(2,4,6)_3P$, in the presence of (1a) behaved essentially in an analogous manner. In acetone, benzene, or chloroform, the reactions of $(2,6)_3P$ and (1a) did not occur under these conditions.

Thermal Degradation of 2-Hydroxyalkylphosphonium Species.—When a methanolic solution of $[(2,6)_3P\text{-}CH_2CMe_2OH]OR$ (2'a) was heated at 100 °C, the ^1H n.m.r. spectrum showed the formation of a new species. A new $C(Me)_2$ proton signal observed as a singlet at δ 2.13 replaced the original doublet at δ 1.18, and new signals for the (2,6) group at δ 7.60 t, 6.77 dd, and 3.59 s also appeared. In addition, a new doublet appeared clearly beside the solvent side band (δ 2.63) at δ 2.63 with J_P of 15 Hz. Resonances at δ 2.13 s and 2.63 d were absent in the spectrum of [$^2H_4$]methanol solution, suggesting that these protons are H-D exchangeable. The presence of an excess of (1a) allowed an additional new singlet to be observed at δ 1.17 due to the formation of 1-methoxy-2-methylpropan-2-ol.

The thermal reaction in methanol was complete in ca. 6 h at 100 °C and treatment of the resultant solution with 60% aqueous perchloric acid gave $[(2,6)_3P\text{-}Me]ClO_4$ (4) in 87% yield. The above ^1H n.m.r. spectrum of the reaction mixture in methanol was found to be quite similar to that of a mixture of compound (4) and acetone (δ 2.14), suggesting thermal

Table 2. [1]H N.m.r. spectral data[a] for tris(2,6-dimethoxyphenyl)-phosphonium perchlorates

Compd.	4-H[b]	3,5-H[c]	2,6-OMe[d]	Other relevant resonances[e]
(2a)	7.56	6.65	3.69	3.80d[16]$_P$(PCH$_2$), 1.14d[2]$_P$(CMe)
(2a)[f]	7.54	6.71	3.66	3.83d[17]$_P$(PCH$_2$), 1.18d[2]$_P$(CMe)
(2b)	7.42	6.49	3.57	7.1br(Ph), 4.1m(PCH$_2$), 1.49d[3]$_D$(CMe)
(2c)	7.42	6.45	3.42	7.2m(Ph), 4.84d[18]$_P$(PCH$_2$)
(2d)	7.51	6.61	3.68	3.68d[17]$_P$(PCH$_2$), 1.36br(C$_2$H$_4$), 0.78s(CMe)
(2e)	7.53	6.62	3.67	1.29d and 1.26d[6](CMe)
(2f)	7.53	6.63	3.66	0.89t[8]$_H$(CMe)
(2g)	7.54	6.64	3.64	7.3br (Ph)
(2h)[g]	7.54	6.63	3.61	3.5br(PCH$_2$)
(3)		6.15[h]	3.66	3.87s(4-MeO), overlapped (PCH$_2$), 1.19d[2]$_P$(PMe)
(3)[f]		6.25[h]	3.66	3.86s(4-MeO), 3.68d[17]$_P$(PCH$_2$), 1.17d[2]$_P$(CMe)
(4)	7.55	6.55	3.57	2.60d[15]$_P$(PMe)
(4)[f]	7.58	6.74	3.59	2.61s[15]$_P$(PMe)
(5)		6.14[h]	3.59	3.89s(4-MeO), 2.49d[15]$_P$(PMe)
(6)	7.52	6.62	2.63	1.23dd[6]$_P$[6]$_H$(CMe), 0.76t[7]$_H$(CMe)
(7)	7.55	6.64	3.61	2.00ddd[7][3][2](CMe)
(8)	7.52	6.61	3.60	5.3br(CH=CH), 3.89dd[18]$_P$[5]$_H$(CH$_2$), 1.44dd[5][5](CMe)
(9)	7.57	6.65	3.61	7.4br (Ph)
(10)	7.56	6.63	3.61	3.34m(PCH$_2$), 1.06t[7]$_H$(CMe)

[a] In CDCl$_3$ (δ, s = singlet, d = doublet, t = triplet, m = multiplet, and br = broad. [b] Triplet with J_H 8—9 Hz. [c] Doublet doublets with J_H 8—9 Hz and J_P 5—6 Hz. [d] Singlet. [e] J_H or J_P (in Hz) given in square brackets. [f] In CD$_3$OD or CH$_3$OH. [g] In CH$_2$Cl$_2$. [h] Doublet with J_P 5 Hz.

Table 3. [13]C N.m.r. spectral data[a] for tris(2,6-dimethoxyphenyl)-phosphonium perchlorates

Compd.	δ (p.p.m.) in CDCl$_3$
(2a)	100.9d[106], 162.3s, 104.4d[8], 135.3s, 55.9s, 38.1d[55], 70.0d[6], 31.9d[7]
(2b)	100.7d[101], 162.0s, 104.3d[7], 135.1s, 55.8s, 38.9d[58], 72.6d[6], 36.0d[7], 147.7d[2], 127.8s, 126.0s, 123.8s
(2c)	100.0d[107], 161.9s, 104.4d[7], 135.1s, 55.7s, 39.6d[62], (74.6),[b] 148.4d[4], 128.3s, 126.4s, 124.4s
(2d)	101.2d[98], 162.3s, 104.4d[7], 135.2s, 60.0s, 39.0d[55], 70.5d[6], 47.3s, 39.9d[7], 32.2s, 27.4s, 22.8s
(2e)	100.2d[99], 162.3s, 104.4d[7], 135.3s, 56.0s, 35.8d[56], 64.3c[4], 25.2d[14]
(2f)	100.5d[99], 162.3s, 104.5d[7], 135.4s, 56.1s, 34.3d[54], 69.3d[5], 32.3d[15], 10.1s
(2g)	100.0d[99], 162.4s, 104.6d[7], 135.3s, 56.1s, 35.5d[56], 70.1s, 143.7d[12], 128.8s, 127.9s, 125.3s
(2h)[c]	100.5d[99], 163.2s, 104.9d[7], 136.0s, 56.5s, 31.0d[54], 58.4s
(3)	92.9d[105], 163.5d[2], 91.1d[7], 165.5d[2], 55.9s, (36.5),[b] 70.0d[6], 31.9d[7]
(4)	101.2d[103], 162.5s, 104.8d[7], 135.7s, 56.2s, 17.4d[64]
(5)	93.1d[107], 163.7s, 91.4d[6], 165.8s, 59.9s, 18.0d[68], 55.9s
(6)	100.2d[99], 162.5s, 104.2d[7], 135.2s, 55.9s, 34.6d[56], 70.9d[4], 63.3s, 20.7d[16], 15.0s
(7)	99.9d[103], 162.5s, 104.6d[7], 135.6s, 56.0s, 115.1d[94], 145.9d[3], 20.6d[24]
(8)	100.1d[97], 162.3s, 104.4d[7], 135.5s, 56.0s, 32.7d[54], 132.4d[18], 120.4d[9], 18.0d[3]
(9)	99.7d[104], 162.6s, 104.7d[7], 135.9s, 56.2s, 112.1d[99], 145.2d[6], 134.6s, 130.3s, 129.2s, 127.5s
(10)	99.5d[99], 162.5s, 104.4d[7], 135.7s, 56.0s, 27.8d[59], 65.3d[2], 66.3s, 15.0s

[a] In the order of C-1, C-2,6, C-3,5, C-4, MeO-2,6, C-1', C-2', and others; s = singlet, d = doublet; J_P (in Hz) given in square brackets. [b] One of the doublet peaks must be obscured by the other peak. [c] In CD$_2$Cl$_2$.

elimination of acetone from (2'a) to give [(2,6)$_3$P-Me]OR (4') in methanol. The presence of acetone in the reaction mixture was further confirmed by gas chromatography.

Thermal elimination of acetone from (2'a) was faster in ethanol than in methanol ($t_{\frac{1}{2}}$, ca. 1 h), reaction being complete in ca. 1 h at 100 °C. Acetone elimination from a mixture of (2,6)$_3$P and (1a) in isopropyl alcohol, proceeded even at room temperature, completing in ca. 5 h.

The perchlorate salt (2a) was stable in alcohols at 100 °C, but in the presence of sodium alkoxide it was degraded to give (4) and acetone. Analogous results were obtained for [(2,4,6)$_3$P-CH$_2$CMe$_2$OH]OR (3') and (3) to give [(2,4,6)$_3$P-Me]OR (5') or [(2,4,6)$_3$P-Me]ClO$_4$ (5) and acetone, respectively. The degradation of (3') was several times slower than that of (2'a), due probably to the lower acidity of the 2-hydroxy proton in (3').

Reaction between compound (2'a) and benzaldehyde or butan-2-one during partial thermal reaction was not observed, indicating that degradation to the methylphosphonium salt and acetone is irreversible.

In the presence of sodium alkoxide the 2-hydroxyalkyl-phosphonium salts (2b)—(2d) was also degraded in a manner analogous to (2a). The ketones were characterized by i.r. and [1]H n.m.r. spectroscopy and by 2,4-dinitrophenylhydrazone formation.

Thermolyses of the salts (2e)—(2h) in basic ethanol, gave different types of product. The salt (2e) gave a mixture of two products, [(2,6)$_3$P-CH$_2$CMeHOEt]ClO$_4$ (6) and possibly [(2,6)$_2$P-CH=CMeH]ClO$_4$ (7), as indicated by the [13]C n.m.r. spectra (Table 3). The relative ratio of the products (6) and (7)

was ca. 80:20—50:50, and the former was isolated pure by recrystallization. In contrast, the salt (2f), gave the allyl-phosphonium salt, [(2,6)$_3$P-CH$_2$CH=CMeH]ClO$_4$ (8), which was identified by the separate preparaton from (2,6)$_3$P and ClCH$_2$CH=CMeH. Thermolysis of the salt (2g) yielded the vinylphosphonium salt, [(2,6)$_3$P-CH=CPhH]ClO$_4$ (9), whilst the salt (2h) gave the 2-ethoxyethylphosphonium salt, [(2,6)$_3$P-CH$_2$CH$_2$OEt]ClO$_4$ (10), which probably formed via [(2,6)$_3$P-CH=CH$_2$]OEt. Compounds (6)—(10) were also thermal degradation products from the [(2,6)$_3$P-CH$_2$CR[1]HOH]OEt intermediates formed in situ from (2,6)$_3$P and the epoxides (1e)—(1h) in ethanol.

The inertness of the P–C bonds to thermolysis can readily be explained by both the steric and electronic effects of the 2,6-methoxy substituents. However, the most attractive explanation involves the formation of an interaction between the phsophorus atom and one or more of the 2,6-methoxy oxygens in the phosphonium species. The presence of such interactions may interfer both sterically and electronically with additional co-ordination by oxy anions, a key step for P–C bond cleavage.[3] The possibility of a simple electronic effect cannot be excluded, since Wittig et al., have reported that a betaine formed from tris(4-methoxyphenyl)phosphine and benzaldehyde was stable to P–C bond cleavage for 16 h at 65 °C,[4] conditions less severe than those of our studies.

The ketone eliminations from the salts (2a—d), and the demethylenations from the terminal epoxides (1a—d) by (2,6)$_3$P, are of interest, since these reactions involve the reversal of a reaction step of the well-known Wittig reaction.[5] A closely related reaction was reported by Jones and Trippett,[6] who

treated Ph_2PNa with *trans*-stilbene oxide in THF, and obtained $Ph_2(PhCH_2)P$.

Formation of the vinylphosphonium salts (7) and (9) and the 2-alkoxyalkylphosphonium salts (6) and (10) from the 2-hydroxyalkylphosphonium salts (2e—h) are essentially identical with those observed for $[Ph_3P-CH_2CH_2OPh]Br$.[7] However, reaction of sodium ethoxide with $[Ph_3P-CH_2CH_2OH]I$ has been shown to cause cleavage of the P–C bond to yield $Ph_2P(O)CH_2CH_2OEt$.[8]

Experimental

[1]H N.m.r. spectra were obtained on a JEOL model JNM-PS-100 spectrometer operating at 100 MHz, using $SiMe_4$ as internal standard. [13]C N.m.r. spectra were recorded on a JEOL model JNM-FX-60S spectrometer operating at 15 MHz using $SiMe_4$ as internal standard. I.r. spectra were recorded on a Hitachi model 215 spectrometer. Mass spectra were obtained on a Hitachi model RMU-6E mass spectrometer.

Reagents.—Tris(2,6-dimethoxyphenyl)phosphine, $(2,6)_3P$, tris(2,4,6-trimethoxyphenyl)phosphine, $(2,4,6)_3P$, and their tertiary phosphonium perchlorates were prepared as described previously.[1] 2-Methyl-1,2-epoxypropane (1a), 1,2-epoxypropane (1e), 1,2-epoxybutane (1f), and α,β-epoxy styrene (1g) were obtained from Tokyou Kasei Co., and were used as purchased. The α-methyl-α,β-epoxystyrene (1b), α-phenyl-α,β-epoxystyrene. (1c), and 4-t-butylcyclohexane-2'-oxirane (1d) were prepared according to the method developed by Corey and Chaykovsky.[9]

Formation of 2-Hydroxyalkylphosphonium Salts.—*Method A.* To a suspenson of $(2,6)_3P$ (0.442 g, 1 mmol) in ethanol (10 cm³) was added (1a) (0.4 cm³, in excess) to give after a few minutes a clear solution. The mixture was then stirred for 0.5—3 h at room temperature after which addition of 60% aqueous perchloric acid (0.4—0.5 cm³) and cooling at 0 °C gave crystalline $[(2,6)_3P-CH_2CMe_2OH]ClO_4$ (2a) (89%); recrystallization from ethanol afforded an analytical sample. Analogous treatment in isopropyl alcohol (room temp., 3—5 h) resulted in the formation of $[(2,6)_3P-Me]ClO_4$ (4) (94%).

Reactions with (1b) and (1c) required prolonged stirring (22—48 h) at room temperature or at 35 °C to give $[(2,6)_3P-CH_2CMePhOH]ClO_4$ (2b) or $[(2,6)_3P-CH_2CPh_2OH]ClO_4$ (2c), respectively. Other epoxides, (1d—h), were treated with $(2,6)_3P$ in a similar manner to (1a) to yield the corresponding 2-hydroxyalkylphosphonium perchlorates, (2d—h). The reaction of $(2,4,6)_3P$ with (1a) proceeded in a manner similar to $(2,6)_3P$ to give $[(2,4,6)_3P-CH_2CMe_2OH]ClO_4$ (3).

Method B. To a suspension of $[(2,6)_3P-H]ClO_4$ (0.523 g, 1 mmol) in ethanol (10 cm³) was added (1a) (0.4 cm³, in excess) followed by $(2,6)_3P$ (0.022 g, 0.05 mmol). The mixture was stirred for 3—5 h to aid precipitation of the salt (2a). The reaction proceeded without forming a homogeneous solution.

Reactions with epoxides (1e)—(1g) were performed a manner similar to (1a) to give the corresponding 2-hydroxyalkylphosphonium perchlorates (2e)—(2g). Similarly, $[(2,4,6)_3P-H]ClO_4$ was treated with (1a) using $(2,4,6)_3P$ as catalyst to give (3).

Method C. A mixture of $(2,6)_3P$ (2 mmol) and 2-chloroethanol (0.5 cm³, in excess) in ethanol (10 cm³) was heated in a sealed glass tube at 100 °C for 6 h. Addition of 60% aqueous perchloric acid (0.8 cm³) followed by cooling to 0 °C resulted in the formation of crystals of $[(2,6)_3P-CH_2CH_2OH]ClO_4$ (2h).

A mixture of $(2,6)_3P$ (1 mmol) and $CH_3CH=CHCH_2Cl$ (0.4 cm³, in excess) in ethanol (10 cm³) was stirred at room temperature for 2 h to give a clear solution. Addition of 60% aqueous $HClO_4$ (0.2 cm³) gave a white precipitate of the allylphosphonium salt $[(2,6)_3P-CH_2CH=CMeH]ClO_4$ (8), which was recrystallized from ethanol.

Thermal Reactions of 2-Hydroxyalkylphosphonium Salts at Basic Conditions.—*Method D.* A solution of (2a) (1 mmol) in ethanol (10 cm³) containing NaOEt (1 mmol) was heated in a sealed glass tube at 100 °C for 1 h. The resultant clear solution was cooled to 0 °C to give white crystals of $[(2,6)_3P-Me]ClO_4$ (4).

Analogous treatments of salts (2b)—(2d) or (3) gave (4) or $[(2,4,6)_3P-Me]ClO_4$ (5) respectively, in good yields. Treatment of (2f—h) gave $[(2,6)_2P-CH_2CH=CMeH]ClO_4$ (8), $[(2,6)_3P-CH=CPhH]ClO_4$ (9), or $[(2,6)_3P-CH_2CH_2OEt]ClO_4$ (10), respectively. Treatment of the salt (2e) (1—48 h at 100 °C) resulted in a mixture, as seen in the observation of two 2,6-OMe proton signals in the [1]H n.m.r. spectra. The mixture was repeatedly recrystallized from ethanol to give $[(2,6)_3P-CH_2CMeHOEt]ClO_4$ (6).

Method E. A solution of $[(2,4,6)_3P-CH_2CMe_2OH]OEt$ was prepared by Method A using $(2,4,6)_3P$ (0.583 g, 1 mmol) and (1a) (0.4 cm³, in excess) in ethanol (10 cm³). The clear solution was heated in a sealed glass tube at 100 °C for 6 h, and then treated with 60% aqueous perchloric acid (0.4 cm³) to yield (5).

Analogous treatments of $(2,6)_3P$ and epoxides (1a—f) resulted in the formation of the same compounds as those obtained by method D, respectively.

Characterization of Ketones.—The filtrate obtained by method E from $(2,6)_3P$ and (1a) was distilled and the distillate employed for the [1]H n.m.r. and gas chromatography analyses for the detection of acetone. The filtrates obtained by method D for (2b), (2c), and (2d) were concentrated to dryness, and the residues used for i.r. and [1]H n.m.r. spectroscopy, as well as for the hydrazone formation using ethanolic 2,4-dinitrophenylhydrazine: the yields of the ketone or hydrazone were 83, 67, and 66% for acetophenone, benzophenone, and 4-t-butylcyclohexanone, respectively.

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