

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 $\text{CH}_2\text{CR}^1\text{R}^2\text{O}$ in alcohol at room temperature readily gave the $[(2,6)_3\text{P}-\text{CH}_2\text{CR}^1\text{R}^2\text{OH}]^+$ species, which were isolated and characterized as the perchlorate salts. Thermolysis of these salts in the presence of the ethoxide anion gave the $[(2,6)_3\text{P}-\text{Me}]^+$ salt and ketone $\text{R}^1\text{R}^2\text{CO}$ [$\text{R}^1, \text{R}^2 = \text{Me, Me; Me, Ph; Ph, Ph}$ (CH_2CH_2)₂ CHBu^t], the $[(2,6)_3\text{PCH}_2\text{CHR}^1\text{OR}]^+$ salt ($\text{R}^1\text{R}^2 = \text{Me, H; H, H}$), the $[(2,6)_3\text{P}-\text{CH}_2\text{CH}=\text{CMeH}]^+$ salt ($\text{R}^1\text{R}^2 = \text{Et, H}$), or the $[(2,6)_3\text{P}-\text{CH}=\text{CPhH}]^+$ salt ($\text{R}^1\text{R}^2 = \text{Ph, H}$), 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.

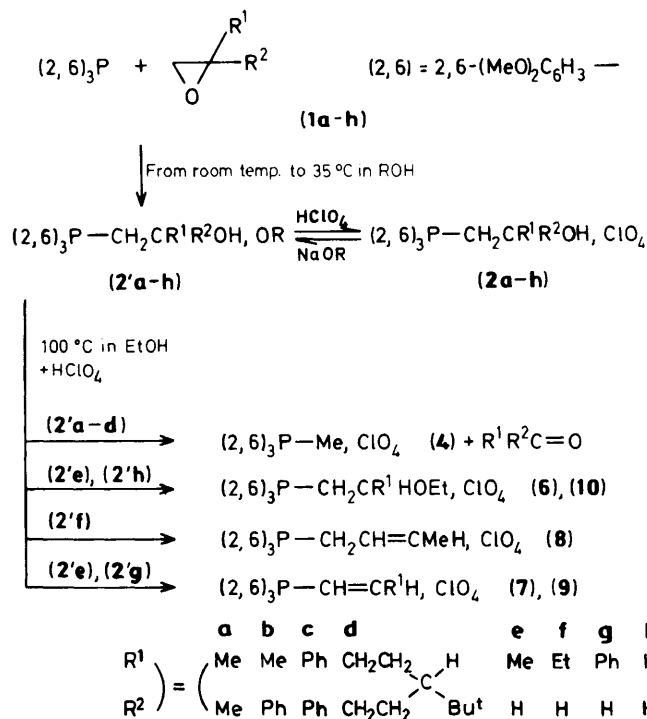
We have recently reported that triphenylphosphines bearing methoxy substituents at the 2,6-positions of the phenyl groups, (2,6)₃P and (2,4,6)₃P [abbr. (2,6) = 2,6-(MeO)₂C₆H₃ and (2,4,6) = 2,4,6-(MeO)₃C₆H₂], are highly basic, and that they exhibit unusually high reactivity towards alkyl chlorides.¹ During 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)CH₂CR¹Cl²OH.

Results and Discussion

Reactions investigated in the present work are summarized in the Scheme. Physical properties, analytical results, and ¹H and ¹³C 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-CH₂CMe₂OH]⁺ClO₄[−] (**2a**), in good yield. Using (2,4,6)₃P, we obtained an analogous salt, [(2,4,6)₃P-CH₂CMe₂OH]⁺ClO₄[−] (**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.



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-Epoxy-cyclohexene did not react under these conditions.

Tertiary phosphonium salts, [(2,6)₃P-H]⁺ClO₄[−] and [(2,4,6)₃P-H]⁺ClO₄[−], 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 ν(O-H), and a very strong band due to ν(ClO₄) at *ca.* 1100 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-R]ClO₄

| Compounds ^b | Method ^c (Yield %) | C% | H% | Cl% | I.r. (Nujol) (cm ⁻¹) |
|--|----------------------------------|--------|-------|-------|----------------------------------|
| [(2,6) ₃ P-CH ₂ CMe ₂ OH]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) ₃ P-CH ₂ CMePhOH]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) ₃ P-CH ₂ CPh ₂ OH]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) ₃ P-CH ₂ C(OH)(C ₂ H ₅) ₂ CHBu ^t]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) ₃ P-CH ₂ CMeHOH]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) ₃ P-CH ₂ CEtHOH]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) ₃ P-CH ₂ CPhHOH]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) ₃ P-CH ₂ CH ₂ OH]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) ₃ P-CH ₂ CMe ₂ OH]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) ₃ P-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) ₃ P-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) ₃ P-CH ₂ CMeHOEt]ClO ₄ (6) | D | 55.2 | 5.9 | 5.9 | 1 100 (vs, ClO ₄) |
| | E | (55.4) | (6.1) | (5.6) | |
| [(2,6) ₃ P-CH ₂ CH=CMcH]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) ₃ P-CH=CPH]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) ₃ P-CH ₂ CH ₂ OEt]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 ¹³C 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 [2H₄]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, CH₂), and 1.29 (s, CMe₂). 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, CMe₂). 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-CH₂CMe₂OH]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 (10⁻³M) 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-H]OMe. When an excess of (**1a**) (10⁻¹M) 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 10⁻³M at 25 °C. Analogous results were obtained for (2,3,6)₃P of which the conductivity on

addition of (**1a**) (10⁻³M) 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)₃P¹ and the increased formation of [(2,4,6)₃P-H]OMe in equilibrium. Conductivity 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-CH₂CMe₂OH]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 [2H₄]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-Me]ClO₄ (**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. ^1H 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] _p (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] _p [3] _p [2] _p (CMe) |
| (8) | 7.52 | 6.61 | 3.60 | 5.3br(CH=CH), 3.89dd[18] _p [5] _H (CH ₂), 1.44dd[5] _p [5] _H (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 CDCl₃ (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 CD₃OD or CH₃OH. ^g In CH₂Cl₂. ^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 CD₂Cl₂.

elimination of acetone from (2'a) to give [(2,6)₃P-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 ($t_{1/2}$, ca. 1 h), reaction being complete in ca. 1 h at 100 °C. Acetone elimination from a mixture of (2,6)₃P 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)₃P-CH₂CMe₂OH]OR (3') and (3) to give [(2,4,6)₃P-Me]OR (5') or [(2,4,6)₃P-Me]ClO₄ (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-hydroxyalkylphosphonium salts (2b)–(2d) was also degraded in a manner analogous to (2a). The ketones were characterized by i.r. and ^1H n.m.r. spectroscopy and by 2,4-dinitrophenylhydrazine 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)₃P-CH₂CMeHOEt]ClO₄ (6) and possibly [(2,6)₂P-CH=CMeH]ClO₄ (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 allylphosphonium salt, [(2,6)₃P-CH₂CH=CMeH]ClO₄ (8), which was identified by the separate preparation from (2,6)₃P and ClCH₂CH=CMeH. Thermolysis of the salt (2g) yielded the vinylphosphonium salt, [(2,6)₃P-CH=CPhH]ClO₄ (9), whilst the salt (2h) gave the 2-ethoxyethylphosphonium salt, [(2,6)₃P-CH₂CH₂OEt]ClO₄ (10), which probably formed *via* [(2,6)₃P-CH=CH₂]OEt. Compounds (6)–(10) were also thermal degradation products from the [(2,6)₃P-CH₂CH₂OH]OEt intermediates formed *in situ* from (2,6)₃P 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 phosphorus atom and one or more of the 2,6-methoxy oxygens in the phosphonium species. The presence of such interactions may interfere 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)₃P, 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 $\text{Ph}_2(\text{PhCH}_2)\text{P}$.

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 $[\text{Ph}_3\text{P}-\text{CH}_2\text{CH}_2\text{OPh}]\text{Br}$.⁷ However, reaction of sodium ethoxide with $[\text{Ph}_3\text{P}-\text{CH}_2\text{CH}_2\text{OH}]\text{I}$ has been shown to cause cleavage of the P–C bond to yield $\text{Ph}_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{OEt}$.⁸

Experimental

¹H N.m.r. spectra were obtained on a JEOL model JNM-PS-100 spectrometer operating at 100 MHz, using SiMe_4 as internal standard. ¹³C 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 suspension 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-CH₂CMe₂OH]ClO₄ (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]ClO₄ (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-CH₂CMePhOH]ClO₄ (2b) or [(2,6)₃P-CH₂CPh₂OH]ClO₄ (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-CH₂CMe₂OH]ClO₄ (3).

Method B. To a suspension of [(2,6)₃P-H]ClO₄ (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 in a manner similar to (1a) to give the corresponding 2-hydroxyalkylphosphonium perchlorates (2e)–(2g). Similarly, [(2,4,6)₃P-H]ClO₄ 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-CH₂CH₂OH]ClO₄ (2h).

A mixture of (2,6)₃P (1 mmol) and $\text{CH}_3\text{CH}=\text{CHCH}_2\text{Cl}$ (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 HClO₄ (0.2 cm³) gave a white precipitate of the allylphosphonium salt [(2,6)₃P-CH₂CH=CHMe]ClO₄ (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]ClO₄ (4).

Analogous treatments of salts (2b)–(2d) or (3) gave (4) or [(2,4,6)₃P-Me]ClO₄ (5) respectively, in good yields. Treatment of (2f–h) gave [(2,6)₂P-CH₂CH=CHMe]ClO₄ (8), [(2,6)₃P-CH=CHPh]ClO₄ (9), or [(2,6)₃P-CH₂CH₂OEt]ClO₄ (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 ¹H n.m.r. spectra. The mixture was repeatedly recrystallized from ethanol to give [(2,6)₃P-CH₂CMeHOEt]ClO₄ (6).

Method E. A solution of [(2,4,6)₃P-CH₂CMe₂OH]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 ¹H 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 ¹H 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.

Acknowledgements

Financial support by a Grant-in-Aid for Scientific Research (No. 60550611) from the Ministry of Education, Science, and Culture is gratefully acknowledged.

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