Electrochemical Preparation and Some Reactions of Alkoxy Triphenylphosphonium Ions

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The formation of an alkoxy triphenylphosphonium ion by anodic oxidation of Ph_3P in the presence of an alcohol was reinvestigated. When a CH_2Cl_2 solution of Ph_3P, $Ph_3P^+H \cdot ClO_4^-$, and an alcohol was subjected to constant-current electrolysis in an undivided cell equipped with a graphite anode and a Pt cathode, the ^{31}P-NMR spectra of the resulting electrolyte showed that alkoxy triphenylphosphonium perchlorates (2) were formed in good to fair yields from primary and secondary aliphatic alcohols, while allylic and benzylic alcohols were transformed to the corresponding alkyl phosphonium ions, and in the case of tertiary aliphatic alcohols, no formation of the corresponding alkoxy or alkyl phosphonium ions was recognized at all. The isolation of 2 thus formed was achieved in good yields by a simple procedure. For the electrolysis, $Ph_3P^+H \cdot BF_4^-$ could be utilized instead of the perchlorate salt, giving an alkoxy triphenylphosphonium tetrafluoroborate (3) from primary and secondary aliphatic alcohols. The reaction of the alkoxy phosphonium ions prepared from β- and α-cholestanol with various nucleophiles such as $Bu_4N^+ \cdot X^-$ (X = Br, Cl, F, N_3, SCN), PhSH, and PhOH was examined. The results indicated that the reaction site of the phosphonium ions is dictated by the identity of the nucleophile. A soft nucleophile was apt to attack at the α-carbon, giving the corresponding S_N2 reaction product in a good yield, while a hard one tended to react at the phosphorus of the phosphonium ion, leading to the regeneration of the cholestanol.

Key words triphenylphosphine; alkoxy triphenylphosphonium ion; anodic oxidation; alcohol; constant-current electrolysis; nucleophilic substitution reaction

Previously, we reported that when a mixture of Ph_3P, an alcohol, and $NaClO_4$ in CH_3CN was subjected to anodic oxidation by controlled-potential electrolysis in a divided cell, the corresponding alkoxy triphenylphosphonium perchlorate (**2**) was obtained in a moderate yield only from an aliphatic primary alcohol.[1] The method seems to be limited by the reaction of **2** with nucleophilic species in the medium, such as Ph_3P, the alcohol, and contaminating H_2O.

In our studies on the electrochemistry of organophosphorus compounds, it has been found that the anodic generation of an acyloxy triphenylphosphonium ion as a synthetically useful active intermediate from Ph_3P and a carboxylic acid can be effectively achieved by employing $Ph_3P^+H \cdot ClO_4^-$ and CH_2Cl_2 as a supporting electrolyte and a solvent, respectively.[2] One of the important roles of $Ph_3P^+H \cdot ClO_4^-$ in the electrolysis is to eliminate the *in situ* formation of an acid anhydride from the acyloxy phosphonium ion and the carboxylic acid. A similar effect of the perchlorate salt can be expected in the electrochemical formation of an alkoxy phosphonium ion. Thus, we have reinvestigated the possibility of using the Ph_3P–$Ph_3P^+H \cdot X^-$–CH_2Cl_2 system as an electrochemical tool to prepare alkoxy triphenylphosphonium ions from various alcohols for the following reasons: (1) examination of the reactivity of isolated alkoxy phosphonium ions, especially those derived from secondary alcohols, in nucleophilic substitution will afford useful information on the mechanism of the Mitsunobu reaction, in which an alkoxy phosphonium ion is suggested to be a key intermediate in the step giving the condensation product of an alcohol with an acidic compound, although controversy remains about this[3,4]; (2) study of the cathodic reduction of the phosphonium ions themselves will shed light on the mechanism of the unique electrochemical one-step deoxygenation of alcohols to the corresponding alkanes reported by us, in which anodically generated alkoxy phosphonium ions might be reduced *in situ* to the product and $Ph_3P=O$.[5]

In this paper, we report a revised electrochemical method to prepare effectively alkoxy phosphonium ions from primary and secondary aliphatic alcohols (Chart 1), together with reactions of the phosphonium ions derived from secondary alcohols, that is, α- and β-cholestanol, with some nucleophiles.

Results and Discussion

Cathodic reduction of $Ph_3P^+H \cdot ClO_4^-$ generates Ph_3P as well as H_2 gas. Accordingly, when a solution of $Ph_3P^+H \cdot ClO_4^-$ and an alcohol is subjected to electrolysis in an undivided cell, the electrochemical reaction initiated by anodic oxidation of Ph_3P can be theoretically achieved without adding the phosphine itself. Thus, the effects of the amount of Ph_3P upon the electrochemical formation of **2** were first examined. As a model compound, β-phenethyl alcohol (**1c**) was chosen. A mixture of **1c**, $Ph_3P^+H \cdot ClO_4^-$ (3 mmol each), and various amounts of Ph_3P in CH_2Cl_2 was subjected to constant-current electrolysis (CCE) (30 mA, 3 F/mol on **1c**) in an undivided cell equipped with a graphite plate anode and a Pt foil

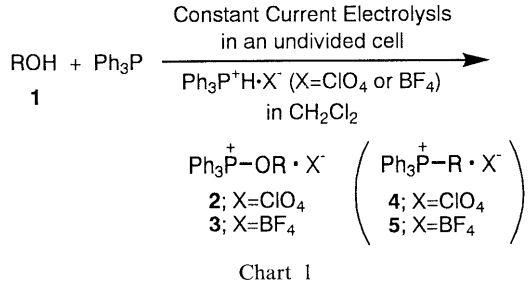

Chart 1

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cathode under an N_2 atmosphere. The crude products obtained in each electrolysis were analyzed by ^{31}P-NMR spectroscopy in $CDCl_3$ using 5% H_3PO_4 in D_2O as an external standard, and the ratio between the alkoxy phosphonium ion **2c** and a by-product, β-phenethyl triphenylphosphonium perchlorate (**4c**), was estimated. As the amount of Ph_3P in the electrolysis was increased, the peak at 61.70 ppm due to **2c** increased and that at 22.61 ppm for **4c** decreased, and in the presence of the phosphine in an amount equimolar with **1c**, only the former peak was observed, along with two peaks at −5.94 and 28.82 ppm attributed to Ph_3P and $Ph_3P=O$, respectively, and the latter peak disappeared, contrary to our expectation that the increment in the amount of the phosphine would cause the formation of a larger amount of **4c**. The findings could be explained as follows, though no definite evidence is available at present: the transformation of **2c** to **4c** is an acid-catalyzed process, and an increase in the amount of Ph_3P will reduce the acidity of the electrolyte solution, tending to prevent the formation of **4c**. On the basis of these results, an equimolar mixture of Ph_3P, $Ph_3P^+H \cdot ClO_4^-$, and **1c** in CH_2Cl_2 was subjected to CCE, leading to the exclusive formation of **2c** in 90% yield, as estimated from the spectroscopic analysis, and the product was isolated in 84% yield by a simple procedure (see Experimental).

With the conditions for the effective formation of **2c** in hand, the electrochemical preparation of **2** from various alcohols depicted in Chart 2 was performed. The results are summarized in Table 1.

When a primary or a secondary aliphatic alcohol such as **1a**—**1e** and **1g** was subjected to CCE, almost quantitative formation of the corresponding alkoxy phosphonium ion **2** was observed on ^{31}P-NMR spectroscopy and **2** was isolated in a fair to good yield, except for **2d**. The low isolated yield of **2d** was due to its instability, which was apparent from the fact that the phosphonium ion decomposed into the starting alcohol **1d** and $Ph_3P=O$ within several hours after its isolation.

A similar spectroscopic analysis showed that the electrolysis of a tertiary aliphatic alcohol **1j** or **1k** did not give a phosphorus-containing compound other than Ph_3P and $Ph_3P=O$, in spite of recovery of the alcohol in a small amount. The results indicated that the alkoxy phosphonium ions generated from **1j** and **1k** would be transformed during the electrolysis into the corresponding alkenes and/or react with the alcohol to give an ether, although no attempt was made to confirm the formation of such products. The ^{31}P-NMR spectrum of a mixture of the crude products obtained on electrolysis in the presence of an allylic alcohol **1l** showed no formation of **2l**, although two peaks were observed at 20.32 and 24.33 ppm (in the region of alkyl phosphonium ions), which are probably due to allyl triphenylphosphonium ion (**4l**) and its isomerized product, 1-propenyl phosphonium ion. Similarly, a benzylic alcohol **1m** was transformed through the electrolysis into **4m**, which was isolated in 66% yield. Thus, alkoxy phosphonium ions generated from allylic and benzylic alcohols by the present method could not be isolated because of their strong tendency to undergo an Arbuzov reaction with Ph_3P, giving alkyl phosphonium ions.

Alkoxy phosphonium tetrafluoroborates (**3**) could be prepared by CCE under essentially the same conditions using $Ph_3P^+H \cdot BF_4^-$ in place of the perchlorate salt. The results are summarized in Table 2. Although **3d** was isolated in a lower yield than that estimated by ^{31}P-NMR spectroscopy of the crude electrolysis mixture, as in the case of **2d**, the other phosphonium ions **3e**—**3i** were isolated in fair to good yields.

As far as we know, only two chemical methods have been reported to prepare and isolate an alkoxy triphenylphosphonium ion. One of them is a Mitsunobu reaction,[6] and the other comprises the activation of $Ph_3P=O$ in the presence of $(CF_3SO_2)_2O$ followed by reaction with an alcohol.[7-9] The former method has proved to be available only for the preparation of the phosphonium ion from a

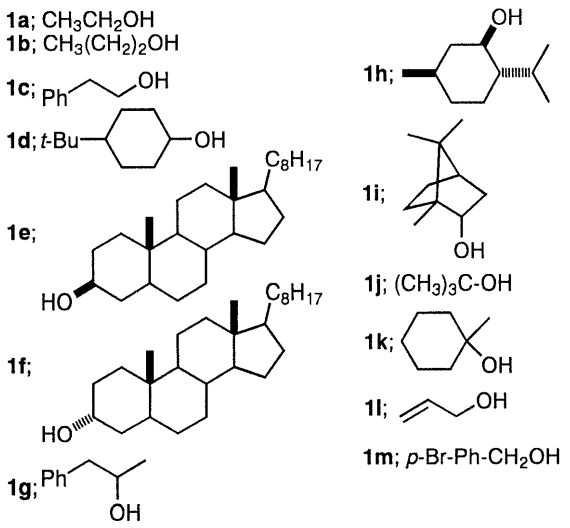

Chart 2

Table 1. Results of CCE of a Mixture of an Alcohol (**1**), Ph_3P, and $Ph_3P^+H \cdot ClO_4^-$ in CH_2Cl_2 in an Undivided Cell

Alcohol	Yield (%) of **2**[a,b]	Alcohol	Yield (%) of **2**[a,b]
1a	78 (68)	**1g**	97 (75)
1b	85 (81)	**1j**	—[c]
1c	90 (84)	**1k**	—[c]
1d	87 (20)	**1l**	—[d]
1e	100 (60)	**1m**	—[e]

a) Determined by ^{31}P-NMR spectroscopy. *b*) The number in parentheses shows the isolated yield. *c*) No formation of **2** or the corresponding alkyl phosphonium ion was observed at all. *d*) 2- and 1-Propenyl phosphonium ions were formed instead. *e*) The corresponding benzyl phosphonium ion was isolated in 66% yield.

Table 2. Results of CCE of a Mixture of an Alcohol (**1**), Ph_3P, and $Ph_3P^+H \cdot BF_4^-$ in CH_2Cl_2 in an Undivided Cell

Alcohol	Yield (%) of **3**[a,b]	Alcohol	Yield (%) of **3**[a,b]
1a	67	**1f**	(49)
1c	93	**1g**	90 (72)
1d	84 (33)	**1h**	(56)
1e	86 (76)	**1i**	(80)

a) Determined by ^{31}P-NMR spectroscopy. *b*) The number in parentheses shows the isolated yield.

Table 3. Results of Reactions of **3e** and **3f** with Various Nucleophiles

Run	Substrate	Nucleophile	Solvent	Reaction time	Products (%)[a]		
1	**3e**	Bu_4NBr	CH_2Cl_2	5 h	**6a** (83)	**7** (4)	**1e** (0)
2	**3e**	Bu_4NCl	CH_2Cl_2	5 h	**6b** (88)	**7** (5)	**1e** (0)
3	**3e**	Bu_4NF	CH_2Cl_2	1 min	**6c** (0)	**7** (3)	**1e** (97)
4	**3e**	Bu_4NN_3	CH_2Cl_2	15 min	**6d** (0)	**7** (Trace)	**1e** (90)
5	**3e**	Bu_4NSCN	CH_2Cl_2	6 h	**6e** (66)	**7** (5)	**1e** (19)
6	**3e**	PhSH[b]	CH_3CN	40 min	**6f** (57)	**7** (2)	**1e** (30)
7	**3e**	PhOH[b]	CH_3CN	1 h	**6g** (0)	**7** (Trace)	**1e** (93)
8	**3f**	Bu_4NBr	CH_2Cl_2	1 h	**8a** (56)	**7** (21)	**1f** (0)
9	**3f**	Bu_4NCl	CH_2Cl_2	1 h	**8b** (65)	**7** (35)	**1f** (0)
10	**3f**	Bu_4NF	CH_2Cl_2	1 min	**8c** (0)	**7** (10)	**1f** (90)
11	**3e**	Bu_4NBr	THF	30 min	**6a** (93)	**7** (4)	**1e** (0)
12	**3e**	Bu_4NCl	THF	30 min	**6b** (82)	**7** (3)	**1e** (15)
13	**3e**	Bu_4NF	THF	1 min	**6c** (0)	**7** (3)	**1e** (95)
14	**3e**	LiBr	THF	30 min	**6a** (92)	**7** (2)	**1e** (0)
15	**3e**	LiCl	THF	1.5 h	**6b** (54)	**7** (8)	**1e** (38)
16	**3e**	LiF[c]	THF	60 h	**6c** (49)	**7** (24)	**1e** (20)

a) Isolated yield. *b*) The reaction was carried out in the presence of K_2CO_3. *c*) The amount was 20 eq with respect to **3e**.

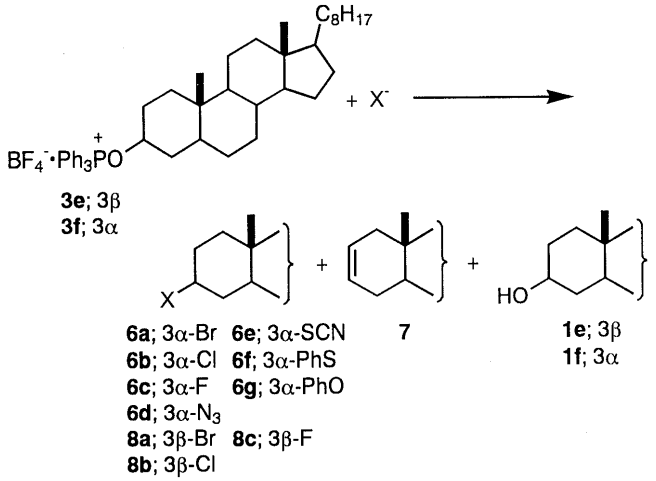

Chart 3

sterically hindered carbohydrate alcohol. The latter seems to be general, since phosphonium ions could be prepared even from steroidal secondary alcohols.[8,9] However, $(CF_3SO_2)_2O$ is not only expensive but also rather difficult to handle, and hence the present method should be more useful as a tool for the preparation of alkoxy phosphonium ions from primary and secondary aliphatic alcohols.

In the reaction of an alkoxy phosphonium ion with a nucleophile, three types of reaction courses can be envisaged, *i.e.*, attack of a nucleophile at the carbon atom α to the oxygen (path A), at a β-hydrogen (path B), and at the phosphorus (path C). Path A will include both S_N1 and S_N2 reactions, and path B will be influenced by the conformation of the phosphonium ion. Taking these points into consideration, **3e** and **3f**, whose absolute configurations and conformations are known, were chosen as model compounds to examine the reactivity of an alkoxy phosphonium ion toward a nucleophile. The reaction of **3e** or **3f** with $Bu_4N^+ \cdot X^-$ in CH_2Cl_2 at room temperature was investigated first, and the results are summarized in Table 3 (see also Chart 3).

The reactions of **3e** with bromide and chloride anions smoothly proceeded *via* path A, and only the stereo-inverted products **6a** and **6b** were obtained in excellent yields, showing that S_N2 reactions occurred predominantly (runs 1 and 2). In each case, only a small amount of **7** was formed *via* path B. Interestingly, the addition of $Bu_4N^+ \cdot F^-$ to the solution of **3e** immediately gave **1e** in a quantitative yield, indicating that fluoride anion favors path C under the conditions used (run 3). A similar result was observed in the reaction with azide anion, where almost no product other than **1e** was obtained (run 4). Thiocyanate anion reacted with **3e**, giving **6e** (66%) and **1e** (19%) through path A and path C, respectively, along with a small amount of **7** (run 5).

Bromination and chlorination of **3f** under the same conditions failed owing to the formation of **7** *via* path B in large amounts, resulting in the formation of **8a** and **8b** in smaller yields than those for **3e** (runs 8 and 9). It is noteworthy that **3f** was totally consumed after the addition of each anion within a shorter time than in the corresponding reactions of **3e**. The results suggest that **3f** with an oxy phosphonium moiety at an axial position has higher reactivity toward a nucleophile as well as a higher tendency to enter into an E2 reaction than **3e** with the phosphonium moiety at an equatorial position. In the reaction of **3f** with $Bu_4N^+ \cdot F^-$ (run 10), no fluorinated product was obtained at all, and **3f** was rapidly decomposed into **1f**, analogously with **3e**.

Table 3 also contains the results for the reaction of **3e** with PhSH and PhOH in CH_3CN in the presence of K_2CO_3 (runs 6 and 7). In the reaction with PhSH, **3e** was transformed into the corresponding sulfide **6f** in 57% yield accompanied with **1e** (30%), while the ether formation from **3e** and PhOH failed, resulting in the isolation of **1e** in 93% yield. Thus, in the reaction with **3e**, a sulfur nucleophile prefers path A while an oxygen nucleophile reacts *via* path C.

The effects of solvent and counter cation upon the halogenation of **3e** were also examined. As shown in run 11, the bromination with Bu_4NBr was accelerated in tetrahydrofuran (THF), leading to the effective formation of **6a** in a much shorter time than in CH_2Cl_2. A similar solvent effect was observed for the reaction of **3e** with Bu_4NCl, although **1e** was formed in 15% yield (run 12).

The addition of Bu_4NF to a THF solution of **3e** brought about the immediate formation of **1e**, as observed in CH_2Cl_2 (run 13). When a lithium salt was utilized as a source of halide ions, the bromination in THF proceeded in a similar way to that with the ammonium salt in the same medium (run 14). A longer time was required for **3e** to be consumed in the reaction with LiCl and the chlorination resulted in a much lower yield, accompanied with **1e** in a larger amount, as compared to the case with Bu_4NCl (run 15). Interestingly, LiF behaved differently from Bu_4NF in the reaction with **3e** (run 16). Thus, the fluorination of **3e** was achieved in 49% yield, although the reaction required 20 times as much LiF as **3e**; otherwise **3e** was not consumed at all even when the mixture was stirred for a long time.

In order to explain the observed results, the following mechanism is proposed. The first step in the reaction of **3e** or **3f** with various nucleophiles is the formation of either a phosphorane or a phosphonium salt with an additive anion as a counter ion, depending on the character of the nucleophile, such as hardness or softness. Namely, a hard nucleophile such as F^-, N_3^-, or phenoxide tends to form a phosphorane, whose decomposition results in the release of the original alcohol (path C). In the case of a softer nucleophile such as Br^-, Cl^-, or sulfur anions, a counter-anion-exchanged phosphonium ion is formed, which is supposed to exist as a three-dimensional ion-pair cluster, as proposed in the nucleophilic substitution reactions of alkoxy phosphonium ions formed in the Lee reaction[10] and isolated as triflate salts,[9b] where "a positive phosphorus in one ion-pair is in part electrically neutralized by a negative anion from another ion-pair" and *vice versa*. The bimolecular reaction in the cluster is assumed to be responsible for the formation of *SN*2 products *via* path A. This assumption is well in line with the observed effect of THF: the medium is less polar than CH_2Cl_2, allowing the effective formation of the cluster, and hence accelerating substitution reactions in the ion-pair.[10] The reaction of **3e** will be affected by the identity of the counter cations of the nucleophiles as well. Li^+ may intervene in the first step, that is, the formation of a phosphorane or an ion-pair cluster, owing to the increment in its chelation to halide ions as the anions become harder. Thus, in the reaction of **3e** with LiCl in THF, the cation can disturb the formation of the ion-pair cluster to some extent, resulting in the formation of **1e** as a by-product *via* a unimolecular reaction of the ion-pair. Furthermore, the presence of Li^+ also seems to hinder the formation of the phosphorane from **3e** and F^-, and to induce the formation of the fluorinated product, probably *via* a simple *SN*2 reaction without forming the corresponding ion-pair cluster.

In summary, the results in Table 3 suggest that **3e** and **3f** react with nucleophiles to give the corresponding substituted products with or without the formation of an ion-pair cluster, and/or to liberate the original alcohols *via* a phosphorane, depending on the identities of the nucleophile, its counter cation, and the solvent. This conclusion, implying that a proper choice of a counter cation of an anionic nucleophile as well as a reaction solvent will reduce the formation of the phosphorane and lead to the effective formation of an *SN*2 reaction product, should be of great value to obtain desired products from alcohols *via* alkoxy phosphonium ions, as in the Mitsunobu and related reactions, although further study is needed to evaluate whether the proposed mechanism is specific to the isolated alkoxy phosphonium ions or is more general.

Experimental

All melting points are uncorrected. Infrared (IR) spectra were taken on a JASCO Valor-III spectrometer. ^1H-, ^{13}C-, and ^{31}P-NMR spectra were obtained at 200, 67.8, and 202 MHz on Varian VXR-200, JEOL EX-270, and JEOL GX-500 spectrometers, respectively, in $CDCl_3$ with tetramethylsilane (TMS) as an internal standard or with 5% H_3PO_4 in D_2O as an external standard. For column chromatography, SiO_2 (Wakogel C-200) was used. CCE was carried out with a Hokuto Denko HA301, HA104, or HA105 potentiostat/galvanostat.

Materials $Ph_3P^+H \cdot ClO_4^-$ was obtained by the addition of 70% $HClO_4$ to a solution of Ph_3P in CH_3CN; the resulting precipitate was filtered off, recrystallized from CH_3CN, and dried *in vacuo*. $Ph_3P^+H \cdot BF_4^-$ was prepared in the same way with 42% HBF_4. All other chemicals were of reagent grade, and were used without further purification. CH_2Cl_2 was distilled from P_2O_5 and stored over molecular sieves 4A. THF and CH_3CN were distilled from potassium and benzophenone and from CaH_2, respectively, under an N_2 atmosphere prior to use.

General Procedure for the Preparation of 2 or 3 from 1 A CH_2Cl_2 solution (30 ml) of Ph_3P (3 mmol), $Ph_3P^+H \cdot X^-$ ($X = ClO_4$ or BF_4) (3 mmol), and **1** (3 mmol) in an undivided cell equipped with a graphite plate anode (12.5 cm^2 each) and a Pt foil cathode was deoxygenated by bubbling N_2 for 20 min, and then subjected to CCE (30 mA) at room temperature under an N_2 atmosphere. The amount of **1** remaining in the electrolyte was followed by TLC. After 3 F/mol against **1** had been passed, the electrolyte was washed with H_2O (50 ml), and the aqueous layer was extracted with CH_2Cl_2 (30 ml × 2). The combined organic layer was dried over $MgSO_4$, and evaporated *in vacuo*. The residue was analyzed by ^{31}P-NMR spectroscopy. In order to isolate an alkoxy triphenylphosphonium ion, ether was added to the residue, then the mixture was stirred for 20 min, and decanted. The procedure was repeated 5 times to afford pure **2** or **3**, which gave satisfactory analytical physical data (Table 4; only characteristic ^1H- and ^{13}C-NMR signals are listed).

General Procedure for the Reaction of 3e or 3f with a Nucleophile To a solution of **3e** or **3f** (0.5 mmol) in CH_2Cl_2 or THF (20 ml), Bu_4NX or LiX (2 mmol) was added. When PhOH or PhSH was utilized as a nucleophile, either of them (2 mmol) was added to a CH_3CN (20 ml) solution of the phosphonium ion (0.5 mmol) in the presence of K_2CO_3 (0.5 g). The resulting mixture was stirred at room temperature until TLC analysis showed that **3e** or **3f** was totally consumed. After removal of the solvent, brine (50 ml) was added to the residue, and the mixture was extracted with ether (50 ml × 3). The combined organic layer was dried over $MgSO_4$, concentrated under reduced pressure, and subjected to silica gel column chromatography (*n*-hexane and/or *n*-hexane–ethyl acetate), to give the products. The products **6a**,[11] **6b**,[11] **6c**,[12] **6e**,[11] and **6f**[11] were identified by comparison of their spectroscopic data with those described in the cited references. Other products **7**, **8a**, and **8b** were also known compounds and gave satisfactory physical data as shown below.

Cholest-2-ene (**7**): Colorless needles (acetone), mp 68—69 °C (lit.[13] 69—70 °C). IR (KBr): 1655 cm^{-1} (lit.[14] 1653 cm^{-1} in CCl_4). ^1H-NMR δ: 5.60 (2H, s), 2.1—0.5 (44H, m). ^{13}C-NMR δ: 125.93 (d), 125.80 (d), 56.50 (d), 56.30 (d), 54.09 (d), 42.46 (s), 41.42 (d), 40.04 (t), 39.79 (t), 39.53 (t), 36.19 (t), 35.83 (d), 35.60 (d), 34.58 (s), 31.83 (t), 30.33 (t), 28.79 (t), 28.25 (t), 28.02 (d), 24.21 (t), 23.88 (t), 22.84 (q), 22.57 (q), 20.92 (t), 18.69 (q), 11.99 (q), 11.66 (q). MS *m/z*: 370 (M^+). *Anal.* Calcd for $C_{27}H_{46}$: C, 87.49; H, 12.51. Found: C, 87.27; H, 12.45.

3β-Bromocholestane (**8a**): Colorless needles (acetone), mp 114—116 °C (lit.[15] 114—115 °C). ^1H-NMR δ: 4.15—3.90 (1H, m), 2.2—0.5 (46H, m). ^{13}C-NMR δ: 56.39 (d), 56.24 (d), 54.21 (d), 52.78 (d), 48.00 (d), 42.57 (s), 40.59 (t), 39.91 (t), 39.80 (t), 39.50 (t), 36.15 (t), 35.78 (d), 35.35 (d), 35.35 (s), 34.18 (t), 31.93 (t), 28.45 (t), 28.23 (t), 28.01 (d), 24.17 (t), 23.83 (t), 22.84 (q), 22.57 (q), 21.04 (t), 18.65 (q), 12.29 (q), 12.06 (q). MS *m/z*: 450 (M^+). *Anal.* Calcd for $C_{27}H_{47}Br$: C, 71.81; H, 10.49. Found: C, 71.64; H, 10.35.

3β-Chlorocholestane (**8b**): Colorless needles (acetone), mp 116—

Table 4. Physical and Spectral Data for Alkoxyl Phosphonium Ions (**2** and **3**)

	mp (°C)	NMR δ			IR ν (cm^{-1})	Elemental analysis (%) Found (Calcd)		
		^{31}P	^{1}H[a]	^{13}C[b]		C	H	Cl
2a	129	61.57	4.41 (2H, quint., J=7 Hz)	69.78 (7.3 Hz)	1093	59.06	4.96	8.71
						(59.25	5.16	8.83)
2b	134	61.54	4.27 (2H, q, J=7 Hz)	73.32 (8.5 Hz)	1096	59.94	5.27	8.43
						(60.03	5.39	8.23)
2c	118—119	61.70	4.56 (2H, q, J=5.4 Hz)	72.89 (8.5 Hz)	1098	64.67	5.01	7.34
						(64.83	5.21	7.27)
2d[c]	56	58.93, 58.53	4.43 (1H, br s)	85.23 (9.7 Hz)	1095		—[d]	
2e	94	58.99	4.28 (1H, br s)	85.05 (9.8 Hz)	1101	72.13	8.34	4.73
						(71.68	8.31	4.77)
2g	98—99	59.61	4.95 (1H, q, J=5.8 Hz)	83.94 (9.8 Hz)	1093	65.27	5.27	7.13
						(65.05	5.35	7.21)
3a	120—121	61.51	4.42 (2H, quint., J=6.8 Hz)	68.98 (8.5 Hz)	1058	60.95	5.11	
						(61.36	5.23)	
3c	120—121	61.48	4.53 (2H, quint., J=5.3 Hz)	72.93 (8.5 Hz)	1059	66.41	5.14	
						(66.36	5.27)	
3d[c]	56	59.36, 58.91	4.41 (1H, br s)	85.13 (8.5 Hz)	1059		—[d]	
3e	104—105	58.91	4.46 (1H, br s)	84.96 (9.8 Hz)	1055	73.36	8.48	
						(73.21	8.58)	
3f	181	59.41	4.98 (1H, br s)	83.14 (8.8 Hz)	1054	73.36	8.48	
						(72.98	8.55)	
3g	103—104	59.58	4.95 (1H, quint., J=6 Hz)	83.88 (9.8 Hz)	1054	66.96	5.41	
						(67.00	5.65)	
3h	99—100	58.97	4.15—4.36 (1H, m)	86.71 (11.0 Hz)	1058	66.68	6.80	
						(66.73	6.95)	
3i	91—92	61.07	4.72 (1H, t, J=7.7 Hz)	90.58 (8.5 Hz)	1054	66.95	6.42	
						(66.58	6.42)	

a) Chemical shifts for α-protons of **2** or **3**. *b*) Chemical shifts for α-carbons of **2** or **3** and coupling constants between carbon and phosphorus atoms. *c*) The phosphonium ion was obtained as a mixture of *trans*- and *cis*-isomers. *d*) The phosphonium ion was not subjected to elemental analysis, due to its instability.

117 °C (lit.[16] 122—123 °C). ^{1}H-NMR δ: 3.75—3.95 (1H, m), 2.1—0.5 (46H, m). ^{13}C-NMR δ: 60.32 (d), 56.41 (d), 56.23 (d), 54.16 (d), 46.77 (d), 42.57 (s), 39.93 (t), 39.59 (t), 39.50 (t), 38.67 (t), 36.14 (t), 35.78 (d), 35.38 (d), 35.29 (s), 33.17 (t), 31.93 (t), 28.46 (t), 28.23 (t), 28.01 (d), 24.17 (t), 23.81 (t), 22.82 (q), 22.57 (q), 21.10 (t), 18.65 (q), 12.26 (q), 12.06 (q). MS m/z: 406 (M^+). *Anal.* Calcd for $C_{27}H_{47}Cl$: C, 79.66; H, 11.64. Found: C, 79.49; H, 11.58.

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References and Notes

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