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Reaction of Triphenylphosphine Radical Cation with 1,3-Dicarbonyl Compounds: Electrochemical One-Step Preparation of Dioxomethylenetriphenylphosphoranes

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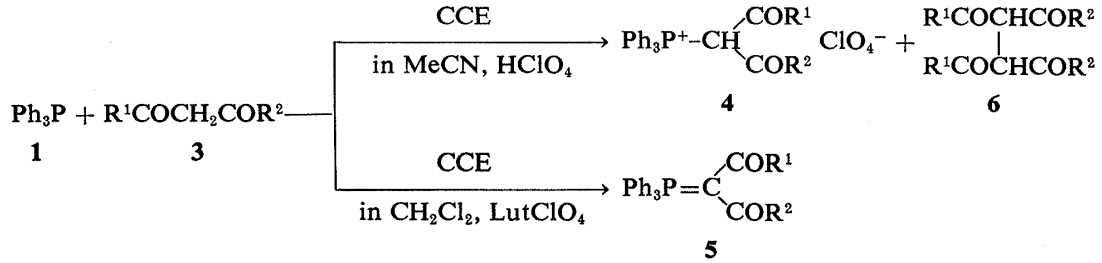
Electrochemical oxidation of Ph_3P (**1**) in MeCN in the presence of 1,3-dicarbonyl compounds, $R^1COCH_2COR^2$ (**3**), with $HClO_4$ as the supporting electrolyte resulted in the formation of the phosphonium salts, Ph_3P^+–$CH(COR^1)COR^2$ ClO_4^- (**4**), provided that R^1 and/or R^2 is a phenyl group. On the other hand, electrolysis in CH_2Cl_2 with 2,6-lutidinium perchlorate gave the phosphoranes, $Ph_3P{=}C(COR^1)COR^2$ (**5**), directly from **1** and **3** in fair to excellent yields: in this case, R^1 or R^2 need not necessarily be a phenyl group. Thus, the electrolysis is shown to be a convenient method to prepare **5** in a single step. Plausible processes for the formation of **4** and **5** are proposed, involving the reaction of electrochemically generated $Ph_3P^{+\cdot}$ with the enol form of **3** as the keystep.

Keywords——triphenylphosphine; 1,3-dicarbonyl compound; dioxomethyltriphenylphosphonium perchlorate; dioxomethylenetriphenylphosphorane; electrochemical oxidation; constant current electrolysis

Triphenylphosphine radical cation [$Ph_3P^{+\cdot}$ (**2**)], generated by one-electron oxidation of Ph_3P (**1**), has been shown to react with compounds of widely differing nucleophilicity, from benzene to aliphatic amines, to give the corresponding phosphonium salts or products derived from them.[1-3] Recently we have reported the preparation of 1-alkenyltriphenylphosphonium salts[4] and allyltriphenylphosphonium salts[5] effected by the electrochemical oxidation of **1** in the presence of alkenes and allylsilanes, respectively. As a continuation of our work on the addition reaction of the radical cation **2** with carbon nucleophiles to form P^+–C bonds, reaction with 1,3-dicarbonyl compounds (**3**) (see Tables I and II) was examined. Electrolysis of a system composed of **1**, **3**, and $HClO_4$ in MeCN gave the phosphonium salts (**4**), while the phosphoranes (**5**) were formed in CH_2Cl_2 with 2,6-lutidinium perchlorate ($LutClO_4$) or tetrafluoroborate ($LutBF_4$) as a supporting electrolyte (Chart 1). Since phosphoranes of type **5** can be employed as the precursors of acetylenes,[6,7] the electrochemical oxidation is expected to have considerable synthetic utility.



CCE: constant current electrolysis

Chart 1

Results and Discussion

The electrolysis was carried out in an undivided cell (see Experimental), unless otherwise stated.

Electrolysis in MeCN

Table I summarizes the results of constant current electrolysis (CCE) of **1** in MeCN containing the dicarbonyl compounds **3** and $HClO_4$. When either of the substituents (R^1 or R^2) in **3** is a phenyl group (**3a**—**3c**), the phosphonium salts **4** were obtained in fair yields together with small amounts of the dimer **6**. The salts **4** were converted to the corresponding phosphoranes **5** by the action of *tert*-BuOK in MeCN.[8] In the case of **3** bearing no phenyl group (**3d** and **3e**), $Ph_3P=O$ was formed almost quantitatively.

Since the oxidation potentials of **3** are higher than that of **1** under the experimental conditions (see Fig. 1 for typical examples),[9] it can be expected that the phosphonium salts **4** are formed *via* the reaction of the radical cation **2** with the enol form of **3** (Chart 2),[10] as suggested for the reaction of **2** with various nucleophiles.[1-4] However, toward the end of the electrolysis when **1** is almost consumed, direct electron transfer from **3** also seems to take place to give the dimer **6** as a by-product. Thus, in a typical experiment, the progress of the electrolysis with **3a** was followed by liquid chromatography. At 60% completion of the electrolysis the yield of **6a** was only 0.4% based on the initial amount of **3a**, while it increased to 3.2 and 4% at 80 and 100% completion, respectively. Dimerization of 1,3-dicarbonyl compounds by electrochemical oxidation has been reported.[11]

At least two factors can be considered to account for the failure to obtain the phosphonium salts **4** from **3d** and **3e**. First, the amount of the enol form (see Chart 2) in the bulk of the electrolysis solution will be smaller in the case of **3d** and **3e** than for **3a**—**3c**.[12,13] Secondly, at the electrode surface the concentration of **3** with a phenyl group must be higher than that of **3** without the phenyl group, because the former dicarbonyl compounds will be specifically adsorbed on the electrode through the phenyl group[14] as suggested by the depressed voltammetric peak of **1** in the presence of **3a** (Fig. 1). Therefore, in the electrolysis with **3d** and **3e**, the radical cation **2** will react with water, added unavoidably to the medium with $HClO_4$,[15] rather than with the dicarbonyl compounds, leading to the almost quantitative formation of $Ph_3P=O$.

The effects of the supporting electrolyte were examined with **3a** as the nucleophile. When $LutClO_4$ or $LutBF_4$ was used in place of $HClO_4$, the phosphorane **5a** (instead of **4a**) and the dimer **6a** were formed[16]: with $LutBF_4$ the yields of **5a** and **6a** were 15 and 12%, respectively. For the preparation of **5**, however, electrolysis in CH_2Cl_2 proved to be preferable (see below). Other supporting electrolytes such as $NaClO_4$, Bu_4NClO_4, and $LiBF_4$ did not give satisfac-

TABLE I. CCE of **1** in the Presence of **3** in the MeCN–$HClO_4$ System[a]

	3		Yield (%)[b] of		Yield (%)[c] of **5** from **4**
	R^1	R^2	**4**	**6**	
a	Ph	Ph	66	4	72
b	Ph	Me	65	4	81
c	Ph	OEt	62	5	71
d	Me	Me	0[d]	—	—
e	Me	OEt	0[d]	—	—

a) General procedure, see Experimental: the ratio of [**1**]:[**3**]:[$HClO_4$] was 1:2:2. *b*) Isolated yield: for **4** based on **1** and for **6** based on **3**. *c*) Isolated yield based on **4**: **4** was refluxed in MeCN containing *tert*-BuOK under N_2 for 8 h. *d*) $Ph_3P=O$ was obtained in almost quantitative yield.

$$1 + HClO_4 \rightleftharpoons Ph_3PH^+ + ClO_4^-$$

$$3 \rightleftharpoons R^1C(OH)=CHCOR^2$$

3′

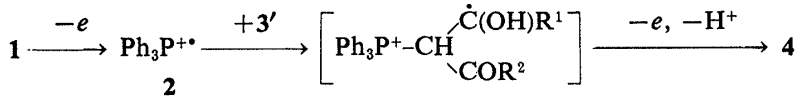


Chart 2

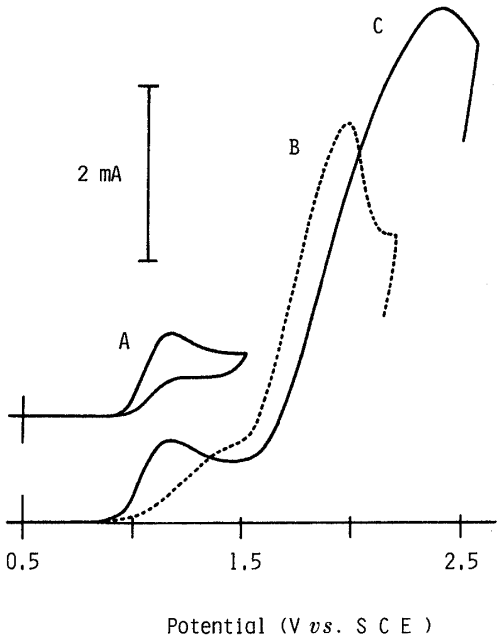


Fig. 1. Cyclic Voltammograms of **1** and **3** in MeCN

A, **1** (11 mmol) and $HClO_4$ (22 mmol) in MeCN (35 ml); B, A+**3a** (22 mol); C, A+**3d** (22 mmol). Conditions: at 27 °C; glassy carbon anode (area = 0.071 cm^2); voltage sweep rate, 50 mV/s. SCE, saturated calomel electrode.

TABLE II. Preparation of **5** by CCE of **1** in CH_2Cl_2 Containing **3** and $LutClO_4$[a]

	3		Yield (%)[b] of **5**	Conversion of **5** to acetylene[c] (yield/%)[d]
	R^1	R^2		
a	Ph	Ph	63[e,f]	PhC≡CCOPh (97)
b	Ph	Me	83	PhC≡CCOMe (62), PhCOC≡CMe (26)
c	Ph	OEt	71	PhC≡CCO_2Et (80)
d	Me	Me	58	[g]
e	Me	OEt	67	[h]
f	MeO	CH_2CO_2Me	30	[i]
g		$-(CH_2)_3-$	35	[j]
h		$-CH_2C(Me)_2CH_2-$	94	[j]
i	Ph	NHPh	*ca.* 100	[i]
j	Me	NHPh	83	[i]
k	Ph	CN for COR^2	56	PhC≡CCN (83)

a) General procedure, see Experimental. *b*) Isolated yield based on **1**. *c*) The phosphorane **5** was refluxed in *o*-dichlorobenzene for 3—8 h. *d*) Isolated yield based on **5**. *e*) $LutBF_4$ was used in place of $LutClO_4$. *f*) The dimer **6a** was obtained in 3% yield based on **3a**. *g*) Not examined, but conversion to MeC≡CCOMe has been reported (ref. 6*d*). *h*) Not examined. *i*) Only tarry materials were obtained. *j*) The reaction of the phosphorane is under investigation.

tory results for the formation of **4** or **5**.

Electrolysis in CH_2Cl_2

In contrast to the results in the MeCN–$HClO_4$ system, CCE in CH_2Cl_2 with $LutClO_4$ or

$LutBF_4$ as the supporting electrolyte gave the phosphorane **5** directly from **1** and **3**[17]: in this case, all of the dicarbonyl compounds **3** reacted with radical cation **2** to afford the products (Table II). Conversion of some of the phosphoranes **5** to acetylenes was examined under conditions somewhat different from those reported[6] and the results are also included in Table II.

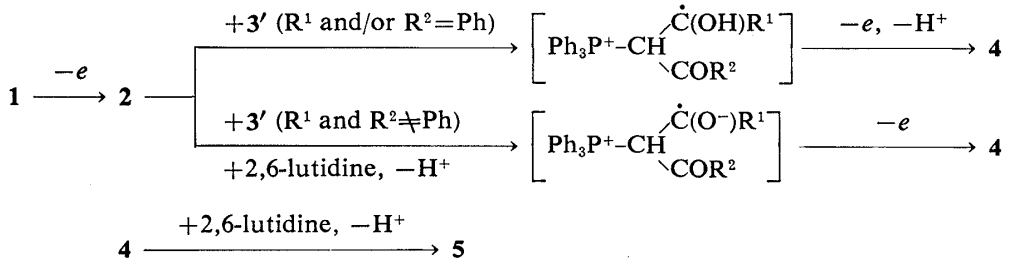
In order to elucidate the role of the supporting electrolyte in the reaction, electrolysis of **1** in CH_2Cl_2 was carried out under several selected conditions, where **3a** and **3d** were chosen as typical dicarbonyl compounds. When $LutClO_4$ was used, both of the phosphoranes **5a** and **5d** were produced as described above (runs 1 and 3 in Table III). With Bu_4NClO_4, on the other hand, the phosphonium salt **4a** was formed from **3a**, though in rather poor yield (run 2), but no product that had originated from **1** and **3d** was obtained (run 4). Since $LutClO_4$ will be easily reduced at the cathode to liberate the free base,[3b,4] these results suggest that (i) the initial product formed from **1** and **3** in CH_2Cl_2 is the phosphonium salt **4**, (ii) a weak base generated *in situ* can effect the conversion of **4** to **5**, and (iii) the formation of **4** from **3** without the phenyl group must be assisted by a base. The third view is consistent with the observation that the phosphonium salts **4** were not formed from **3d** and **3e** in the $MeCN–HClO_4$ system. The reaction at the cathode in the electrolysis with Bu_4NClO_4 will not be simple. Although quaternary ammonium salts have been reported to produce tertiary amines upon cathodic reduction,[18] such processes would take place at very high negative potentials. Under the present experimental conditions, the discharge of the solvent (CH_2Cl_2) might occur preferentially, when chloride ion is thought to be liberated.[19] The possibility of the reduction of

Table III. CCE of **1** in the Presence of **3a** or **3d** in CH_2Cl_2[a]

Run	3	Supporting electrolyte	Electrolysis cell and additive	Yield (%)[b] of 4 and 5	
1	**3a**	$LutClO_4$	Undivided cell	0	49
2	**3a**	Bu_4NClO_4	Undivided cell	23	0
3	**3d**	$LutClO_4$	Undivided cell	0	58[c]
4	**3d**	Bu_4NClO_4	Undivided cell	0	0
5	**3d**	Bu_4NClO_4	Divided cell $NaHCO_3$ (57 mmol)[d]	0	2
6	**3d**	Bu_4NClO_4	Divided cell Na_2CO_3 (57 mmol)[d]	0	44

a) Essentially the same procedure was employed as had been used to obtain the results in Table II. *b*) Isolated yield based on **1**. *c*) Quoted from Table II. *d*) Suspended in the anode compartment.

at the anode



at the cathode

$$2\ LutClO_4 \xrightarrow{+2e} 2(2,6\text{-lutidine}) + H_2 + 2ClO_4^-$$

Chart 3

anodically generated species at the cathode cannot be ruled out. In any case, however, it is likely that a base, which acts in a manner similar to 2,6-lutidine, is not produced at the cathode in the electrolysis with Bu_4NClO_4. These arguments are supported by the results obtained on electrolysis with Bu_4NClO_4 in the presence of suspended bases ($NaHCO_3$ and Na_2CO_3) in a divided electrolysis cell (runs 5 and 6), where participation of cathodically generated species in the anodic reactions is eliminated. The phosphorane **5d** was obtained from **3d**, and the yield increased with the basicity of the suspended base.

Based on the results described so far, the overall process for the formation of **5** in the CH_2Cl_2–$LutClO_4$ system is proposed to be as shown in Chart 3. Although the process from **2** to **4** is represented as stepwise reactions, it cannot be distinguished from a process in which further one-electron transfer and the deprotonation take place concurrently with the attack of **3** on the radical cation **2**.

It is well known that α-acylphosphoranes, $Ph_3P=C(R)COR'$ (**7**), are useful intermediates for the synthesis of acetylenes.[6,7] The preparation of **7** most frequently employed involves the reaction of the Wittig reagents, $Ph_3P=CHR$, with acid halides or acid anhydrides. However, in this method with acid halides, though not always with acid anhydrides, half of the reagent is converted to the phosphonium salt, $Ph_3P^+-CH_2R\ X^-$ (X^- = halide ion or acid anion), and the separation of **7** from the salt is sometimes difficult. Since the phosphoranes **5** are representatives of the compounds **7** as precursors of acetylenes, except for the terminal acetylene equivalents reported recently,[7] the electrochemical preparation of **5** described in the present study, involving a simple one-step procedure from **1** under mild conditions, has potential synthetic utility. Furthermore, the phosphoranes such as **5g** and **5h** are hard to obtain by conventional methods. Studies on the synthetic application of these compounds are in progress.

Experimental

All melting points are uncorrected. Infrared (IR) and proton nuclear magnetic resonance (^{1}H-NMR) spectra were recorded on JASCO A-202 and Hitachi R-22 spectrometers, respectively. Cyclic voltammetry was carried out as described previously.[20] CCE was performed using a Hokuto Denko HA-301 potentiostat/galvanostat, but the use of a conventional DC power supply (50 V–2A) also seems to be effective. A 50 ml sample tube (diameter, 3.5 cm; height, 7.5 cm) was employed as the undivided electrolysis cell, which was equipped with a graphite plate anode (2 × 10 cm) and a platinum plate cathode (1 × 10 cm) through a silicon stopper. A beaker (volume, 50 ml) was used as the divided cell: the cathode compartment was composed of a glass cylinder (diameter, 25 mm) with a sintered glass disk at the bottom, which was suspended in the beaker through a rubber stopper. A solution of Bu_4NClO_4 (0.63 M) in CH_2Cl_2 was placed in the cylinder as the catholyte. The same electrodes as described above were used.

Materials——The phosphine **1** was recrystallized from hexane. 1,3-Dicarbonyl compounds **3a**—**3j** were obtained from commercial sources and were used without further purification. Compound **3k** was synthesized by the reported method.[21] $LutClO_4$ and $LutBF_4$ were prepared as described previously.[22] MeCN was purified by the method of Kiesele,[23] and CH_2Cl_2 was distilled from P_2O_5. Other chemicals were of reagent grade, and were used without further purification.

General Procedure for the Preparation of 5——A solution of **1** (11 mmol), **3** (22 mmol), and $LutClO_4$ or $LutBF_4$ (22 mmol) in CH_2Cl_2 (35 ml) was subjected to CCE (30 mA; current density, 1 mA/cm^2) in the undivided cell at ambient temperature until 2 F per mol of **1** had been consumed. The electrolyzed solution was concentrated to *ca.* 2 ml under reduced pressure below 30 °C. Water (100 ml) was added to the residue and the mixture was extracted with $CHCl_3$ (3 × 100 ml). The organic layer, after being dried over anhydrous $MgSO_4$, was evaporated under reduced pressure. The residue was subjected to column chromatography on silica gel with hexane–AcOEt as an eluant to give the phosphorane **5**: the optimum solvent ratio was dependent on the particular phosphorane and was found by thin layer chromatography. Electrolysis in the divided cell was performed by essentially the same procedure.

Dibenzoylmethylenetriphenylphosphorane (**5a**): mp 185—187 °C (from AcOEt–hexane) (lit.[6d] 191—192 °C). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1520. NMR ($CDCl_3$) δ: 6.85—7.90 (25H, m, ArH). *Anal.* Calcd for $C_{33}H_{25}O_2P$: C, 81.80, H, 5.20. Found: C, 81.76; 4.96.

Benzoyltriphenylphosphoranylideneacetone (**5b**): mp 175—178 °C (from AcOEt) (lit.[6d] 172—173 °C). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1570, 1530. NMR ($CDCl_3$) δ: 1.86 (3H, s, $COCH_3$), 7.3—8.0 (20H, m, ArH). *Anal.* Calcd for

$C_{28}H_{23}O_2P$: C, 79.61; H, 5.49. Found: C, 79.80; H, 5.43.

Ethyl Benzoyltriphenylphosphoranylideneacetate (**5c**): mp 141—142 °C (from AcOEt) (lit.[6b] 142—143 °C). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1660, 1540. NMR ($CDCl_3$) δ: 0.63 (3H, t, J=7 Hz, CH_3), 3.75 (2H, q, J=7 Hz, CO_2CH_2), 7.4—8.1 (20H, m, ArH). *Anal.* Calcd for $C_{29}H_{25}O_3P$: C, 76.98; H, 5.57. Found: C, 77.14; H, 5.43.

Acetyltriphenylphosphoranylideneacetone (**5d**): mp 167—172 °C (from AcOEt–hexane) (lit.[6d] 167—169 °C). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1530. NMR ($CDCl_3$) δ: 2.24 (6H, s, $COCH_3$), 7.30—7.80 (15H, m, ArH). *Anal.* Calcd for $C_{23}H_{21}O_2P$: C, 76.65; H, 5.87. Found: C, 76.82; H, 5.84.

Ethyl Acetyltriphenylphosphoranylideneacetate (**5e**): mp 156—159 °C (from AcOEt–hexane) (lit.[6a] 152—154 °C). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1650, 1550. NMR ($CDCl_3$) δ: 0.67 (3H, t, J=8 Hz, CH_3), 2.46 (3H, s, $COCH_3$), 3.73 (2H, q, J=8 Hz, OCH_2), 7.30—7.80 (15H, m, ArH). HR-MS: Calcd for $C_{24}H_{23}O_3P$ (M^+) m/z: 390.1386, Found: 390.1384.

Dimethyl 3-Oxo-2-triphenylphosphoranylideneglutarate (**5f**): mp 129—130 °C (from AcOEt–hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1660, 1560. NMR ($CDCl_3$)δ: 3.12 (3H, s, CO_2CH_3), 3.70 (3H, s, CO_2CH_3), 3.84 (2H, s, CH_2), 7.25—7.85 (15H, m, ArH). *Anal.* Calcd for $C_{25}H_{23}O_5P$: C, 69.12; H, 5.34. Found: C, 69.37; H, 5.19.

2-Triphenylphosphoranylidenecyclohexa-1,3-dione (**5g**): mp 210.5—214 °C (from hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1550. NMR ($CDCl_3$) δ: 1.90—2.20 (2H, m, $-CH_2-$), 2.30—2.55 (4H, m, $COCH_2\times2$), 7.30—7.85 (15H, m, ArH). *Anal.* Calcd for $C_{24}H_{21}O_2P$: C, 77.41; H, 5.68. Found: C, 77.61; H, 5.72.

5,5-Dimethyl-2-triphenylphosphoranylidenecyclohexa-1,3-dione (**5h**): mp 209—212 °C (from hexane). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1550. NMR ($CDCl_3$) δ: 1.13 (6H, s, $CH_3\times2$), 2.30 (4H, s, $COCH_2\times2$), 7.20—7.80 (15H, m, ArH). *Anal.* Calcd for $C_{26}H_{25}O_2P$: C, 77.98; H, 6.29. Found: C, 78.24; H, 6.05.

Benzoyltriphenylphosphoranylideneacetanilide (**5i**): mp 188—193 °C (from AcOEt). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1620, 1520. NMR ($CDCl_3$) δ: 6.75—7.75 (26H, m, ArH). *Anal.* Calcd for $C_{33}H_{26}NO_2P$: C, 79.34; H, 5.25; N, 2.80. Found: C, 79.56; H, 5.08; N, 2.74.

Acetyltriphenylphosphoranylideneacetanilide (**5j**): mp 180—184 °C (from AcOEt). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1610, 1530. NMR ($CDCl_3$) δ: 1.38 (3H, s, CH_3), 6.80—7.85 (20H, m, ArH). *Anal.* Calcd for $C_{28}H_{23}NO_2P$: C, 77.05; H, 5.31; N, 3.21. Found: C, 77.22; H, 5.48; N, 3.11.

2-Cyano-2-triphenylphosphoranylideneacetophenone (**5k**): mp 209—213 °C (from AcOEt–hexane)(lit.[6b] 208 °C). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2170, 1550. NMR ($CDCl_3$) δ: 7.30—8.10 (20H, m, ArH). *Anal.* Calcd for $C_{27}H_{20}NOP$: C, 79.99; H, 4.97; N, 3.45. Found: C, 80.28; H, 4.82; N, 3.48.

Electrolysis in the MeCN–$HClO_4$ System——A solution of **1** (11 mmol), **3** (22 mmol), and 70% $HClO_4$ (22 mmol as $HClO_4$) in MeCN (35 ml) was subjected to CCE as described above. Caution: $HClO_4$ should be added slowly to the mixture of **1** and **3** in MeCN with stirring. The electrolyzed solution was concentrated to *ca.* 10 ml under reduced pressure below 30 °C. Ether (300 ml) was added to the residue. The phosphonium salt **4** separated out as colorless crystals, which were filtered off, washed with ether, and recrystallized from MeCN–ether. The combined filtrate was evaporated under reduced pressure and the residue was subjected to column chromatography on silica gel with hexane–AcOEt (10 : 1) as an eluant to give the dimer **6**.

(Dibenzoylmethyl)triphenylphosphonium Perchlorate (**4a**): mp 218—222 °C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690 (w), 1670 (w), 1650 (w), 1590, 1105. NMR (CD_3CN) δ: 7.30—8.10 (26H, m, ArH and CH). *Anal.* Calcd for $C_{33}H_{26}ClO_6P$: C, 67.76; H, 4.48; Cl, 6.06. Found: C, 68.00; H, 4.38; Cl, 5.88.

(Acetylbenzoylmethyl)triphenylphosphonium Perchlorate (**4b**): mp 213—218 °C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1630, 1600, 1105. NMR (CD_3CN) δ: 2.10 (3H, s, $COCH_3$), 7.30—8.10 (21H, m, ArH and CH). *Anal.* Calcd for $C_{28}H_{24}ClO_6P$: C, 64.31; H, 4.63; Cl, 6.78. Found: C, 64.29; H, 4.48; Cl, 6.79.

(Benzoylcarboethoxymethyl)triphenylphosphonium Perchlorate (**4c**): mp 173 °C. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 1670, 1100. NMR (CD_3CN) δ: 0.90 (3H, t, J=7 Hz, CH_3), 4.05 (2H, q, J=7 Hz, CO_2CH_2), 6.95 (1H, d, J=13 Hz, P^+-CH), 7.30—8.10 (20H, m, ArH). *Anal.* Calcd for $C_{29}H_{26}ClO_7P$: C, 62.99; H, 4.74. Found: C, 62.79; H, 4.82.

1,1,2,2-Tetrabenzoylethane (**6a**): mp 219—222 °C (from AcOH) (lit.[24] 211—213 °C). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1690. NMR ($CDCl_3$) δ: 6.80 (2H, s, >CH–CH<), 7.15—7.55 (12H, m, ArH), 7.78—7.95 (8H, m, ArH). *Anal.* Calcd for $C_{30}H_{22}O_4$: C, 80.70; H, 4.97. Found: C, 80.63; H, 4.79.

1,2-Diacetyl-1,2-dibenzoylethane (**6b**): A mixture of keto and enol forms. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1720 and 1670 (keto form), 1600 (enol form). NMR ($CDCl_3$) δ: 2.03 (6H, s, $CH_3\times2$), 6.90 (2H, s, >CH-CH< for the keto form), 7.10—8.20 (10H, m, ArH). From the NMR spectrum, the ratio of [keto]/[enol] was estimated to be 1/5.4.

Diethyl 2,3-dibenzoylsuccinate (**6c**) was a mixture of *meso* and *dl* forms (1 : 1) at the time of isolation. After recrystallization from hexane, however, only the *meso* form was obtained: mp 128 °C (lit.[25] 126 °C). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1740, 1680. NMR ($CDCl_3$) δ: 0.95 (6H, t, J=9 Hz, $CH_3\times2$), 3.95 (4H, q, J=9 Hz, $OCH_2\times2$), 5.58 (2H, s, >CH–CH<), 7.44—7.60 (6H, m, ArH), 8.10—8.22 (4H, m, ArH). *Anal.* Calcd for $C_{22}H_{22}O_6$: C, 69.10; H, 5.80. Found: C, 69.09; H, 5.85.

Conversion of 4 to 5——A mixture of **4** (3.6 mmol) and *tert*-BuOK (18 mmol) in dry MeCN (20 ml) was refluxed with stirring under N_2 for 8 h. The reaction mixture, after addition of aqueous NH_4Cl (10%, 50 ml), was extracted with $CHCl_3$ (3×50 ml). The extract was treated as described above to give the corresponding phosphorane **5**.

Preparation of Acetylenes——A solution of **5** (1 mmol) in *o*-dichlorobenzene (5 ml) was refluxed for 3—8 h. The reaction mixture was subjected to column chromatography on silica gel (hexane–AcOEt, 10 : 1) to give the

corresponding acetylene. The products are all known compounds[6b,d] and gave the expected analytical results.

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8) The conversion of **4** to **5** can be effected with a weaker base such as 2,6-lutidine or Na_2CO_3 as suggested by the results described below. However, since the electrolysis in CH_2Cl_2 was found to be preferable for the preparation of **5** (Table II), further modification of the method was not attempted.
9) The voltammetric peak potentials of **3** in MeCN (0.1 M $LutClO_4$ or $LutBF_4$) were as follows (the values were little affected by addition of $HClO_4$): **3a**, 1.71; **3b**, 1.80; **3c**, 1.77; **3d**, 1.90; **3e**, 1.92; **3f**, 2.1; **3g**, 1.50; **3h**, 1.60; **3i**, 1.63; **3j**, 1.65; **3k**, 2.1 V *vs.* SCE. (concn. of **3**, 2 mmol; voltage sweep rate, 50 mV/s). The values for **3a** and **3d** do not coincide with those read from Fig. 1. This discrepancy is due to the difference in the concentration of the substrate in the two experiments.
10) The voltammetric peak potential of **1** in MeCN containing 2 mol eq of $HClO_4$, which is *ca.* 140 mV more positive than that of **1** without the acid, agrees well with that of $Ph_3PH^+ ClO_4^-$ prepared separately, indicating that **1** is almost completely protonated under the electrolysis condition [*cf.* H. Ohmori, H. Maeda, K. Konomoto, K. Sakai, and M. Masui, *Chem. Pharm. Bull.*, **35**, 4473 (1987)]. However, the exact nature of the initial electrode process generating the radical cation **2** under the experimental conditions is not clear, though the overall process is considered to be as depicted in Chart 2. A voltammetric study of the oxidation of **1** in acidic MeCN is in progress and will be reported elsewhere.
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15) Since 70% $HClO_4$ obtained from a commercial source was used without any treatment, the reaction medium inevitably contained a small amount of water.
16) The electrolyzed solution was treated according to the procedure employed for the work-up of the solution from electrolysis carried out in CH_2Cl_2 (see Experimental and note 17).
17) It was confirmed that, in a designed mixture of the phosphonium salt **4a** (2 mmol) and $LutBF_4$ (22 mmol) in CH_2Cl_2 (35 ml), **4a** was recovered in 86% yield by the work-up described in the experimental section, indicating that formation of **4** in the electrolysis solution as the major product would have been detected if it had actually occurred.
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