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One-Step Preparation of 1-Alkenyltriphenylphosphonium Perchlorates by Electrochemical Oxidation of Triphenylphosphine in the Presence of Alkenes

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Electrochemical oxidation of triphenylphosphine in dichloromethane at a graphite anode in the presence of olefins has been shown to be a convenient method for the preparation of 1-alkenyltriphenylphosphonium perchlorates under mild conditions.

Keywords—triphenylphosphine; 1-alkenyltriphenylphosphonium perchlorate; alkene; electrochemical oxidation; constant current electrolysis

Triphenylvinylphosphonium bromide (Schweizer's reagent)¹⁾ and related 1-alkenylphosphonium salts are useful building blocks for the synthesis of carbocyclic²⁾ and heterocyclic³⁾ compounds, allylamines,⁴⁾ and 1,4-dienes.⁵⁾ Applications of 1-cycloalkenyltriphenylphosphonium salts to the synthesis of carbocyclic and heterocyclic compounds and optically active organophosphorus compounds have also been reported.^{6,7)} However, the preparation of the phosphonium salts usually involves rather troublesome multistep procedures.^{1,8,9)} On the other hand, we found recently that electrochemical oxidation of triphenylphosphine (**1**) in the presence of olefins (**2**) can be an efficient method to prepare 1-alkenyltriphenylphosphonium salts (**3**)¹⁰⁾: 1-cycloalkenyl derivatives (C₅—C₈) were obtained in 50—70% yields. This paper reports further examples of electrochemical preparation of **3** (Chart 1), including triphenylvinylphosphonium perchlorate (**3f**).

Chart 1

Results and Discussion

As described previously,¹⁰⁾ the phosphonium salt **3** was obtained by constant current electrolysis of a mixture of **1** and **2** in dry dichloromethane containing 2,6-lutidinium perchlorate (LutClO₄) in an undivided electrolysis cell. The results are shown in Table I.

Since the oxidation potentials of the olefins used are higher than that of **1**,¹¹⁾ the process for the formation of **3** can be represented as shown in Chart 2 by analogy with the reactions of triphenylphosphine radical cation (**4**) with other nucleophiles.¹²⁾ LutClO₄ acts as a proton carrier, that is, it is reduced to the free base at the cathode and the latter accepts the proton liberated at the anode.

In the electrolysis with **2a**, **2c**, and **2d**, the phosphonium salts listed in Table I were

TABLE I. Electrochemical Preparation of 3^{a)}

Olefin 2 (amount (mmol))	Product 3 ^{b)}	Yield (%) ^{c)}
a 1-Methylcyclohexene (15)	(2-Methylcyclohexen-1-yl)P ⁺ Ph ₃	41
b Cyclohexene (15)	(Cyclohexen-1-yl)P ⁺ Ph ₃	53 ^{d)}
c Styrene (3)	C ₆ H ₅ CH=CH-P ⁺ Ph ₃	79
d 4-Methylstyrene (3)	<i>p</i> -Me-C ₆ H ₄ CH=CH-P ⁺ Ph ₃	ca. 100
e 1,3-Cyclohexadiene (5)	(1,3-Cyclohexadien-1-yl)P ⁺ Ph ₃	92 ^{e)}
f Ethylene (saturated)	CH ₂ =CH-P ⁺ Ph ₃	30 ^{f)}

a) General procedure, see Experimental (amount of 1, 3 mmol). b) Counter anion, ClO₄⁻.
 c) Isolated yield based on 1. d) Quoted from ref. 10. e) Obtained as a crude product, see the text.
 f) At 0°C, see Experimental.

Chart 2

isolated, and no other compound derived from 1 and the olefins was obtained. The yield of 3a was lower than that of 3b under the same electrolysis conditions. In 2a only one position is available for the attack of the radical cation 4 to give 3a, that is, the 2-position, while 3b will be formed by the reaction of 4 with 2b at either of the two olefinic carbons. In the case of 2c and 2d, the radical cation 4 seems to attack preferentially at the position in the molecule with highest frontier electron density.¹³⁾ The proton nuclear magnetic resonance (¹H-NMR) spectra of 3c and 3d, which exhibit signals due to two vinyl protons with *J*_{HH} = 18 Hz, suggest¹⁴⁾ that the phosphonium salts are *trans* isomers. Although the phosphonium salt 3e was suggested, on the basis of spectroscopic data (see Experimental), to be the major component of the product isolated in the electrolysis with 2e, it could not be separated from small amounts of impurities. When the product was treated with sodium hydroxide according to the known procedure,⁹⁾ (1,3-cyclohexadien-1-yl)diphenylphosphine oxide (5e) was obtained in 62% yield. In an attempt to prepare the phosphonium salts of the type, R-CH₂-CH=CH-P⁺Ph₃ ClO₄⁻ (3g), electrolysis of 1 with 1-heptene was examined. An oily product mixture containing some phosphonium salt was obtained, but separation of the mixture into each component has not yet been achieved. In this case, treatment of the mixture with sodium hydroxide did not give the expected alkenyldiphenylphosphine oxide: Ph₃PO was isolated from the reaction.

The present results together with those reported previously¹⁰⁾ may suggest the possibility of preparing various 1-alkenyltriphenylphosphonium salts by electrochemical oxidation. However, further investigation is required to obtain the phosphonium salts 3g and to improve the yield of the vinylphosphonium salt 3f.

Experimental

All melting points are uncorrected. Infrared (IR) and ¹H-NMR spectra were measured with Nippon-Bunko A202, and Hitachi R-20 (60 MHz) or JEOL GX-400 (400 MHz) spectrometers, respectively. Constant current electrolysis was carried out using a Hokuto Denko HA-301 and HA-111 potentiostat/galvanostat.

Materials—LutClO₄ was prepared as described previously.¹⁵⁾ Dichloromethane was distilled from P₂O₅ and stored over molecular sieves. Other organic compounds were obtained from commercial sources and were purified by distillation or recrystallization.

General Procedure for the Preparation of 3—A 50 ml sample tube fitted with a silicon stopper was used as the electrolysis cell. A graphite plate anode (10.5 × 2 cm²) and a stainless steel plate cathode (2.8 × 2 cm²) were placed in

the cell at a distance of *ca.* 1 cm through the stopper. A solution of **1** (3 mmol) and **2** (amount, see Table I) in dry, deoxygenated CH_2Cl_2 (40 ml) containing 0.2 M LuClO_4 , and anhydrous K_2CO_3 (3 g, suspended) were placed in the electrolysis cell. The system was subjected to electrolysis (20 mA; current density, *ca.* 1 mA/cm²) at ambient temperature under an N_2 atmosphere until 2 F per mol of **1** (579 C, *ca.* 8 h) had been consumed: the N_2 gas was supplied from a balloon connected to the cell by a hypodermic needle. The electrolyzed solution, after the K_2CO_3 had been removed by filtration, was evaporated to *ca.* 1–2 ml under reduced pressure. Water (100 ml) was added to the residue, and the mixture was extracted with CHCl_3 (50 ml $\times$ 4). The extracts were dried with anhydrous MgSO_4 and concentrated to *ca.* 5 ml under reduced pressure. The phosphonium salt **3** separated out when the residue was added dropwise to ether (100 ml) with stirring.

(2-Methy-1-cyclohexen-1-yl)triphenylphosphonium Perchlorate (**3a**): mp 178–180 °C (from CH_2Cl_2 –ether). IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 1590 (C=C), 1100 (ClO_4^-). NMR (CDCl_3) δ : 1.2–2.5 (11H, m), 7.5–8.2 (15H, m). *Anal.* Calcd for $\text{C}_{25}\text{H}_{26}\text{ClO}_4\text{P}$: C, 65.72; H, 5.74; Cl, 7.76. Found: C, 65.71; H, 5.73; Cl, 7.84.

(β -Styryl)triphenylphosphonium Perchlorate (**3c**): mp 189–190 °C (from CH_2Cl_2 –AcOEt). IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 1600 (C=C), 1100 (ClO_4^-). NMR (CDCl_3) δ : 7.17 (1H, dd, $J_{\text{PH}}=23$ Hz, $J_{\text{HH}}=18$ Hz), 7.40–7.45 (3H, m, H^m and H^p), 7.51 (1H, dd, $J_{\text{PH}}=21$ Hz, $J_{\text{HH}}=18$ Hz), 7.65–7.95 (17H, m, Ph_3P and H^o). *Anal.* Calcd for $\text{C}_{26}\text{H}_{22}\text{ClO}_4\text{P}$: C, 67.18; H, 4.77; Cl, 7.63. Found: C, 67.10; H, 4.71; Cl, 7.45.

[β -(4-Methylstyryl)triphenylphosphonium Perchlorate (**3d**): mp 221–223 °C (from CH_2Cl_2 –AcOEt). IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 1600 (C=C), 1100 (ClO_4^-). NMR (CDCl_3) δ : 2.46 (3H, s, CH_3), 7.14 (1H, dd, $J_{\text{PH}}=23$ Hz, $J_{\text{HH}}=18$ Hz), 7.35 (2H, brd, $J=9$ Hz, H^m), 7.41 (1H, dd, $J_{\text{PH}}=21$ Hz, $J_{\text{HH}}=18$ Hz), 7.6–8.0 (17H, m, Ph_3P and H^o). *Anal.* Calcd for $\text{C}_{27}\text{H}_{24}\text{ClO}_4\text{P}$: C, 67.72; H, 5.05; Cl, 7.40. Found: C, 67.94; H, 5.11; Cl, 7.17.

Electrolysis of **1** (786 mg) in the presence of **2e** (400 mg) followed by work-up as described above gave a crystalline solid as the product (1210 mg). The following spectral data, together with the ¹³C-NMR spectra of vinyl- and allylphosphonium salts,¹⁶ suggest that (1,3-cyclohexadien-1-yl)triphenylphosphonium perchlorate (**3e**) is the main component of the product. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 1620 and 1585 (conjugated diene), 1100 (ClO_4^-). ¹H-NMR (CD_3CN) δ : 2.37–2.45 (4H, m), 6.23–6.27 (1H, m, H on C3), 6.42–6.48 (1H, m, H on C4), 6.71 (1H, dd, $J_{\text{PH}}=20$ Hz, $J_{\text{HH}}=5.5$ Hz, H on C2), 7.68–7.93 (15H, m, Ar). ¹³C-NMR ($\text{DMSO}-d_6$) δ [J_{PC} (Hz), assignment]: 113.4 [84.7, C1], 146.5 [9.2, C2], 123.8 [16.0, C3], 136.8 [9.2, C4], 21.7 [8.4, C5 or C6], 22.9 [6.9, C6 or C5], 117.0 [89.3, P⁺-C of Ph], 134.1 [10.7, *o*-C], 130.4 [13.0, *m*-C], 135.1 [3.1, *p*-C]. Treatment of the product (900 mg, *ca.* 2 mmol as **3e**) with NaOH in H_2O –EtOH according to the reported procedure⁹ followed by column chromatography on silica gel [AcOEt–hexane (5:1)] gave (1,3-cyclohexadien-1-yl)diphenylphosphine oxide (**5e**) (351 mg, 62%): mp 139–140 °C (from hexane). IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 1630 and 1600 (conjugated diene). NMR (CDCl_3) δ : 2.2–2.4 (4H, m), 6.00–6.12 (2H, m), 6.38 (1H, brdd, $J_{\text{PH}}=11$ Hz, $J_{\text{HH}}=3.5$ Hz), 7.35–7.95 (10H, m). *Anal.* Calcd for $\text{C}_{18}\text{H}_{17}$ OP: C, 77.13; H, 6.11. Found : C, 76.86; H, 6.02.

Triphenylvinylphosphonium Perchlorate (3f)—Ethylene was bubbled through the solution of **1** (786 mg) in dry CH_2Cl_2 (40 ml) containing 0.2 M LuClO_4 and suspended K_2CO_3 for 30 min. The mixture was electrolyzed at 0 °C as described above. Work-up of the electrolyzed solution gave **3f** (350 mg): mp 134–136 °C (from CH_2Cl_2 –ether). IR $\nu_{\text{max}}^{\text{CHCl}_3}$ cm⁻¹: 1590 (C=C), 1100 (ClO_4^-). NMR (CDCl_3) δ : 5.8–7.0 (3H, m), 7.3–8.0 (15H, m). *Anal.* Calcd for $\text{C}_{20}\text{H}_{18}\text{ClO}_4\text{P}$: C, 61.79; H, 4.67; Cl, 9.12. Found: C, 62.11; H, 4.63; Cl, 9.22.

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