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An Improved Electrochemical Preparation of Alkoxytriphenylphosphonium Salts

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Constant current electrolysis of triphenylphosphine in acetonitrile containing an alcohol and benzoic or succinic acid in a one-compartment cell gave better yields of the title compounds than the previously reported controlled potential electrolysis in a divided cell. Constant voltage electrolysis was also found to be effective. The phosphonium salts reacted with carboxylic acids to form esters in high yields.

Keywords——alkoxytriphenylphosphonium perchlorates; triphenylphosphine; anodic oxidation; constant current electrolysis; constant voltage electrolysis; ester formation

Alkoxyphosphonium ions have been shown to be potential alkylating agents.[1,2] We have previously reported the preparation of alkoxytriphenylphosphonium perchlorates (**2**) *via* anodic oxidation of triphenylphosphine (**1**) in the presence of alcohols.[2] However, the method involves rather troublesome controlled potential electrolysis (C.P.E.) in a divided electrolysis cell, and half of the starting phosphine (**1**) is recovered as the protonated form. Modification of the electrochemical method to overcome these defects should encourage the application of **2** as alkylating agents. We have examined constant current electrolysis (C.C.E.) in a one-compartment cell, which is more practical for synthetic purposes than C.P.E. in a divided cell.

$$\underset{\mathbf{1}}{Ph_3P} \xrightarrow[\text{in MeCN, NaClO}_4\text{, ROH}]{\text{anodic oxidation}} \underset{\mathbf{2}}{[Ph_3P^+-OR][ClO_4^-]}$$

Results and Discussion

C.C.E. of **1** and an alcohol in acetonitrile in the presence of benzoic or succinic acid (equimolar with **1**) was found to give **2** (R=Me, Et, and Pr) in fair yields. Typical results are compared with those[2] of C.P.E. in a divided cell in Table I. The carboxylic acids were added to the system in order to cause the discharge of protons to be the primary process at the cathode and to prevent the products (**2**) from being reduced. Use of an excess of the acids did not improve the yields of **2**. The effects of acid strength on the yield of **2** (R=Et) were examined under the conditions described in Table I. The following results were obtained [acid (arranged in the decreasing order of acidity in water), % yield of **2** (R=Et)]: trifluoroacetic, 9; formic, 8; *m*-bromobenzoic, 34; glycolic, 34; *p*-chlorobenzoic, 42; benzoic, 51; adipic, 46; *p*-methoxybenzoic, 40; acetic, 28; propionic, 29. The decrease in the yield with acids stronger than benzoic acid may be partly ascribed to the partial protonation of **1**, but a full explanation of the results is not yet possible. The effects of electrolysis current and the amount of ethanol were also tested. An electrolysis current of 200—300 mA (area of the anode, *ca.* 12 cm^2) and an amount of ethanol more than 70 times that of **1** were required to obtain a reasonable yield of **2** (R=Et).

To simplify the electrolysis further, constant voltage electrolysis (C.V.E.) of **1** was examined, for which a conventional DC power supply can be used in place of a potentiostat. C.V.E. of **1** in acetonitrile containing ethanol and benzoic acid gave **2** (R=Et) in 54% yield (see experimental section).

Table I. Yields (%) of **2** formed on Electrolysis of **1** in Acetonitrile ($0.2\ \text{M}\ NaClO_4$) containing Alcohols[a]

ROH	C.C.E. in the presence of benzoic acid	C.C.E. in the presence of succinic acid	C.P.E. in a divided cell[c]
MeOH	51[d]	51[d]	33
EtOH	51	48	37
PrOH	45	42	31
Bu^tOH	4[e,f]	3[e,f]	Trace
$PhCH_2OH$	0[f]	0[f]	0

[a] Based on the isolated products after recrystallization.

[b] In an open beaker with a graphite plate (effective area, *ca.* 12 cm^2) and a platinum foil as the anode and the cathode, respectively: **1**, 2 mmol; carboxylic acid, 2 mmol; ROH, 200 mmol; MeCN, 50 ml; electrolysis current, 200 mA. Under these conditions, formation of an ester (*cf.* Table II) as a by-product was negligible.

[c] Results of our previous work (ref. 2).

[d] Without the acid, the yield was less than 10%.

[e] Determined by PMR spectroscopy of the product mixture (*cf.* ref. 2).

[f] The major products were $[Ph_3P^+–R][ClO_4^-]$ and Ph_3PO.

The results described so far suggest that the electrochemical preparation of **2** can be effected by a simple procedure, though further studies on the electrolysis conditions might further improve the yield. For the preparation of **2** (R=Me, Et, and Pr), the corresponding alcohols can be used as the solvent instead of acetonitrile. With higher alcohols, however, the use of acetonitrile will be more practical.

As an additional example of the application of **2** as alkylating agents, reactions with carboxylic acids were investigated. The results (Table II) are comparable with those of the reported methods of ester formation using **1** as one of the reagents.[3] One advantage of the present method is the stability of the reagents. Thus, the phosphonium salts (**2**, R=Me and Et) are stable for over one year in stoppered bottles at room temperature.

Table II. Ester Formation with **2**[a]

R in **2**	Carboxylic acid	Yield (%) of ester[b]
Me	$PhCO_2H$	~100
Et	$PhCO_2H$	84
Et	*p*-$Cl-C_6H_4CO_2H$	86
Et	*p*-$MeO-C_6H_4CO_2H$	77
Et	*o*-$HO-C_6H_4CO_2H$	68
Et	CH_3CO_2H	77
Et	$HOCH_2CO_2H$	91

[a] The phosphonium salts (0.4 mmol) and the acids (0.2 mmol) were refluxed in ROH (8 ml) for 5 h.

[b] Based on the amount of carboxylic acid. The yield was determined by GLC with PEG-20 M as the packing.

Experimental

Materials——Triphenylphosphine (**1**) was recrystallized from hexane and stored under reduced pressure. Sodium perchlorate and acetonitrile were purified as described previously.[4] Primary alcohols were purified by conventional methods. All other chemicals were of reagent grade and were used without further purification.

Apparatus——C.C.E. was carried out in an open beaker (50 ml) using a Hokuto Denko HA-104 potentiostat-galvanostat connected with a Hokuto Denko HF-201 coulometer. A graphite plate (effective area, *ca.* 12 cm^2) and a platinum foil were used as the anode and the cathode, respectively. C.V.E. was performed using a Kikusui Electronics PAB 32-1.2 regulated DC power supply. The electrolysis cell assembly was the same as that employed in C.C.E.

Electrolysis Procedure——Typical examples are described below.

(a) C.C.E.: A mixture of **1** (525 mg), benzoic acid (244 mg), and ethanol (8 ml) in acetonitrile (50 ml) containing 0.2 M $NaClO_4$ was subjected to C.C.E. (200 mA) for 32 min[5] at room temperature. The electrolysis solution was not protected from atmospheric moisture. The electrolyzed solution was evaporated to dryness under reduced pressure, and the residue was extracted with chloroform (3×30 ml). The chloroform was removed under reduced pressure and the residue, after being washed with benzene (3×5 ml), was recrystallized from ethanol–ether to give **2** (R=Et) as colorless crystals (415 mg), the infrared and proton magnetic resonance spectra of which coincided with those of an authentic sample.[2] Ph_3PO and $[Ph_3P^+–Et]$ $[ClO_4^-]$ were formed as by-products.

(b) C.V.E.: A mixture of essentially the same composition as that described above was subjected to C.V.E. The cell voltage was adjusted so that the initial current amounted to 200—250 mA (5—10 V). The electrolysis was discontinued after about 2 F per mole of **1** had been consumed. The electrolyzed solution was worked up as described above.

References and Notes

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5) The theoretical time required for a two-electron oxidation of 2.0 mmol of **1** at 200 mA is 32.17 min.