

removed by evaporation. Water was added to the residue and the sparingly soluble crystals were filtered and dried. Recrystallization from isopropyl ether gave 0.064 g (36%) of 3-hydroxy-1,4,4-trimethyl-5-trichloromethyl-2-pyrrolidinone (7) as colorless plates, mp 148–149°. *Anal.* Calcd. for $C_8H_{12}Cl_3NO_2$: C, 36.88; H, 4.64; N, 5.38. Found: C, 37.04; H, 4.57; N, 5.30. IR ν_{\max}^{KBr} cm^{-1} : 3395 (OH), 1686 (C=O). NMR ($CDCl_3$) δ : 1.22 (3H, s, CH_3), 1.49 (3H, s, CH_3), 3.17 (3H, s, NCH_3), 3.91 (1H, d, $J=4$ Hz, $>CHO-$), 4.11 (1H, s, $>CH$), 4.46 (1H, d, $J=4$ Hz, OH).

Reaction of 3 with Zinc in AcOH—A mixture of 0.26 g of 3 and 0.65 g of zinc dust in AcOH (4 ml) was heated at 70° for 1 hr with stirring. The precipitates were filtered off, and the filtrate was evaporated to dryness under reduced pressure. Water was added to the residue and insoluble material was extracted with ether. The ethereal extract was dried over anhydrous $MgSO_4$. Removal of the solvent left a crystalline residue which on recrystallization from isopropyl ether gave 0.114 g (50%) of 5-dichloromethyl-1,4,4-trimethyl-2-pyrrolidinone (8) as colorless needles, mp 141–142°. *Anal.* Calcd. for $C_8H_{13}Cl_2NO_2$: C, 42.50; H, 5.79; N, 6.15. Found: C, 43.04; H, 5.76; N, 6.15. IR ν_{\max}^{KBr} cm^{-1} : 3266 (OH), 1686 (C=O). NMR ($CDCl_3$) δ : 1.19 (3H, s, CH_3), 1.26 (3H, s, CH_3), 3.17 (3H, s, NCH_3), 3.65 (1H, d, $J=3$ Hz, $>CHN<$), 3.79 (1H, br. $>CHO-$), 4.67 (1H, br. OH), 6.06 (1H, d, $J=3$ Hz, $CHCl_2$).

Acknowledgement The authors are indebted to Mr. K. Narita and other members of the Analysis Center of this college for microanalyses.

[Chem. Pharm. Bull.]
27(7)1700–1703(1979)

UDC 547.438.1.04 : 541.138.04

Phosphorylation of Alcohols *via* Anodic P-Halogenation of Dialkyl Hydrogen Phosphites¹⁾

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(Received February 13, 1979)

Trialkylphosphates, $(RO)_2P(O)OR'$, were prepared from dialkyl hydrogen phosphites, $(RO)_2PHO$, and lithium chloride in $R'OH$ by constant current electrolysis at a glassy carbon anode. Electrolysis at an anode having a larger area and at a lower current density gives better yields of the products. The electrolytic phosphorylation was also performed in acetone and in acetonitrile.

Keywords—electrochemical oxidation; constant current electrolysis; anodic phosphorylation; anodic P-halogenation; dialkyl hydrogen phosphites; trialkyl phosphates

Various methods have been reported for the phosphorylation of alcohols.³⁾ One of the methods used to prepare mixed trialkyl phosphates involves the reaction of alcohols with dialkyl halophosphonates,⁴⁾ which can be conveniently prepared from dialkyl hydrogen phosphites and halogens.⁵⁾ As a continuation of our studies on anodic substitution reactions involving organophosphorus compounds,⁶⁾ an electrochemical modification of the methods

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was attempted, which avoids the use of molecular halogens. In contrast to the extensive studies on anodic C-halogenation⁷⁾ and recent reports on anodic N-halogenation,⁸⁾ little attention seems to have been paid to the corresponding P-halogenation.⁹⁾

Results and Discussion

Dimethyl (Ia), diethyl (Ib), and di-isopropyl hydrogen phosphite (Ic) were chosen as model compounds; and methanol, ethanol, and propanol as alcohols. When alcoholic solutions

TABLE I. Results of Anodic Phosphorylation^{a)}

Run No.	Phosphite	Alcohol	Current efficiency (%) ^{b)}	Yield of II ^{c)} (%)
1	Ia	MeOH	(100) ^{d)}	46
2		EtOH	71	57
3		<i>n</i> -PrOH	42 ^{e,f)}	63 ^{e)}
4	Ib	MeOH	67	48
5		EtOH	77	70
6		<i>n</i> -PrOH	48 ^{e,f)}	64 ^{e)}
7	Ic	MeOH	67	57
8		EtOH	78	72

a) Five mmol of I and 2 g of LiCl in 40 ml of alcohol; glassy carbon plate anode (2.5 × 4 cm); current density, 0.75 Adm⁻²; at 0°.

b) Based on the amount of I consumed after passage of 2 F per mol of I (0.27 Ahr). Current efficiency was estimated in a separate experiment, except for run Nos. 3 and 6.

c) Based on the amount of II isolated by distillation after passage of 4 F per mol of I.

d) See the text.

e) Current density 0.25 Adm⁻².

f) After passage of 4 F per mol of I.

TABLE II. Effects of Current Density, Total Electricity Passed, and Temperature on the Yield of IIc from Ic and MeOH^{a)}

Run No.	Current density (Adm ⁻²)	Amount of electricity (F/mol of Ic)	Temp. (°C)	Current efficiency ^{b)} (%)	Chemical yield ^{c)} (%)
9	1.88 ^{d)}	2	0	38	14
10	0.25 ^{e)}	2	0	74	32
11	0.5 ^{f)}	2	0	64	27
12	1.0 ^{g)}	2	0	64	23
13	0.75	2	0	68	27
14	0.75	4	0	50	66
15	0.75	6	0	33	87
16	0.75	8	0	25	92
17	0.75	2	20	100	88
18	0.75	2	34	100	79

a) Five mmol of Ic and 2 g of LiCl in 40 ml of MeOH; glassy carbon plate anode (2.5 × 4 cm).

b) Based on the amount of Ic consumed.

c) Based on the amount of II c (R' = Me) estimated by NMR spectroscopy (see 'Experimental').

d) Size of anode 1 × 4 cm; the amount of current is the same as that in run Nos. 13—18 (150 mA).

e) Amount of current 50 mA.

f) 100 mA.

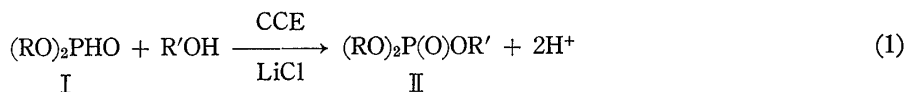
g) 200 mA.

7) N.L. Weinberg, "Technique of Electroorganic Synthesis," ed. by N.L. Weinberg, John Wiley and Sons Inc., New York and London, 1974, Chapter IV and 1975, Chapter VII.

8) H. Miyazaki, *Denki Kagaku*, **44**, 409 (1976); *idem, ibid.*, **45**, 244, 475, and 553 (1977); *idem, ibid.*, **46**, 270 (1978).

9) During preparation of the manuscript, a report on anodic bromination of dialkyl hydrogen phosphites has appeared: S. Torii, H. Tanaka, M. Ukita, and N. Sayo, The 7th Symposium on Organosulfur and Organophosphorus Compounds, Kyoto, Feb. 1979, Extended Abstract pp. 73—75.

of I and lithium chloride were subjected to constant current electrolysis (CCE) under various conditions, corresponding phosphates (II) were formed (Eq. 1). Typical results are



summarized in Tables I and II. Details of the procedures are described in the Experimental section.

In the electrolysis of Ia in methanol (run No. 1 in Table I), Ia was consumed after the passage of 2F per mol of the substrate, but the yield of IIa (R'=Me) was rather low. When the electrolysis was carried out with an increased amount of Ia (20 mmol in 100 ml of MeOH), the yield of IIa increased (63%). No clear explanation can be given for these results at present.

When Ib (5.5 mmol) was added to a pre-electrolyzed solution of lithium chloride in methanol (LiCl, 2 g; MeOH, 40 ml; 150 mA \times 4 hr; at 0°), half of Ib was consumed within 1 hr without further electrolysis and formation of IIb (R'=Me) was observed. These results, together with the facts that chloride ion is oxidized at 1.05 V *vs.* saturated calomel electrode (SCE) under these conditions whereas I is not oxidized below 1.50 V, suggest that equations 2—4 comprise a possible route for the anodic phosphorylation. However, the results obtained in the present study do not exclude a contribution of the reaction involving R'OCI as an intermediate which chlorinates the substrate, as suggested in the anodic chlorination of olefins.⁷⁾



The following points can be noted in Table II. (a) The chemical yield of II increases with decreasing electrolytic current (run Nos. 10—13). This is consistent with the results obtained in chemical chlorination of I, where the yield of chlorophosphonate increased when chlorine was passed slowly into I.¹⁰⁾ (b) At a given electrolytic current, the current efficiency and the yield of II are higher for a run with a wider electrode surface (run Nos. 9 and 13). (c) Prolonged electrolysis improves the yield of II (run Nos. 13—16). However, the value of the current efficiency in run No. 14 indicates that Ic was completely consumed after the passage of the cited quantity of electricity. The increase in the yield observed in run Nos. 15 and 16 suggests that an intermediate is formed from I (probably the corresponding chlorophosphonate, III) and the conversion of the intermediate to II is slower than its formation. Increase in temperature seems to accelerate both reactions (run Nos. 17 and 18).

Phosphorylation was also attempted in acetone and acetonitrile. When a solution of Ib and lithium chloride in acetone containing *ca.* 2% methanol was subjected to electrolysis (current density, 0.75 Adm⁻²; 4F per mol of Ib; at 0°), IIb (R'=Me) was formed, but in low yield (17%). Essentially the same results were obtained on electrolysis in acetonitrile. On using sodium iodide in place of lithium chloride, however, IIb (R'=Me) was isolated in 39 and 42% yield on electrolysis in acetone and in acetonitrile, respectively, under the above electrolytic conditions. Similarly, cyclohexanol was phosphorylated with Ia and sodium iodide in acetone, and IIa (R'=c-C₆H₁₁) was isolated in 30% yield.

Experimental

Materials—Dialkyl hydrogen phosphites were purified by distillation. Alcohols and acetone were purified by conventional procedures. Acetonitrile was purified as described previously.⁹⁾ Lithium chloride and sodium iodide were of reagent grade and were used without further purification.

10) H. McCombie, B.C. Saunders, and G.J. Stacey, *J. Chem. Soc.*, 1945, 380.

Apparatus—Constant current electrolysis was carried out using a Hokuto Denko HA-104 Potentiostat/Galvanostat. An H-type electrolysis cell was used. The anode compartment was separated with a sintered glass disk fitted with a methyl cellulose plug which was prepared by slurring methyl cellulose (350—500 cps) in warm acetonitrile containing sodium perchlorate. Infrared (IR) and nuclear magnetic resonance (NMR) spectra were obtained using Hitachi EPI-2 and R20-A spectrometers, respectively.

Constant Current Electrolysis—Typical examples of the procedure are described below.

(a) General Procedure for the Runs in Table I: A solution of I (5 mmol) and LiCl (2 g) in R'OH (40 ml) was placed in the anode compartment, and MeOH (20 ml) containing HClO₄ (2 ml) in the cathode compartment. The system was subjected to constant current (150 mA) electrolysis with a glassy carbon anode (2.5 × 4 cm) and a stainless steel cathode until 1950 C of electricity (4F per mol of I) had been passed at 0°. Water (30 ml) was added to the anolyte, and the mixture was extracted with chloroform (5 × 30 ml). The chloroform extract, after drying over anhydrous magnesium sulfate, was freed of solvent under reduced pressure. Distillation of the residue under reduced pressure gave II as a colorless oil, which gave the expected analytical results. The IR and NMR spectra of the product were compared with those of an authentic sample.

Current efficiency was estimated in a separate experiment. Thus, a solution of I (5 mmol) and LiCl (2 g) in R'OH (40 ml) was subjected to electrolysis under the conditions described above until 975 C of electricity had been passed. The anolyte was freed of solvent under reduced pressure, and the residue was extracted with chloroform-*d*₃ (3 × 3 ml). The chloroform layer, after adding 0.2 ml of acetonitrile, was adjusted to 10.0 ml in a volumetric flask with chloroform-*d*₃, and subjected to NMR spectroscopy. Current efficiency was estimated from the decrease in the P-H signal of I.

(b) General Procedure for the Runs in Table II: The electrolysis procedure was essentially as described in (a). Current efficiency and chemical yield were estimated in terms of the NMR P-H signal of I and the P-OMe signal of II, respectively, after the anolyte had been treated as described above.

(c) Electrolysis in Acetone: A solution of Ia (5 mmol), NaI (7 g), and cyclohexanol (0.8 ml) in acetone (40 ml) was subjected to electrolysis as described in (a): the catholyte was composed of HClO₄ (2 ml) in acetone (20 ml). Water (30 ml) was added to the anolyte, and the mixture was extracted with chloroform (5 × 30 ml). The chloroform layer was washed successively with aq. Na₂S₂O₃ (10%, 30 ml), aq. HCl (10%, 30 ml), and water (30 ml), and then dried over anhydrous magnesium sulfate. The chloroform was evaporated off under reduced pressure, and the residue was subjected to column chromatography on silica gel with chloroform as an eluant. Removal of the eluant by evaporation followed by distillation of the residue under reduced pressure gave IIa (R' = *c*-C₆H₁₁) as a colorless oil (1.4 mmol). The IR and NMR spectra of the product coincided with those of an authentic sample.

Acknowledgement The authors are grateful to Dainippon Seiyaku Co., Ltd. for performing elemental analysis of the electrolysis products.