1425 w, 1442 w, 1463 m, 1481 w, 1494 w, 1525 m, 1548 m, 1589 s, 1612 s, 1652 m, 1680 w, 1699 w, 1730 w, 1740 w, 1770 w, 2880 w, 2970 br.w.

 $\frac{\text{Bis}(2-\text{fluoro}-2,2-\text{dinitroethyl})\text{bis}(2-\text{chloro}-2,2-\text{dinitroethyl})\text{orthocarbonate (III)}. A sample of 0.3 g FeCl₃ was added to a solution of 3.9 g (0.01 mole) bis(2-fluoro-2,2-dinitroethyl)dichloroformal and 3.8 g (0.022 mole) 2-chloro-2,2-dinitroethanol in 15 ml abs. ClCH₂CH₂Cl and then treated by analogy to procedure a for (I). The yield of (III) was 4.3 g (65%). IR spectrum (<math>\nu$, cm⁻¹): 770 w, 795 w, 824 m, 870 m, 880 w, 1100 m, 1140 br.s, 1180 w, 1338 s, 1400 w, 1460 w, 1542 w, 1612 s, 2700 w, 2940 w, 2980 br.w.

 $\frac{\text{Bis}(2-\text{fluoro}-2,2-\text{dinitroethyl})\text{bis}(2,2-\text{difluoro}-2-\text{nitroethyl})\text{orthocarbonate (IV)}}{\text{sample of 0.3 g FeCl}_3 was added to a solution of 3.9 g (0.01 mole) bis(2-fluoro-2,2-dinitroethyl)dichloroformal and 2.84 g (0.022 mole) 2,2-difluoro-2-nitroethanol in 15 ml abs. ClCH₂CH₂Cl and then treated by analogy to procedure a for (I). The yield of (IV) was 3.9 g (68%). IR spectrum (<math>\nu$, cm⁻¹): 770 w, 820 m, 865 m, 883 m, 965 w, 1040 w, 1125 s, 1150 s, 1180 br.s, 1338 s, 1375 m, 1417 m, 1468 w, 1629 s, 1680 m, 1735 w, 3000 br.w, 3040 w.

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CATHODE-CATALYZED TRANSESTERIFICATION

OF ALKYLPHOSPHONATES

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The cathodic electrolysis of aliphatic alcohols and alkylphosphonates in acetonitrile with 0.5 N Et_4NClO_4 as the base electrolyte leads to mono- and ditransesterified phosphonates. The yield and ratio of these products is a function of the nature of the starting reagents and amount of current passed.

Interest in the transesterification of esters of alkylphosphonic acids is related to the possibility of synthesizing higher and cyclic esters from readily available lower esters. However, the reported variants of this reaction [1-4], as a rule, require heating and base catalysis. The yields of the final products are not always satisfactory.

In the present work, we show that the transesterification of alkylphosphonate esters (I) may be carried out under cathodic catalysis conditions at ~20°C. The essence of this method lies in the generation of the alcoholate ion from the alcohol on a vitreous carbon or platinum electrode [5,6]. This ion then enters a nucleophilic replacement reaction at the phosphorus atom in phosphonate (I), leading to mono- (II) and ditransesterified products (III).

$$(R^{2}0)_{2}P(0)R^{3} \xrightarrow{R^{1}0^{-}} R^{1}0(R^{2}0)P(0)R^{3} \xrightarrow{R^{1}0^{-}} (R^{1}0)_{2}P(0)R^{3} \xrightarrow{(1)} (II) \xrightarrow{R^{2}0^{-}} (II) \xrightarrow{(II)} (III) \xrightarrow{(1)} (III) \xrightarrow{(1)$$

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TABLE 1. Yields of Mono- (II) and Ditransesterified Products (III) upon the Electrolysis of Phosphonates (I) in 0.5 N Et_4NClO_4 in Acetonitrile Containing 15 vol. % R^1OH with a Vitreous Carbon (VC) or Platinum Cathode

Experi-			(I) *	(lath a da	ρ	Yield,	*** %
number	R'OH	R ²	R³	Cathode	F/mole	(11)	(III)
1	n-PrOH	Me	Me	VC	2.30	_	65
2	n-BuOH	Me	Me	VC	0.50	48	-
3	n-BuOH	Me	Me	VC	1,05	50	1 10
4	n-BuOH	Me	Me	VC	2,30	_	61
5	n-BuOH	Me	Me	Pt	2,30		68
6	i-C ₅ H ₁₁ OH	Mie	Me	VC	1,00	45	15
7	i-C ₅ H ₁₁ OH	Me	Me	Pt	2,10		63
8	n-C ₆ H ₁₃ OH	Me	Me	VC	1,01	46	16
9	n-C ₆ H ₁₃ OH	Me	Me	Pt	2,20	-	65
10	n-C ₆ H ₁₃ OH	Et	Me	VC	1,50	65	5
11	n-BuOH	Me	CH (OMe) ₂	VC	1.80	11 ***.	5
12	n-C ₆ H ₁₃ OH	Et	$CH_2CH(OEt)_2$	VC	2,00	- `	3 0
13	n-BuOH	Me	Ph	VC	2,00	-	60

*The conversion of (I) was 60% upon the passage of 0.5 F/mole, 80-90% upon the passage of \geq 1 F/mole, and 90-100% upon the passage of \geq 2 F/mole.

**The yield of the isolated products was calculated relative to the amount of (I) taken.

""The ratio of (II) to (III) in the mixture was determined by gas-liquid chromatography.

The yield and ratio of products (II) and (III) are largely functions of the nature of starting phosphonate (I) and amount of current passed (Table 1). Thus, dimethyl methyl-phosphonate ($\mathbb{R}^2 = \mathbb{R}^3 = \mathbb{M}e$) readily undergoes electrochemical transesterification (ECTE) with various alcohols such as n-propyl, n-butyl, isopentyl, and n-hexyl alcohols. Passing 0.5 F/mole leads to the exclusive formation of monosubstituted product (II) (Table 1, experiment 2). Passing ≥ 1 F/mole leads to a mixture of mono- and disubstituted esters (Table 1, experiment 3). Disubstituted ester (III) is the only electrolysis product upon passage of ≥ 2 F/mole (Table 1, experiments 1, 4, 5, 7, and 9).

The use of acetonitrile as the solvent and tetraethylammonium perchlorate as a base electrolyte with a low tendency for ion pair formation provides for high reactivity of the alcoholate ions at the cathode, this permits us to carry out ECTE of phosphonates (I) at ~20°C. We should note that ECTE proceeds with high conversion of (I) and is extremely selective. Under the electrolysis conditions, (I)-(III) do not enter side bulk or electrode processes. Monitoring by thin-layer and gas-liquid chromatography showed that the consecutive conversion of (I) to (II) and then to (III) occurs during the electrolysis (scheme 1). The overall yield of (II) and (III) according to the gas-liquid chromatographic data taking account of the conversion of (I) is close to quantitative. On the other hand, the yield of the products calculated relative to the amount of (I) taken after treatment of the reaction mixture was ≤ 70 %. The partial decomposition of (II) and (III) apparently occurs upon distillation, especially at high temperatures. We should add that the ECTE method recently described by Masumizu et al. [7] for esters of carboxylate acids proceeds with only 32-50% conversion, while the yields of the products isolated by high efficiency liquid chromatography do not exceed 52% taking account of conversion.

Diethyl esters of alkylphosphonic acids also undergo ECTE (Table 1, experiment 10). However, in this case, a greater amount of current is required for complete conversion. Monosubstituted ester (II) is the major product even when Q = 1.5 F/mole. The replacement of the second ethoxy group is significantly hindered in such compounds.

The introduction of the electron-donor dimethoxymethyl group $(R^3 - CH(OMe)_2)$ significantly complicates the ECTE. Although (II) and (III) are formed in this case, the yields of these products are low (Table 1, experiment 11). On the other hand, the ECTE reaction does not occur at all in the presence of a diethoxymethyl group in diethyl phosphonate and the starting phosphonate is recovered almost completely after the electrolysis.

terificatio	uo					
	Phosphonate		Bp, °C (p, mm Ho)		NMR spectrum in	n CDC1 ₃ (IMS)
R	R ²	Ra		frail (n. + r)(du	. δP_{-CH_3} , ppm (J PCH, Hz)	ыс. 8 _С р. ррт (J _{PC} , Hz)
n-Pr	n-Pr	Me	93-94°(10)	1,4180(22) [9, 10]	1,40(17,0)	9,56(144,4)
Me	n-Bu	Me	$98-101^{\circ}(10)$	1,4187(22) [10]	1,39(17,0)	9,06(144,3)
n-Bu	n-Bu	Me	124-125° (10)	1,4240(22) [1,9]	1,38(17,0)	10,14(144,4)
Me	i-C3H11	Me	115-118° (10)	1,4330 (22)	1,39(17,0)	9,21 (144,3)
i-CsH11	-CsIII	Me	138° (10)	1,4275(22) [9]	1,39(17,0)	10,07 (144,3)
Me	n-CeH13	Me	128-131°(10)	1,4278(21)	1,39(17,0)	9,19(143,8)
n-C ₆ H ₁₃	n-C ₆ H ₁₃	Me	172-174° (10)	1,4334(21) [1]	1,39(17,0)	10,24(145,2)
Et	n-CeH13	. Me	132-135°(12)	1,4251(24) [1]	1,39(17,0)	10,36(144,3)
n-Bu	n-Bu	Ph	96-97° (0,01)	1,4845 (24)	J	128,65 (188,0)
n-C ₆ H ₁₃	$n^{-}C_{6}H_{13}$	CH ₂ CH (OEt) 2	115-122° (0,01)	1,4368 (24)	2,1(19,0)	

TABLE 2. Physicochemical Indices of Phosphonates R¹O(R²O)P(O)R³ Obtained by Electrochemical Transes-Ľ, When the diethoxymethyl is removed from the phosphorus atom by one methylene unit, transesterification becomes possible although the yield of product (III) is low (Table 1, experiment 12). The introduction of a phenyl group with is a poorer electron donor than the above mentioned substituents permits rather smooth ECTE (Table 1, experiment 13). However, when a strong electron-withdrawing group such as CN ($\mathbb{R}^3 - CH_2CN$) is introduced into the α position of (I), transesterification does not proceed at all. In this case, loss of the labile α -hydrogen proceeds initially at the cathode.^{*} We also cannot exclude the possibility of α -deprotonation of the phosphonate due to its reaction with the alcoholate ion generated at the cathode. The carbanion site arising at the α site has strong electron-donor properties and hinders nucleophilic substitution at the phosphorus atom. On the other hand, the phosphonate carbanion readily reacts with carbonyl compounds such as benzaldehyde, leading to an olefin through the Horner reaction [8].

$$(EtO)_{2}P(O)CH_{2}CN---- \underbrace{ \begin{array}{c} \xrightarrow{n-BuO^{-}} \times \longrightarrow & (II) + (III) \\ & \downarrow \\ & \downarrow \\ & \downarrow \\ & -H^{-e} \end{array}}_{(EtO)_{2}P(O)CHCN} \xrightarrow{PhCHO}_{-(EtO)_{2}PO_{2}^{-}} PhCH=CHCN$$

$$(3)$$

Hence, phosphonates not containing strong electron-donor substituents at the α -carbon atom or not having a labile hydrogen at this position undergo the ECTE reaction. Mono- or ditransesterified esters may be obtained by the ECTE method depending on the amount of current passed. This process permits us to obtain higher esters of alkylphosphonic acids from available lower esters. Furthermore, this reaction may be useful for obtaining cyclic alkylphosphonates. The feasibility of such a process was demonstrated in the case of the transesterification of (MeO)₂P(O)Me by 1,3-butanediol.

$$(MeO)_{2}P(O)Me + MeCH(OH)CH_{2}CH_{2}OH \xrightarrow{2F/mole}_{-2MeO^{-}} O \overset{O}{\overset{\parallel}{\overset{\parallel}{\underset{Me}{\overset{}}}} -Me$$

$$Me \qquad (4)$$

However, the product yield is low and further study is required in order to improve the yield.

EXPERIMENTAL

The electrolyses were carried out in a glass diaphragm cell at ~20°C. A $50 \cdot \text{cm}^2$ vitreous carbon plate or $60 \cdot \text{cm}^2$ platinum mesh was used as the cathode, while a platinum mesh was used as the anode. The catholyte was stirred using a magnetic stirrer.

A sample of 100 ml 0.5 N Et_4NClO_4 in abs. acetonitrile containing 0.065 mole phosphonate (I) and 15 vol. \$ alcohol was added to the cathodic section of the cell. The anolyte was 100 ml of the base electrolyte. The electrolysis was carried out in a galvanostatic regime; the current strength was 0.10-0.15 A. After passage of the required current, the catholyte was evaporated under vacuum and the residue was diluted with 350 ml ether. The base salt precipitate was filtered off. After recrystallization, this salt may be reused. The ethereal solution was washed with five 50-ml portions of water, dried over Na₂SO₄, and evaporated. The residue consisting of phosphonate (II) and/or (III) was distilled in vacuum (Table 2). Extraction of the wash water with CH_2Cl_2 with subsequent drying over Na₂SO₄ and distillation gave starting dimethyl methylphosphonate.

The structures of the phosphonates obtained (Table 2) were supported by ¹H and ¹³C NMR spectra taken on a Tesla BS497 spectrometer at 100 MHz and by chromato-mass spectra taken on a Varian MAT 3H-A spectrometer. The mass spectra of all the compounds have molecular ion peaks. The physicochemical indices were found to correspond to reported values [1, 9, 10].

The possibility of such a process was demonstrated in our recent work [8] on phosphonates with various electron-withdrawing substituents in the α position, which served as the basis for the development of an electrochemical variant of the Horner reaction.

Thin-layer chromatography was carried out on Silufol plates with 10:1 ethyl acetate/methanol as the eluent. Gas-liquid chromatography was carried out on a 0.3 ×250-cm glass column packed with SE-30 using a Chrom-5 chromatograph.

The product in experiment 11 (Table 1) was isolated as a mixture of (II) and (III) at 95-100°C (0.08 mm). The structures of these compounds were indicated by chromato-mass spectrometry and ¹³C NMR spectroscopy in CDCl₃ with TMS as the standard (δ_{C-P} , ppm (J_{PC}, Hz)): 100.8 (206) for MeO(n-BuO)P(O)CH(OMe)₂ and 101.1 (206) for (n-BuO)₂P(O)CH(OMe)₂. The treatment of the catholyte and separation of PhCH-CHCN (bp 71-75°C (0.01 mm), n_D²⁴ 1.5960) in the experiment with (EtO)₂P(O)CH₂CN and PhCHO was carried out by analogy to our previous procedure [8]. The product formed in the electrolysis of (MeO)₂P(O)Me and 1,3-butanediol after treatment of the reaction mixture was identified by gas-liquid chromatography by comparison with an authentic sample and chromato-mass spectrometry.

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