CONCLUSIONS

Reaction of dimethylvinylethynylcarbinol with the fluorinated alcohols 1,1,3-trihydrotetrafluoropropanol, 1,1,5-trihydrooctafluoropentanol, and 1,1,7-trihydrodecafluoroheptanol has given the ethers, the properties of which have been determined.

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ELECTROCHEMICAL SYNTHESIS OF ARYL PHOSPHONATES

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The electrochemical oxidation of trialkyl phosphites $(RO)_3P$ at platinum and glass–carbon electrodes in the presence of aromatic compounds ArH results in the formation of O,O'-dialkyl arylphosphonates [1, 2]. It was of interest to study in greater detail the effects of experimental conditions (current density, concentrations of phosphite and aromatic compounds, etc.) on the synthesis of arylphosphonates. We here describe the electrochemical synthesis of arylphosphonates at glass-carbon electrodes in acetonitrile in the presence of Na_3PO_4.

EXPERIMENTAL

The electrochemical oxidation of trialkyl phosphites in MeCN was carried out at an SU-2000 glass–carbon electrode with 0.1 M $NaClO_4$. A stationary disk electrode was used for the voltammetric measurements. Preparative electrolysis was carried out under dry argon in a diaphragm cell with an anolyte capacity of 100 cm^3 under galvanostatic conditions (current density 4-5 mA/cm^2), anode area 50 cm^2. The cathode was a nickel spiral with a surface area of 10 cm^2. The potential of the operating electrode was measured relative to an Ag electrode in an 0.01 M solution of $AgNO_3$ in MeCN. ^{31}P NMR spectra were obtained on a KGU-4 NMR instrument at a frequency of 10.2 MHz, relative to 85% H_3PO_4. Positive values for the chemical shifts are given towards lower field.

DISCUSSION OF RESULTS

In the anodic oxidation of trialkyl phosphites both at glass–carbon and platinum electrodes, a definite wave occurs at potentials of 1.6-1.7 V with a current peak corresponding to the transfer of 0.6-0.7 electrons from the depolarizer molecule to the electrode. The model compounds used for the calculation of the one-electron level was trimesitylphosphine, which gives stable cation-radicals on electrochemical oxidation [3]. Figure 1 shows the potentiodynamic polarization curves for the oxidation of triethyl phosphite in the absence and in the presence of benzene. In the presence of benzene, the height of the oxidation wave for triethyl phosphite increases substantially. The anode current for the oxidation of benzene, observable only at potentials >2.0 V, can be ignored in this region of potentials. Similar results were obtained at the glass-carbon electrode for tributyl, tri-n-propyl, and triisopropyl phosphites. In the presence of benzene, toluene, ethylbenzene, or cumene the oxidation waves for all the phosphites examined increased up to the 1e level, indicating that the phoshpite cation-radicals react with the aromatic compounds.

The preparative oxidation of trialkyl phosphites in the presence of aromatic compounds and Na_3PO_4, used as a proton acceptor, afforded the corresponding arylphosphonates (Table 1) by the following suggested reaction sequence:

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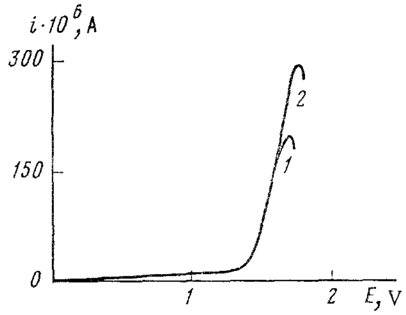

Fig. 1. Polarization curves for oxidation at a stationary glass–carbon electrode: 1) triethyl phosphite (C, $5 \cdot 10^{-3}$ M); 2) triethyl phosphite (C, $5 \cdot 10^{-3}$ M) + benzene (C, $1 \cdot 10^{-1}$ M). Base electrolyte, 0.1 M $NaClO_4$, scanning rate 4.8 V/min.

$$(RO)_3P - e^- \rightleftarrows (RO)_3P^{+\cdot}$$

$$(RO)_3P^{+\cdot} + ArH \rightarrow (RO)_3\dot{P}Ar + H^+$$

$$(RO)_3\dot{P}Ar - e^- \rightarrow (RO)_3\overset{+}{P}Ar$$

$$Na_3PO_4 + H^+ \rightarrow Na_2HPO_4 + Na^+$$

The quasiphosphonium cations $(RO)_3\overset{+}{P}Ar$ formed are converted into $ArP(O)(OR)_2$ in the presence of alcoholic sodium alkoxides

$$Ar\overset{+}{P}(OR)_3 + RONa \rightarrow ArP(O)(OR)_2 + ROR + Na^+$$

The occurrence of this reaction is indicated by the presence in the ^{31}P NMR spectrum of the reaction mixture following electrolysis of a single signal at 50-52 ppm. Following treatment of the reaction mixture with sodium alkoxide, this signal disappears and a signal for the arylphosphonate appears with δ ^{31}P +17 to +18 ppm. It follows that sodium alkoxide is the most convenient and effective reagent for the dealkylation of the quasiphosphonium salts. Pyridine, which was used previously [1], was inconvenient, since the N-alkylpyridinium compound formed by alkylation hinders extraction of the required product, thereby reducing the yield. Sodium iodide, used in [2], contaminates the arylphosphonate with iodine, which complicates the purification of the products.

Examination of the effects of current density, the concentrations of phosphite and aromatic compound, and the amount of Na_3PO_4 in the electrolyte gvae the following results. As the concentration of ArH increases, the yields of $ArP(O)(OR)_2$ increase. In all experiments, therefore, we used as large an excess as possible of ArH over the trialkyl phosphite. Increasing the amounts and the state of subdivision of the Na_3PO_4 also increased the yields of $ArP(O)(OR)_2$. Finally, the highest yields of $ArP(O)(OR)_2$ were obtained at the highest possible current densities.

These results lead to the conclusion that the main reason for reduced yields of $ArP(O)(OR)_2$ [1, 2] are reaction of the phosphite with the perchloric acid liberated, and with the quasiphosphonium cations

$$(RO)_3P + H^+ \rightarrow (RO)_3\overset{+}{P}H \rightarrow \rightarrow \text{breakdown products} \qquad (1)$$

$$(RO)_3P + Ar\overset{+}{P}(OR)_3 \rightarrow \rightarrow R\overset{+}{P}(OR)_3 + ArP(O)(OR)_2 \qquad (2)$$

$$(RO)_3P + R\overset{+}{P}(OR)_3 \rightarrow \rightarrow R\overset{+}{P}(OR)_3 + RP(O)(OR)_2$$

TABLE 1. Results of Preparative Electrolysis at a Glass-Carbon Electrode in the Presence of Aromatic Compounds ArH

$(RO)_3P$	ArH	$ArP(O)(OR)_2$	Yield,* %	bp, °C (p, mm Hg)	n_D^{20}	Isomer composition, %			P, %	
						ortho	meta	para	found	calculated
$(EtO)_3P$	PhH	$C_6H_5P(O)(OEt)_2$	86	100 (1)	1,4916	—	—	—	14,20	14,46
$(EtO)_3P$	PhMe	$MeC_6H_4P(O)(OEt)_2$	95	130 (3)	1,4993	40	28	32	13,25	13,57
$(EtO)_3P$	PhEt	$EtC_6H_4P(O)(OEt)_2$	93	112 (1)	1,4995	33	33	34	12,52	12,79
$(n\text{-}PrO)_3P$	PhH	$C_6H_5P(O)(OPr\text{-}n)_2$	84	106–108 (1)	1,4895	—	—	—	12,54	12,79
$(n\text{-}PrO)_3P$	PhMe	$MeC_6H_4P(O)(OPr\text{-}n)_2$	90	110–112 (1)	1,5033	39	28	33	11,86	12,09
$(i\text{-}PrO)_3P$	PhMe	$MeC_6H_4P(O)(OPr\text{-}i)_2$	70	98–100 (1)	1,5120	39	27	34	11,75	12,09
$(n\text{-}BuO)_3P$	PhH	$C_6H_5P(O)(OBu\text{-}n)_2$	87	115–116 (1)	1,4848	—	—	—	11,67	11,51

*See [1, 2].

Reduced yields of the required products could also be due to reaction of the phosphite cation-radicals with water present in the "dry" solvent when perchlorates are used as the base electrolyte

$$(RO)_3P^{+\cdot} + H_2O - 2e \rightarrow (RO)_3PO + 2H^+ \qquad (3)$$

A large excess of ArH suppresses reaction (3), the presence of Na_3PO_4 prevents protonation and destruction of the phosphite by perchloric acid, and the use of maximum current densities and moderate concentrations of phosphite reduces alkylation of the starting material by quasiphosphonium cations (although it does not entirely eliminate it). When the reaction is carried out under these conditions, the yields of arylphosphonates are considerably increased.

CONCLUSIONS

Electrochemical oxidation of trialkyl phosphites in the presence of aromatic hydrocarbons at glass—carbon electrodes with the addition of Na_3PO_4 gives arylphosphonates in high yields.

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SUBSTITUTION REACTIONS INVOLVING ORGANOALUMINUM COMPOUNDS.

COMMUNICATION 2.* SYNTHESIS OF SUBSTITUTED ALLENES FROM PROPARGYL ACETATES

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It is known [2] that the acetylene—allene rearrangement which occurs on substitution is one of the most reliable routes to substituted allenes. Much attention has recently been devoted to the substitution of acetylenic alcohols and halides by organomagnesium and organolithium compounds [3, 4]. These reactions proceed rapidly and selectively when catalyzed by transition metals, copper compounds being particularly active [5].

We have previously reported [1] the reaction of propargyl acetates with organoaluminum compounds (OAC) to give substituted allenes. A necessary condition for the reaction to occur is catalysis by Cu(I) salts. This communication describes a study of the effects of different reaction parameters (reaction temperature, solvent, structure of the substrate and the reagent) on the yields of allenes. A variety of transition metals were tried as catalysts.

The reactions of substituted propargyl acetates with a variety of OAC (R_3Al, R_2AlR', R_2AlCl, $RAlCl_2$, R_2AlOR, $LiAlR_4$) have been examined. The best results in terms of the selectivity of the reaction were obtained with the trialkylalanes R_3Al and R_2AlR', yields of allenes of 45-86% being obtained, whereas with R_2AlOR', R_2AlCl, and $RAlCl_2$ the yields were much lower. The reaction goes well in ethereal solvents (diethyl ether, dipropyl ether, and THF). In CH_2Cl_2 the reaction is more vigorous, but without selectivity, and in addition to allenes considerable amounts of by-products are formed. In hydrocarbons (hexane or heptane), the rate of reaction is much slower, and complete conversion of the acetate does not occur.

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*For Communication 1, see [1].

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