

Anodic Oxidation of Organophosphorus Compounds. Part 1. Anodic Alkylamination of Triphenylphosphine

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Anodic oxidation of triphenylphosphine has been investigated by cyclic voltammetry and controlled potential electrolysis at a glassy-carbon electrode in acetonitrile. Electrolyses of triphenylphosphine in the presence of various primary amines result in the formation of monoalkylaminotriphenylphosphonium salts in 50–70% yield. The reaction sequence is suggested to be one-electron oxidation of the phosphine, nucleophilic attack of primary amine on the resulting cation radical, and a further one-electron transfer and loss of a proton.

NUMEROUS and systematic studies have been reported on the anodic oxidation of the organic compounds containing nitrogen,¹ but little attention has been paid to that of organophosphorus compounds in spite of the well known similarities and differences in the chemical property between nitrogen and phosphorus. Several groups of investigators have found that triphenylphosphine (Ph_3P) is oxidized at platinum^{2,3} and carbon paste electrodes⁴ in acetonitrile to give triphenylphosphinium cation radical, which reacts with small amounts of water present in the solvent to give triphenylphosphine oxide (Ph_3PO).^{2,4} Thus a possibility of anodic substitution reactions at phosphorus atom to afford stable products has been suggested.

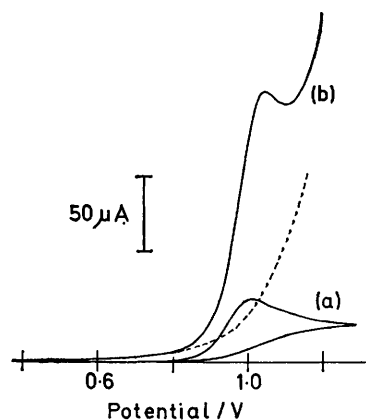
We report here the results of cyclic voltammetry and controlled potential electrolysis of Ph_3P in acetonitrile at a glassy-carbon electrode with and without added aliphatic primary amines. Anodic alkylamination to give stable compounds may be a novel example among various anodic substitution reactions hitherto reported.⁵

In acetonitrile containing 0.1M-sodium perchlorate, Ph_3P showed a single anodic peak at 1.00 V but no cathodic peak down to -0.1 V in the reverse scan (Figure). All potentials were measured against aqueous saturated calomel electrode (s.c.e.). The i_p value of the anodic wave was proportional to the concentration of Ph_3P up to 50mm. At a fixed Ph_3P concentration (5mm),

¹ N. L. Weinberg, 'Technique of Electroorganic Synthesis,' ed. N. L. Weinberg, Wiley, New York and London, 1974, ch. IV; R. F. Nelson, *ibid.*, chs. V and IX.

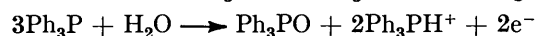
² G. Schiavon, S. Zecchin, G. Cogoni, and G. Bontempelli, *J. Electroanal. Chem.*, 1973, **48**, 425.

a linear relationship between the i_p value and the square root of the scan rate was obtained at scan rates of 0.012–3.12 V s^{-1} . There was no evidence of a reversible process



Cyclic voltammogram of Ph_3P (5mm) (a) in acetonitrile, (b) in acetonitrile containing 1% n-propylamine; 0.1M- NaClO_4 , 0.05 V s^{-1} . Dashed line represents the background current of acetonitrile containing 1% n-propylamine

at any scan rate examined. Electrolysis of Ph_3P in acetonitrile at 1.0 V gave a coulometric n -value of 0.9–1.0, and formation of Ph_3PO and Ph_3PH^+ was recognized.



³ Yu. M. Kargin, E. V. Nikitin, G. V. Romanov, O. V. Parakin, B. S. Mironov, and A. N. Pudovic, *Doklady Akad. Nauk S.S.S.R.*, 1976, **226**, 1101 (*Chem. Abs.*, 1976, **85**, 11,611f).

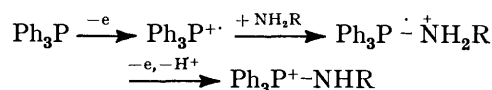
⁴ Von H. Matschiner, L. Krause, and F. Krech, *Z. anorg. Chem.*, 1970, **373**, 1.

⁵ L. Ebersson and K. Nyberg, *Tetrahedron*, 1976, **32**, 2185.

According to the stoichiometry suggested the n -value should be 0.66.^{2,*} The observed n -value indicates that the acetonitrile used contained a considerable amount of water. Thus on electrolysis of Ph_3P in the presence of 10% water an n -value of 2.0 was obtained, and Ph_3PO was formed almost quantitatively. All these results are essentially the same as those obtained at a platinum electrode.²

Effects of primary amines on the voltammogram of Ph_3P was examined. The i_p value increased with the concentration of amine and gradually reached a limiting value. The ratio of the limiting i_p value to that in the absence of amine was approximately three at voltage scan rate of 0.05 V s^{-1} (Figure),[†] and decreased with increase in the scan rate. Under these conditions the plot of i_p value against the square root of the scan rate was no longer linear but convex, indicating that some chemical reactions take place between two successive electron transfers. Controlled potential electrolyses of Ph_3P in acetonitrile containing an excess of primary

identification of the products are described in the Experimental section. Without electrolysis the phosphonium salts were not formed at all under the same conditions at least for five days. The coulometric n -values were considerably larger than two (Table 1) probably because part of the primary amines were oxidized at the anode potential applied (see Figure).[‡] However, the n -value required for the formation of the phosphonium salts will be 2. This is supported by the results obtained on electrolysis of Ph_3P in acetonitrile containing 10% water (see above), and by the fact that the ratio of voltammetric peak height of Ph_3P in the presence of 10% water to that in the absence of water was essentially the same as the ratio of i_p values observed in the presence of an excess of primary amine (*ca.* 3). The following scheme is suggested for the formation of the phosphonium salts.



Several methods of preparation of monoalkylaminotriphenylphosphonium salts have been reported.^{8,9} The electrochemical method described in this paper can be compared with that of Appel *et al.*⁹ which involves one-step reaction of amines and carbon tetrachloride with Ph_3P . The electrochemical method requires shorter time for the reaction.

EXPERIMENTAL

Materials.— Ph_3P was recrystallized from *n*-hexane and stored under reduced pressure. Primary amines were distilled before use. Sodium perchlorate was purified as described previously.¹⁰ Acetonitrile was distilled first from calcium hydride and then from phosphorus pentaoxide after treatment by the method of Mann *et al.*¹¹

Apparatus.—Cyclic voltammetry and controlled potential electrolysis were carried out essentially as described previously.¹² An NF Circuit Design Block FG-100 function generator, Hokuto Denko HA-104 Potentiostat/Galvanostat, Kawasaki Electronica TM-2520D dual-channel transient memory connected with a L-2001 pre-amplifier, and a Toa Dempa XYR-2A recorder were used for obtaining i_p vs. $V^{1/2}$ relationship. All voltammetric measurements were carried out at $25 \pm 0.05 \text{ }^\circ\text{C}$. I.r. and n.m.r. spectra were obtained using a Hitachi EPI-2 and R-20A spectrometers, respectively.

Controlled Potential Electrolysis.—Typical examples of the procedure are described.

(a) *Electrolysis in acetonitrile.* Ph_3P (20.1 mg) was

⁶ I. Pintér, J. Kovács, and A. Messmer, *Carbohydrate Res.*, 1977, **53**, 117.

⁷ C. J. Woerner and W. M. Gulick, jun., *Electrochim. Acta*, 1977, **22**, 445.

⁸ H. H. Sisler, A. Sarkis, H. S. Ahuja, R. J. Drago, and N. L. Smith, *J. Amer. Chem. Soc.*, 1959, **81**, 2982; L. Horner and H. Oediger, *Ann.*, 1959, **627**, 142; H. Zimmer and G. Singh, *J. Org. Chem.*, 1963, **28**, 483.

⁹ R. Appel, R. Kleinstuck, K. D. Ziehn, and F. Knoll, *Chem. Ber.*, 1970, **103**, 3631.

¹⁰ M. Masui and H. Ohmori, *J.C.S. Perkin II*, 1972, 1882.

¹¹ J. F. O'Donnell, J. T. Ayres, and C. K. Mann, *Analyt. Chem.*, 1965, **37**, 1161.

¹² H. Sayo and M. Masui, *J.C.S. Perkin II*, 1973, 1640.

TABLE 1

Results of controlled potential electrolysis of Ph_3P in acetonitrile^a

| Amount of Ph_3P (mg) | Additions | n -Value | Products identified (yield/%) ^b |
|--------------------------------------|------------------------------------|------------|--|
| 20.1 ^c | None | 0.95 | Ph_3PO , ^d $\text{Ph}_3\text{P}^+\text{H}^+$ ^d |
| 266.3 ^c | 10% (w/v) water | 2.05 | Ph_3PO (96.6) |
| 262.3 | <i>n</i> -Propylamine ^e | 3.92 | $\text{Ph}_3\text{P}^+\text{NHP}^{\text{r}} \text{ClO}_4^-$ (57.6) |
| 339.2 | Isopropylamine ^e | 3.08 | $\text{Ph}_3\text{P}^+\text{NHP}^{\text{r}} \text{ClO}_4^-$ (50.1) |
| 264.7 | Isobutylamine ^e | 3.61 | $\text{Ph}_3\text{P}^+\text{NHBu}^{\text{t}} \text{ClO}_4^-$ (56.2) |
| 263.6 | <i>t</i> -Butylamine ^e | 3.95 | $\text{Ph}_3\text{P}^+\text{NHBu}^{\text{t}} \text{ClO}_4^-$ (67.8) |
| 262.3 | Cyclohexylamine ^e | 2.50 | $\text{Ph}_3\text{P}^+\text{NH-cyclohexyl} \text{ClO}_4^-$ (60.5) |

^a The volume of anolyte was 100 ml unless otherwise noted. Sodium perchlorate (0.1M) was used as supporting electrolyte. Electrolysis was carried out under a stream of dry nitrogen. Those runs with added primary amines were carried out at 0.95 V at $0 \text{ }^\circ\text{C}$ and those without amine at 1.0 V at room temperature. ^b Based on the isolated product after recrystallization. ^c The volume of anolyte was 40 ml. ^d See Experimental section. ^e Concentration of amine was 1% (v/v).

amines gave monoalkylaminotriphenylphosphonium perchlorates as main products. Typical results are summarized in Table 1. Details of the procedures and

* It has been reported that the water content of nominally anhydrous acetonitrile solutions is enough for the occurrence of the reaction.²

† The i_p value in the presence of excess primary amine was corrected by subtracting the background current arising from slow oxidation of the amine (see Figure).

‡ The possibility that part of the phosphonium salt was deprotonated by an excess of primary amine to afford triphenylphosphinalkylimine cannot be excluded because the latter was stated to be formed from aminophosphonium salt in dichloromethane by the action of triethylamine.⁶ Actually when *t*-butylaminotriphenylphosphonium perchlorate was dissolved in acetonitrile containing 1% *t*-butylamine and 0.1M-sodium perchlorate and then set aside for 10 h, the solution showed a small anodic peak around 0.9 V. Anodic oxidation of triphenylphosphinephenylimine has been reported.⁷

subjected to electrolysis in acetonitrile (40 ml) containing 0.1M-NaClO₄ at 1.0 V until the current became <2% of the initial value (*ca.* 80 min). During the course of the electrolysis a slow stream of dry nitrogen was bubbled through the anolyte. From the current-time curve 6.98 C, which corresponded to $n = 0.95$, was found to be consumed. The anolyte was adjusted to 50.0 ml by addition of acetonitrile containing 0.1M-NaClO₄ in a volumetric flask. The resulting

layer was washed with three 20-ml portions of water, dried with MgSO₄, and evaporated to dryness under reduced pressure. The colourless crystals obtained were recrystallized from benzene-light petroleum to give Ph₃PO (273 mg; m.p. 156°), the i.r. spectra of which coincided with that of authentic sample.

(c) *Electrolysis in acetonitrile containing an excess of primary amine.* Electrolysis was carried out at 0 °C to

TABLE 2
Physical and spectroscopic data of Ph₃P⁺NHR ClO₄⁻

| R | M.p. (°C) | Elemental analysis (%) | | | | | N.m.r. ^a [δ(p.p.m.)] | I.r. ^b (ν/cm ⁻¹) | |
|-----------------|-------------|------------------------|------|-----|------|-----|---------------------------------|--|---|
| | | Found | C | H | N | P | | | Cl |
| Pr ⁿ | 119.5—120.5 | Found | 60.2 | 5.6 | 3.5 | 7.2 | 8.5 | 0.78 (3 H, t), 1.25—1.95 (2 H, m), 2.55—3.28 (2 H, q), 5.10—5.62 (1 H, m), ^c 7.26—8.10 (15 H, m) | 3 500—3 400, 3 030—2 930, 1 595, 1 490, 1 450, 1 150—1 070, 995 |
| | | Calcd. | 60.1 | 5.5 | 3.3 | 7.4 | 8.4 | | |
| Pr ⁱ | 154—155 | Found | 60.1 | 5.7 | 3.4 | 7.4 | 8.6 | 1.15—1.45 (6 H, d), 2.90—3.50 (1 H, m), 5.13—5.65 (1 H, t), ^c 7.30—8.05 (15 H, m) | 3 225, 2 950, 1 595, 1 495, 1 450, 1 130—1 070, 1 000 |
| | | Calcd. | 60.1 | 5.5 | 3.3 | 7.4 | 8.4 | | |
| Bu ^t | 121 | Found | 60.4 | 5.9 | 3.5 | 7.2 | 8.4 | 0.67—0.95 (6 H, d), 1.50—2.20 (1 H, m), 2.35—3.18 (2 H, m), 5.10—5.65 (1 H, m), ^c 7.20—8.15 (15 H, m) | 3 300—3 200, 2 950, 1 600, 1 495, 1 450, 1 140—1 050, 1 000 |
| | | Calcd. | 60.9 | 5.8 | 3.2 | 7.1 | 8.2 | | |
| Bu ^t | 168 | Found | 61.0 | 6.0 | 3.1 | 7.2 | 8.3 | 1.29 (9 H, s), 4.90—5.15 (1 H, d), ^c 7.40—8.15 (15 H, m) | 3 250—3 150, 2 950, 1 600, 1 495, 1 450, 1 110—1 060, 1 000 |
| | | Calcd. | 60.9 | 5.8 | 3.2 | 7.1 | 8.2 | | |
| Cyclohexyl | 163—165 | Found | 62.0 | 6.0 | 3.2 | 6.6 | 8.0 | 0.73—2.13 (10 H, m), 2.50—3.03 (1 H, m), 5.12—5.58 (1 H, t), ^c 7.40—8.10 (15 H, m) | 3 250—3 150, 2 900, 1 595, 1 490, 1 450, 1 120—1 060, 995 |
| | | Calcd. | 62.7 | 5.9 | 3.05 | 6.7 | 7.7 | | |

^a The n.m.r. spectra (60 MHz) were recorded in CDCl₃ with Me₄Si as internal standard. ^b For KBr discs. ^c These signals were assigned to the proton on the nitrogen atom.

solution showed no voltammetric peak due to Ph₃P, but on addition of 2,6-lutidine (0.50 ml) showed an oxidation peak at 1.0 V which coincided with that of authentic Ph₃P under the same conditions, indicating that part of the starting Ph₃P had been protonated on electrolysis. By comparing the peak height with that of authentic sample 32% of Ph₃P was found to be recovered. The solution, after 2,6-lutidine had been added, was subjected to high-speed liquid chromatography using a Waters 6000-A solvent delivery system with a U6K universal injector and a JASCO UVI-DEC-1 spectrophotometer [Bondapack C₁₈-Corasil (37—50 μm); $\frac{1}{8}$ in × 2 ft column; 45% aqueous methanol; 25 ml min⁻¹; at 225 nm]. Ph₃PO was found to be formed in 58% yield.

(b) *Electrolysis in acetonitrile with added water.* Ph₃P (266.3 mg) was subjected to electrolysis in acetonitrile (40 ml) containing 10% water and 0.1M-NaClO₄ at 1.0 V. The resulting solution was evaporated to dryness under reduced pressure and the residue was shaken with a mixture of chloroform (50 ml) and water (20 ml). The chloroform

minimize the releasing of primary amine by the stream of nitrogen. However, electrolysis at room temperature did not give different products. Ph₃P (262.3 mg) was subjected to electrolysis in acetonitrile (100 ml) containing 1% n-propylamine and 0.1M-NaClO₄ at 0.95 V. The electrolysis was continued until the current dropped approximately to the background value (*ca.* 460 min). The anolyte was evaporated to dryness under reduced pressure and the residue was extracted three 20-ml portions of chloroform. The chloroform extract was evaporated under reduced pressure, and the residue was dissolved in ethanol and reprecipitated with ether. The precipitate was recrystallized from ethanol-ether to give white crystals (241.8 mg) which were identified as n-propylaminotriphenylphosphonium perchlorate by elemental analysis and i.r. and n.m.r. spectra. Other monoalkylaminotriphenylphosphonium perchlorates were obtained similarly. The physical and spectroscopic data of them are summarized in Table 2.

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