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Reaction of Electrochemically Generated Triphenylphosphine Radical Cation with Amides and Ureas

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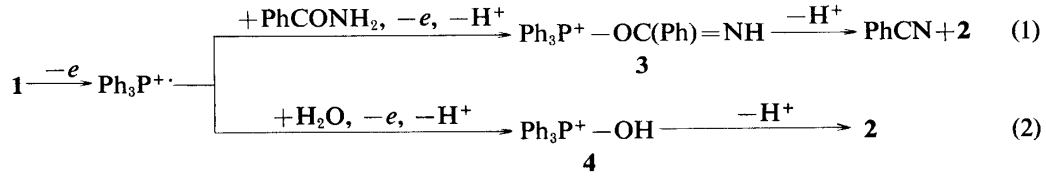
Constant-current electrolysis of triphenylphosphine in dichloromethane in the presence of primary amides and *N*,*N*′-disubstituted ureas resulted in the formation of nitriles and carbodiimides, respectively. Dehydrosulfurization of thiobenzamide and *N*,*N*′-dicyclohexylthiourea was also effected by electrolysis under the same conditions, but probably through mechanisms different from those of dehydration of the corresponding amide and urea.

Keywords——constant-current electrolysis; triphenylphosphine; primary amide; *N*,*N*′-disubstituted urea; nitrile; carbodiimide

In the radical cations generated electrochemically from trivalent phosphorus compounds, the positive charge and the unpaired electron are localized mainly on the phosphorus atom. Thus the radical cations, which are relatively strong electrophiles, have been shown to react at the phosphorus atom with reagents of widely differing nucleophilicity: water;[1-3] phosphorus compounds themselves;[4] aromatic and heteroaromatic compounds such as benzene, thiophene, *etc.*;[1,5,6] hexafluorosilicate ion;[7] alcohols, thiols, and disulfides;[8] aliphatic amines;[3] and *N*-hydroxy compounds such as oximes and hydroxamic acids.[9] As a continuation of our work on the addition reaction of electrochemically generated triphenylphosphine radical cation,[3,8,9] we examined the reaction with primary amides and *N*,*N*′-disubstituted ureas, leading to the formation of nitriles and carbodiimides, respectively.

Results and Discussion

In acetonitrile containing 0.1 M sodium perchlorate, Ph_3P (**1**) showed a single irreversible anodic peak at 1.0 V *vs*. S.C.E., as observed previously.[1,3,8,9] The voltammetric peak of **1** was little affected by the addition of an equimolar amount of benzamide: the latter showed an oxidation peak at 2.35 V under the experimental conditions. However, when **1** (2 mmol) was subjected to constant-current electrolysis (C.C.E.) in acetonitrile (0.1 M $NaClO_4$) in the presence of benzamide (2 mmol) and 2 F per mol of **1** were allowed to pass, formation of benzonitrile (22%) together with Ph_3PO (**2**) was recognized. These results suggest, by analogy with other anodic addition reactions of **1**,[1,3,8,9] that benzamide reacts with the radical cation of **1** to give the phosphonium ion (**3**), from which benzonitrile and **2** are formed [reaction (1) in Chart 1]. Since the acetonitrile used is unavoidably contaminated by a small amount of water, and benzamide must be a weak nucleophile, the reaction of water with the radical cation of **1** [reaction (2) in Chart 1; the principal process in the absence of the amide[10]] will take place concurrently with reaction (1). In both reactions (1) and (2), two protons are liberated along with the transfer of two electrons and the former will be accepted by **1**, the strongest base present in the medium, to convert **1** to an electrochemically inactive form. Thus, benzamide will exhibit essentially no effect on he voltammetric peak of **1**, provided that



$$1 \xrightarrow{-e} Ph_3P^{+\cdot} \xrightarrow{+PhCONH_2,\ -e,\ -H^+} \underset{\mathbf{3}}{Ph_3P^+-OC(Ph)=NH} \xrightarrow{-H^+} PhCN+\mathbf{2} \quad (1)$$

$$Ph_3P^{+\cdot} \xrightarrow{+H_2O,\ -e,\ -H^+} \underset{\mathbf{4}}{Ph_3P^+-OH} \xrightarrow{-H^+} \mathbf{2} \quad (2)$$

Chart 1

TABLE I. Results of C.C.E. of **1** in the Presence of $RCONH_2$[a]

Amide R	Yield (%)[b] of RCN	Amide R	Yield (%)[b] of RCN
Me	75	Me–CH=CH	57
Et	97	Ph	89
Pr	95	$PhCH_2$	88

[a] In CH_2Cl_2 (40 ml) containing 0.1 M $LutClO_4$ with suspended Al_2O_3 (0.5 g); amount of **1**, 15 mmol; amount of amide, 10 mmol; current density, 13.3 mA/cm^2; quantity of electricity, 1.8 F per mol of **1**. An undivided electrolysis cell was used throughout with a graphite plate as the anode and a platinum foil as the cathode (see Experimental).

[b] Determined gas chromatographically based on $RCONH_2$ used.

$$Ph_3P^{+\cdot} \xrightarrow{+RNHCONHR,\ -e,\ -H^+} \underset{\mathbf{5}}{Ph_3P^+-OC(NHR)=NR} \xrightarrow{-H^+} RN=C=NR+\mathbf{2}$$

Chart 2

TABLE II. Results of C.C.E. of **1** in the Presence of RNHCONHR′[a]

Urea R	Urea R′	Yield (%)[b] of RN=C=NR′	Urea R	Urea R′	Yield (%)[b] of RN=C=NR′
Et	Et	59	*tert*-Bu	*tert*-Bu	91
iso-Pr	iso-Pr	92	Ph	Ph	5
cyclo-C_6H_{11}	cyclo-C_6H_{11}	72[c]	Ph	iso-Pr	21

[a] In CH_2Cl_2 (40 ml) containing 0.1 M $LutBF_4$ with suspended Al_2O_3 (0.5 g); amount of **1**, 12 mmol; amount of urea, 10 mmol; current density, 4 mA/cm^2; quantity of electricity, 1.9 F per mol of **1**. An undivided electrolysis cell was used throughout with a graphite plate as the anode and a platinum foil as the cathode (see Experimental).

[b] Determined gas chromatographically based on RNHCONHR′ used.

[c] Supporting electrolyte, 0.1 M $LutClO_4$.

the conversion of **3** to the products is fast in the time-scale of cyclic voltammetry.[11)]

Since the phosphonium ion (**3**) was thought to be unstable, isolation of the ion was not attempted. Instead, application of reaction (1) to the preparation of nitriles was examined. C.C.E. under the following conditions gave favorable results (Table I): solvent, CH_2Cl_2 with suspended alumina; supporting electrolyte, 2,6-lutidinium perchlorate ($LutClO_4$); relatively high concentration of **1**; current density, around 10 mA/cm^2. Dichloromethane is known to be a solvent which is suitable for electrolysis under dry conditions.[12)] $LutClO_4$ is considered to act as a proton carrier, that is, it will be reduced to the free base at the cathode and the latter, taking the place of **1**, will accept the proton liberated at the anode.

Electrolysis of **1** in the presence of *N,N′*-disubstituted ureas, which are structurally related to primary amides, proceeded similarly to give carbodiimides, probably *via* the phosphonium ion (**5**) (Chart 2). The results are summarized in Table II. In this case, the use of

2,6-lutidinium fluoroborate ($LutBF_4$) in the place of $LutClO_4$ gave better yields of carbodiimides except for dicyclohexylcarbodiimide. A current density (*ca.* 4 mA/cm^2) smaller than in the case of amides was found to be preferable. With a larger current density, the concentration of the ureas at the electrode surface probably becomes insufficient to trap the radical cation of **1** effectively, because of the rather poor solubility of the ureas in the medium.

In connection with the results obtained above, the possibility of electrochemical dehydrosulfurization of thioamides and thioureas was examined. When a solution of **1** and thiobenzamide in CH_2Cl_2 containing 0.1 M $LutClO_4$ was subjected to C.C.E. under the conditions listed in Table I, benzonitrile was formed in 71% yield and formation of Ph_3PS was confirmed. Similar electrolysis performed on a mixture of **1** and *N,N'*-dicyclohexylthiourea gave dicyclohexylcarbodiimide in 56% yield. In these electrolyses, the nitrile and the carbodiimide are also considered to be formed *via* the phosphonium ions, $Ph_3P^+{-}SC(Ph){=}NH$ (**6**) and $Ph_3P^+{-}SC(NHC_6H_{11}){=}NC_6H_{11}$ (**7**), respectively. At present, however, the exact processes leading to **6** and **7** cannot be specified, because the thioamide and the thiourea are oxidized more easily[13)] than **1** and several possibilities arise.[14)]

Several methods have been reported for the conversion of $RC(X)NH_2$ and $RNHC(X)NHR'$ (X=O or S) to nitriles[15,16)] and carbodiimides,[17-19)] respectively. The electrochemical methods can be compared with those which involve reaction of the above compounds with **1** and carbon tetrachloride.[15,17)] However, the electrochemical methods do not require warming or heating of the reaction mixture and can be conducted even under cooling.

Experimental

Materials——The phosphine (**1**) was recrystallized from hexane and stored in the dark under reduced pressure. *tert*-BuNHCONH-*tert*-Bu and iso-PrNHCONHPh were prepared by the reaction of *tert*-BuNCO and PhNCO with *tert*-$BuNH_2$ and iso-$PrNH_2$, respectively. Authentic samples of RN=C=NR', except for R=R'=iso-Pr and cyclo-C_6H_{11}, were prepared by the known methods.[17,19)] Other organic compounds were obtained from commercial sources and were purified by distillation or recrystallization. CH_2Cl_2 was washed successively with sulfuric acid, water, saturated $NaHCO_3$ solution, and water, dried with $CaCl_2$, and then distilled from P_2O_5 under an atmosphere of dry nitrogen. $LutClO_4$ and $LutBF_4$ were prepared by adding a 70% solution of $HClO_4$ (160 g) and a 42% solution of HBF_4 (210 g), respectively, to 2,6-lutidine (110 g) at 0 °C, and they were each recrystallized from AcOEt–EtOH, dried at room temperature or at 50 °C, respectively, under reduced pressure, and stored over P_2O_5.

Apparatus——Cyclic voltammetry was performed as described previously.[3,8)] C.C.E. was carried out using a Hokuto Denko HA-104 potentiostat/galvanostat connected with a Hokuto Denko HF-201 coulometer.

C.C.E.——(a) General Procedure for the Runs in Table I: A 50 ml sample tube with a silicon stopper was used as the electrolysis cell. A graphite plate anode (2 × 1.7 cm) and a platinum foil cathode (3 × 1.5 cm) were placed in the cell by hanging them with two pieces of platinum wire through the stopper. The distance between the electrodes was kept at *ca.* 1 cm. A solution of **1** (15 mmol) and $RCONH_2$ (10 mmol) in CH_2Cl_2 (40 ml) containing 0.1 M $LutClO_4$, and Al_2O_3 (0.5 g; dried at 200 °C and 10 mmHg for 5 h) were placed in the electrolysis cell. The system was subjected to C.C.E. (current density, 13.3 mA/cm^2) until 1.8 F per mol of **1** (2606 C) had been passed. The electrolyzed solution was adjusted to 50.0 ml with CH_2Cl_2 in a volumetric flask, and RCN was determined by gas liquid chromatography (GLC).

In the run with $PhCONH_2$, the solution used for the GLC analysis was concentrated at room temperature under reduced pressure, and the residue was chromatographed on a short column of silica gel with $CHCl_3$ as the eluant to remove the supporting electrolyte. Distillation of the effluent gave PhCN, which was identified by comparing its infrared (IR) spectrum with that of an authentic sample.

(b) General Procedure for the Runs in Table II: The same electrolysis cell as described above was used. A solution of **1** (12 mmol) and RNHCONHR' (10 mmol) in CH_2Cl_2 (40 ml) containing 0.1 M $LutBF_4$, and the dried Al_2O_3 (0.5 g) were placed in the cell. The system was subjected to C.C.E. (current density, 4 mA/cm^2) until 1.9 F per mol of **1** (2200 C) had been passed. RN=C=NR' was determined by GLC as described above.

In the run with iso-PrNHCONH-iso-Pr, the CH_2Cl_2 was removed under reduced pressure and the residue was extracted with hexane (20 ml × 3). Distillation of the extract gave iso-PrN=C=N-iso-Pr, which was identified by comparing its IR spectrum with that of an authentic sample.

The electrolyses with $PhCSNH_2$ and $C_6H_{11}NHCSNHC_6H_{11}$ were carried out as described in (a) and (b), respectively.

References and Notes

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

2) von H. Matschiner, L. Krause, and F. Krech, *Z. anorg. Chem.*, **373**, 1 (1970).

3) H. Ohmori, S. Nakai, and M. Masui, *J. Chem. Soc., Perkin Trans. 1*, **1978**, 1333.

4) W. B. Gara and B. P. Roberts, *J. Chem. Soc., Chem. Commun.*, **1975**, 949; *idem, J. Chem. Soc., Perkin Trans. 2*, **1978**, 150.

5) Yu. M. Kargin, E. V. Nikitin, O. V. Parakin, G. V. Romanov, and A. N. Pudovik, *Dokl. Akad. Nauk SSSR*, **241**, 131 (1978) [*Chem. Abstr.*, **89**, 119655*v* (1978)]; *idem, ibid.*, **242**, 1108 (1978) [*Chem. Abstr.*, **90**, 31059*p* (1979)]; E. V. Nikitin, O. V. Parakin, Yu. A. Ignatév, A. S. Romakhin, G. V. Romanov, Yu. M. Kargin, A. N. Pudovik, and T. Ya. Stepanova, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1979**, 2396 [*Chem. Abstr.*, **92**, 66746*d* (1980)]; *idem, ibid.*, **1980**, 939 [*Chem. Abstr.*, **93**, 56824*j* (1980)]; Yu. M. Kargin, E. V. Nikitin, O. V. Parakin, G. V. Romanov, and A. N. Pudovik, *Phosphorus and Sulfur*, **8**, 55 (1980); E. V. Nikitin, A. S. Romakhin, O. V. Parakin, G. V. Romanov, Yu. M. Kargin, and A. N. Pudovik, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **1981**, 2170 [*Chem. Abstr.*, **95**, 202909*a* (1981)]; E. V. Nikitin, A. S. Romakhin, O. V. Parakin, G. V. Romanov, I. P. Kosachev, Yu. M. Kargin, and A. N. Pudovik, *Dokl. Akad. Nauk SSSR*, **262**, 1182 (1982) [*Chem. Abstr.*, **96**, 181369*c* (1982)]; *idem, ibid.*, **266**, 402 (1982); *idem, Izv. Akad. Nauk SSSR, Ser. Khim.*, **1983**, 626.

6) H. Ohmori, S. Nakai, and M. Masui, *J. Chem. Soc., Perkin Trans. 1*, **1979**, 2023.

7) E. V. Nikitin, O. V. Parakin, G. V. Romanov, Yu. A. Ignatév, A. S. Romakhin, Yu. M. Kargin, and A. N. Pudovik, *Dokl. Akad. Nauk SSSR*, **252**, 922 (1980) [*Chem. Abstr.*, **93**, 122532*r* (1980)]; *idem, Zh. Obshch. Khim.*, **52**, 1207 (1982) [*Chem. Abstr.*, **97**, 81627*n* (1982)].

8) H. Ohmori, S. Nakai, M. Sekiguchi, and M. Masui, *Chem. Pharm. Bull.*, **28**, 910 (1980); H. Ohmori, S. Nakai, H. Miyasaka, and M. Masui, *ibid.*, **30**, 4192 (1982).

9) H. Ohmori, S. Nakai, and M. Masui, *Chem. Pharm. Bull.*, **28**, 2247 (1980).

10) It has been reported that the water content of nominally anhydrous acetonitrile solution is enough for the occurrence of the reaction (refs. 1 and 3).

11) If the conversion of **3** to the products did not take place within the time-scale of cyclic voltammetry, the peak current of **1** would increase slightly: that is, in reaction (1) two molecules of **1** are required for overall two-electron transfer, while three molecules of **1** are required in reaction (2). On the other hand, if the rate of the process **1** to **3** was negligible compared to that of **1** to **4**, the formation of nitrile would not be observed.

12) J. P. Helps, K. S. V. Stanthanam, and A. J. Bard, *J. Am. Chem. Soc.*, **89**, 1752 (1967).

13) On cyclic voltammetry in acetonitrile containing 0.1 M $NaClO_4$, thiobenzamide and *N*,*N′*-dicyclohexylthiourea showed an irreversible anodic peak at 0.95 and 0.65 V, respectively.

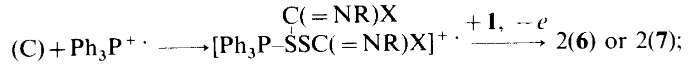
14) The following processes, at least, may be possible:

$$\mathrm{XCSNHR}\ (\mathrm{X=Ph,\ R=H\ or\ X=C_6H_{11}NH,\ R=C_6H_{11}}) \xrightarrow{-e} [\mathrm{XCSNHR}]^{+\cdot}\ \mathrm{(A)}$$

$$\xrightarrow{+\mathbf{1}} [\mathrm{XC(NHR)=S{-}PPh_3}]^{+\cdot} \xrightarrow{-e,-\mathrm{H}^+} \mathbf{6}\ \text{or}\ \mathbf{7};$$

$$\mathrm{(A)} \xrightarrow{-\mathrm{H}^+} [\mathrm{XC(N=R)S}]^{\cdot}\ \mathrm{(B)},\ 2\mathrm{(B)} \rightarrow \mathrm{XC(=NR)SSC(=NR)X\ (C)}$$

$$\xrightarrow{+\mathbf{1}} \mathbf{6}\ \text{or}\ \mathbf{7} + \mathrm{XC(=NR)S^-\ (D)},\ \mathrm{(D)} \xrightarrow{-e} \mathrm{(B)};$$



$$\mathrm{(C)} + \mathrm{Ph_3P^{+\cdot}} \longrightarrow [\mathrm{Ph_3P{-}}\overset{\mathrm{C(=NR)X}}{\mathrm{S}}\mathrm{SC(=NR)X}]^{+\cdot} \xrightarrow{+\mathbf{1},\ -e} 2(\mathbf{6})\ \text{or}\ 2(\mathbf{7});$$

$$\mathrm{(B)} + \mathrm{Ph_3P^{+\cdot}} \rightarrow \mathbf{6}\ \text{or}\ \mathbf{7}.$$

15) E. Yamato and S. Sugasawa, *Tetrahedron Lett.*, **1970**, 4383; R. Appel, R. Kleinstück, and K.-D. Ziehn, *Chem. Ber.*, **104**, 1030 (1971).

16) von H. J. Bestmann, J. Lienert, and L. Mott, *Justus Libigs Ann. Chem.*, **718**, 24 (1968); M.-I. Lim, W.-Y. Ren, and R. S. Klein, *J. Org. Chem.*, **47**, 4594 (1982) and references cited therein; C. I. Chiriac, *Rev. Roum. Chim.*, **28**, 33 (1983).

17) R. Appel, R. Kleinstück, and K.-D. Ziehn, *Chem. Ber.*, **104**, 1335 (1971).

18) M. Mikolajczyk and P. Kielbasińsky, *Tetrahedron*, **37**, 233 (1981); K. Wagner, K. Findeisen, W. Schäfer, and W. Dietrich, *Angew. Chem. Int. Ed. Engl.*, **20**, 819 (1981); A. Williams and I. T. Ibrahim, *Chem. Rev.*, **81**, 589 (1981).

19) C. Palomo and R. Mestres, *Synthesis*, **1981**, 373; *idem, Bull. Soc. Chim. Fr.*, **1981**, II-361; P. Molina, M. Alajarin, A. Arques, and J. Sáez, *Synth. Commun.*, **12**, 573 (1982) and references cited therein; A. V. R. Rao, M. N. Rao, K. Garyali, and P. Kumar, *Chem. Ind.* (London), **1984**, 270.