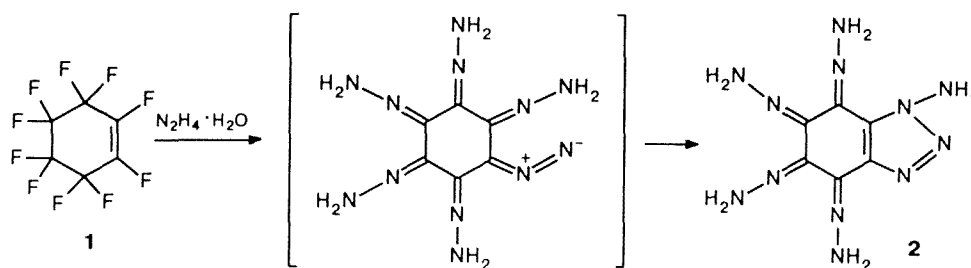


Scheme 1



[M-N₂]⁺ (3.80); 207 [M-N₃H]⁺ (1.92); 194 [M-2N₂]⁺ (11.54); 179 [M-2N₂, NH]⁺ (11.50); 164 [M-2N₂, N₂H₂]⁺ (40.38); 149 [M-2N₂, N₃H₃]⁺ (11.58); 134 [M-2N₂, N₄H₄]⁺ (9.62); 120 [M-2N₂, N₅H₅]⁺ (15.38); 105 [M-2N₂, N₆H₅]⁺ (38.46); 92 [C₆H₅NH] (57.69); 78 [C₆H₆] (53.82); 77 [C₆H₅] (57.69); 76 [C₆H₄] (47.68); 68 [C₂N₃H₂] (65.38); 52 [C₄H₄] (100); 42 [C=N-NH₂] (7.82); 32 [N₂H₄] (89.20); 28 [N₂] (100); 17 [NH₃] (100).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 94-03-08548).

References

1. I. L. Knunyants, Yu. T. Struchkov, M. D. Bargamova, and A. A. Espenbetov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 1097 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 1001 (Engl. Transl.)].
2. T. J. Brice and J. H. Simons, *J. Am. Chem. Soc.*, 1951, **73**, 4016.
3. G. G. Bargamov, K. A. Lysenko, and M. D. Bargamova, *Izv. Akad. Nauk, Ser. Khim.*, 1995, 2465 [*Russ. Chem. Bull.*, 1995, **44**, 2361 (Engl. Transl.)].

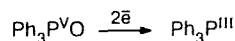
Received December 26, 1995;
in revised form January 25, 1996

Electrochemical deoxygenation of triphenylphosphine oxide

V. V. Yanilkin,* V. S. Gromakov, and F. F. Nigmatzyanov

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan' Scientific Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420083 Kazan', Russian Federation.
Fax: +7 (843 2) 75 2253

Electrochemical reduction of phosphine oxides directly at the electrode involves cleavage of the P—C bond¹ or hydrogenation of the aromatic fragment.² We found that electrolysis carried out with a soluble aluminum anode in a 0.1 M solution of anhydrous aluminum trichloride as the supporting electrolyte leads to the reduction of the phosphoryl group of the triphenylphosphine oxide and yields triphenylphosphine.



The electrolysis of 3.8 g of $Ph_3P=O$ was carried out in a diaphragmless glass cell ($V = 50$ mL) with a graphite cathode in an acetonitrile—benzene (2 : 1) mixture at a constant current of 0.4 A for 2.5 h. When the electrolysis was completed, the solution was treated with 50 mL of

cold water and extracted with hexane, and the organic layer was washed with water and dried with CaCl_2 . The substance obtained after evaporation of the solvent (2.54 g) was analyzed by TLC and ^{31}P NMR spectroscopy. The mixture was found to contain the starting compound (Ph_3PO , δ 24.94) and triphenylphosphine (PPh_3 , δ -6.15). The current yield of the latter was 24 % and the substance yield was 30.5 %, judging from the integral intensities of the corresponding signals in the ^{31}P NMR spectrum. Aluminum is ionized at the anode (the current yield of Al^{3+} is 140 %), while at the cathode, the Al^{3+}

ions are reduced. Apparently, the process of the formation of Ph_3P includes the generation of aluminum ions in a low oxidation state or Al^0 , which then reduce triphenylphosphine oxide.

References

1. J. M. Saveant and Binh Su Khac, *J. Electroanal. Chem.*, 1978, **88**, 27.
2. L. Horner and H. Neumann, *Chem. Ber.*, 1969, **102**, 3953.

Received December 26, 1995;
in revised form February 26, 1996

Synthesis of trifluoroacetates of *N*-(2-hydroxyethyl)-substituted trifluoroacetaminosuccinodiamide and succinimide

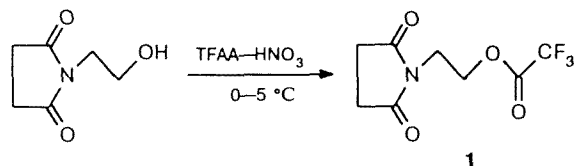
B. S. Fedorov and V. V. Arakcheeva*

*Institute of Chemical Physics in Chernogolovka, Russian Academy of Sciences,
142432 Chernogolovka, Moscow Region, Russian Federation.
Fax: +7 (096) 515 3588*

Previously¹ it was demonstrated that the treatment of mannitol and sorbitol with a trifluoroacetic anhydride—nitric acid system ($\text{TFAA}-\text{HNO}_3$) resulted in the formation of the corresponding hexanitrate in 45 % yields. Similar results were obtained on the nitration of 1,1,4,4-tetranitrobutan-2,3-diol and its derivatives.²

We have found that another reaction pathway takes place when *N*-(2-hydroxyethyl)succinimide is treated with the same system, namely, acylation of the hydroxy group occurred instead of *O*-nitration (Scheme 1).

Scheme 1



Trifluoroacetate **1** was isolated as a white crystalline substance in a 43 % yield when the reaction mixture was diluted with water; m.p. 87–89 °C. ^1H NMR (CD_3CN , SiMe_4), δ : 2.60 (s, 4 H, CH_2); 3.78 (t, 2 H, NCH_2 , $^3J_{\text{CH}_2-\text{CH}_2} = 6.0$ Hz); 4.44 (t, 2 H, $\text{CH}_2\text{OC}(\text{O})$, $^3J_{\text{CH}_2-\text{CH}_2} = 6.0$ Hz). IR ($\text{ClCH}_2\text{CH}_2\text{Cl}$, film), ν/cm^{-1} : 1111, 1159 (C–F); 1225 (C(O)O); 1694 (C=O, imide); 1796 (C=O in $\text{CF}_3\text{C}(\text{O})\text{O}$); 2922, 2951, 2982 (CH_2).

In the case of *N,N'*-bis(2-hydroxyethyl)trifluoroacetaminosuccinodiamide, which contains N–H bonds in amide groups, *N*-nitration of the amide nitrogen atoms occurs along with *O*-acylation (Scheme 2).

Compound **2**, which was hitherto unknown, was obtained as a white crystalline substance in a 95 % yield; m.p. 79.0–80.5 °C (from a $\text{CCl}_4-\text{ClCH}_2\text{CH}_2\text{Cl}$ mixture). ^1H NMR (CD_2Cl_2 , SiMe_4), δ : 3.73 (m, 2 H, CH_2O , ABX-system, $\Delta\nu = 31.6$ Hz, $|^2J_{\text{AB}}| = 18.3$ Hz, $^3J_{\text{AX}} = 5.1$ Hz, $^3J_{\text{BX}} = 5.5$ Hz); 4.40–4.70 (m, 8 H, $\text{OCH}_2\text{CH}_2\text{N}$); 5.90 (br.m, 1 H, CH, ABX-system); 7.38 (br.d, 1 H, $\text{NHCO}(\text{CF}_3)$, $^3J_{\text{NH}-\text{CH}} = 7.5$ Hz). IR (KBr),