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C—N Bond Cleavage in the Electrochemical Reduction of 1,2,4,5-Tetrafluoro-3,6-dinitrobenzene

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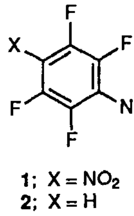
The electrochemical reduction of 1,2,4,5-tetrafluoro-3,6-dinitrobenzene in *N,N*-dimethylformamide gives 1,2,4,5-tetrafluoro-3-nitrobenzene, among other reaction products.

Electrochemical reduction of aromatic nitro compounds usually results in the formation of nitroso, hydroxylamino and amino compounds or of the products of subsequent chemical transformations of these compounds.[1,2] We have found no examples in the literature of elimination of the nitro group during the electrolysis of nitroarenes.



1; X = NO_2
2; X = H

On investigating the electrochemical reduction of 1,2,4,5-tetrafluoro-3,6-dinitrobenzene **1** in *N,N*-dimethylformamide (DMF), we have found 1,2,4,5-tetrafluoro-3-nitrobenzene **2** among the reaction products. Thus, the radical anion of **1** has been recorded by EPR spectroscopy, formed by reduction of compound **1** at −50 to −10 °C ($a_N = 0.80$ G, $a_F = 3.57$ G) (1 G = 10^{-4} T). At temperatures above −10 °C, this radical disappears and the EPR spectrum of the radical anion of com-

Mendeleev Commun., 1992, 2(1), 37–38

pound **2** is observed.[3] The reduction of compound **1** in DMF in the presence of 5% D_2O leads to the 4-deuterio-2,3,5,6-tetrafluoronitrobenzene radical anion ($a_D = 0.60$ G, $a_F{}^2 = 6.20$ G, $a_F{}^2 = 2.30$ G, $a_N = 9.70$ G).

Voltammograms of compound **1** in DMF show the reduction peak of compound **3** in addition to that of the starting compound ($E_p = -0.47$ V) (the peak height ratio for compounds **1** and **2** is approximately 20:1). The former peak potential ($E_p = -0.87$ V) is equal to that of an authentic sample of compound **2**. Preparative electrolysis of compound **1** at -0.50 V leads to product **2** in 25% yield (determined by GLC).

Voltammetric measurements, preparative electrolysis and electrochemical generation of the radical anions were carried out using a platinum working electrode and a saturated calomel electrode as reference. The supporting electrolyte was 0.1 mol dm^{-3} tetraethylammonium perchlorate.

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