(1)

M. E. Niyazymbetov, and V. A. Petrosyan

The identical product compositions obtained upon the electrochemical oxidation of 1,1dinitrocarbanions [1, 2] and the reaction of such anions with XeF_2 have led us to propose that the one-electron oxidation of these carbanions occurs upon reaction with XeF_2 [3, 4]. In the elaboration of XeF_2 as a one-electron oxidizing agent, we undertook a study of the reaction of this compound with nitroazole anions. The corresponding radicals are formed upon the electrochemical oxidation of such anions on a platinum electrode [5].

In the present communication, we present the results of a study of the reaction between XeF_2 and the potassium salt of 3-nitro-1,2,4-triazole (I). A sample of 1.5 mmoles XeF_2 was added with vigorous stirring to a suspension of 1 mmole (I) in 20 ml abs. acetonitrile at 20°C. The KF precipitate was filtered off after 30 min. The final solution had neutral pH and contained nonionized 3-nitro-1,2,4-triazole (II) (70-80% yield) and unidentified impurities in trace amounts as indicated by thin-layer chromatography and PMR spectroscopy.

Solutions of XeF₂ in acetonitrile are stable for prolonged periods [6]. XeF₂ begins to react with acetonitrile only at the boiling point of this solvent or in the presence of strong Lewis acids such as BF_3 and SbF_5 as catalysts [7]. Thus, (II) cannot form as a result of the protonation of starting (I) in acetonitrile containing XeF_2 .

By analogy with our previous proposals [5, 8], the likely reason for the formation of (II) is abstraction of a hydrogen atom from the solvent molecule by nitrotriazole radical (Ia) formed upon the one-electron oxidation of (I) by XeF_2^* according to the following scheme:

The reaction between anion (I) and XeF_2 at 20°C in acetonitrile containing 30 vol. % benzene gives a 3:2 mixture of (II) and 1-phenyl-3-nitro-1,2,4-triazole (III). Triazole (III) was identified using thin-layer chromatography and PMR spectroscopy by comparison with an authentic sample [8]. The yield of (III) was 25-35%, and this product is apparently the result of the reaction of radical (Ia) with a benzene molecule according to Scheme 2 [8]:

$$(I) \xrightarrow{\text{XeF}_2} (Ia) \xrightarrow{N}_{N} (Ib) \xrightarrow{N}_{N} (Ib) \xrightarrow{N}_{N} (III) + (II) (II) (III) + (II) (III) + (III) (II$$

*The XeF₂, radical-anion formed in this case apparently decomposes to give XeF, and F.

662

A. E. Trubitsin, A. A. Mel'nikov, M. S. Pevzner, I. V. Tselinskii,

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, Moscow. Lensovet Leningrad Technological Institute. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 3, pp. 736-738, March, 1989. Original article submitted July 25, 1988.

Scheme (2) involves the intermediate formation of cyclohexadienyl radical (Ib) (σ complex), whose rearomatization may occur by two equally probable pathways: a) subsequent one-electron oxidation with deprotonation and b) abstraction of a hydrogen atom by radical (Ia).

In principle, (III) may also be formed through the benzene radical-cation (product of the reaction of benzene and XeF_2 [9]) according to Scheme (3):

$$\bigotimes \frac{\operatorname{XeF}_{2}}{-\operatorname{XeF}_{2}} \left[\bigotimes\right]^{\dagger} \xrightarrow{(I)} (Ib) \xrightarrow{\operatorname{XeF}_{2}} (III)$$
(3)

However, this pathway appears less likely since benzene has a higher oxidation potential $(E_{1/2} = 2.02 \text{ V} [10])$ than anion (I) $(E_{1/2} = 1.77 \text{ V} [5])$.

Thus, XeF₂ may act as a one-electron oxidizing agent not only relative to 1,1-dinitrocarbanions but also toward nitroazole anions, which do not readily undergo oxidation. This reaction is apparently the first case of the chemical generation of the 3-nitro-1,2,4-triazole radical.

EXPERIMENTAL

The PMR spectra were taken on a Perkin-Elmer R-12 spectrometer at 60 MHz in $(CD_3)_2CO$ with HMDS as the internal standard. The thin-layer chromatographic analysis was carried out on Silufol UV-254 plates with 25:1 $CHCl_3$ -2-propanol as the eluent. The sample of (III) obtained for comparison was prepared according to our previous procedure [8]. In order to isolate (II), the solution after the reaction of XeF_2 with (I) was filtered. The solvent was evaporated and the residue was recrystallized from ethanol to give ~70-80% yield (II). In order to separate (II) and (III), the reaction mixture after the reaction of XeF_2 and (I) in the presence of benzene was treated analogously. The total yield of (II) and (III) relative to the amount of (I) taken was about 70%. The (II)/(III) ratio was found to be 3:2 using the integral intensities of the PMR signals for the protons at C^5 of the triazole rings in (II) (δ = 8.85 ppm) and (III) (δ = 9.35 ppm). The potassium salt of 3-nitro-1,2,4-triazole (I) was obtained by neutralization of the corresponding N-H acid by KOH in ethanol.

CONCLUSIONS

Xenon difluoride in acetonitrile is capable of oxidizing the anion of 3-nitro-1,2,4triazole to form the corresponding radical.

LITERATURE CITED

- 1. V. A. Kokorekina, V. A. Petrosyan, and L. G. Feoktistov, The Electrochemical Synthesis of Monomers [in Russian], Izd. Nauka, Moscow (1980), p. 83.
- V. A. Petrosyan and M. E. Niyazymbetov, Izv. Akad. Nauk SSSR, Ser. Khim., 603 (1987). 2.
- I. V. Tselinskii, A. A. Mel'nikov, and A. E. Trubitsin, Zh. Org. Khim., 23, 1657 (1987). 3.
- I. V. Tselinskii, A. A. Mel'nikov, and A. E. Trubitsin, Zh. Org. Khim., 24, 688 (1988). 4.
- M. E. Niyazymbetov, V. A. Petrosyan, A. A. Gakh, and A. A. Fainzil'berg, Izv. Akad. 5. Nauk SSSR, Ser. Khim., 2390 (1987).
- 6. H. Meinert and G. Kaushka, Z. Chem., 9, 70 (1969).
- H. Meinert and S. Rüdiger, Z. Chem., 9, 35 (1969).
 V. A. Petrosyan, M. E. Niyazymbetov, M. S. Pevzner, and B. I. Ugrak, Izv. Akad. Nauk SSSR, Ser. Khim., 1643 (1988).
- 9. M. Ya. Turkina and I. P. Gragerov, Zh. Org. Khim., 11, 340 (1975).
- 10. V. A. Petrosyan and M. E. Niyazymbetov, Izv. Akad. Nauk SSSR, Ser. Khim., 368 (1988).