Russian Chemical Bulletin, International Edition, Vol. 51, No. 8, pp. 1466—1467, August, 2002

Oxidative coupling of the azide ion with anions of primary nitroalkanes. Synthesis of 1-azido-1-nitroalkanes

I. V. Tselinskii, S. F. Mel´nikova,* and S. A. Fedotov

Saint Petersburg State Technological Institute (Technical University),
26 Moskovsky prosp., 198013 St. Petersburg, Russian Federation.
E-mail: sfm@tu.spb.ru

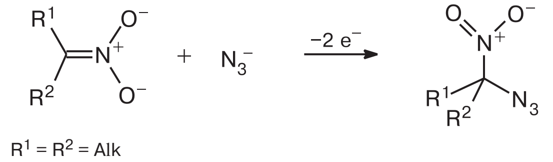
The reaction of salts of 1-*aci*-nitroethane and 1-*aci*-nitrobutane with sodium azide and ammonium peroxodisulfate in the methylene chloride—water two-phase system affords 1-azido-1-nitroethane and 1-azido-1-nitrobutane, respectively.

Key words: 1-azido-1-nitroalkanes, oxidative azidation, one-electron oxidation, 1-nitroalkanes.

One of the main methods for introduction of various functional groups into the α-position of primary and secondary nitroalkanes is the oxidative coupling of nitrocarbanions with the corresponding anions (for example, nitronate, cyanide, nitrite, and arylsulfonate anions[1—3]) either by a chemical oxidant ($AgNO_3$, $K_3Fe(CN)_6$, $(NH_4)_2S_2O_8$), or under electrolysis conditions.

Oxidative azidation of secondary nitroalkanes has been described[4—6] (Scheme 1).

Scheme 1



Involvement of primary nitroalkanes in this reaction has been unknown to present time.

In addition, 1-azido-1-nitroalkanes are promising synthons for the formation of various polynitrogen structures, for example, azidopolynitro compounds.

We found that the reaction of $(NH_4)_2S_2O_8$ and NaN_3 with nitroethane (**1a**) and 1-nitrobutane (**1b**) afforded azido derivatives **2a,b** (Scheme 2).

Scheme 2

$$\underset{\mathbf{1a,b}}{RCH_2NO_2} + NaN_3 \xrightarrow[CH_2Cl_2—H_2O]{NaOH,\ (NH_4)_2S_2O_8} \underset{\mathbf{2a,b}}{RCH(NO_2)N_3}$$

R = Me (**a**), Pr^n (**b**)

This reaction to occur successfully needs nitroalkane to be transformed into the *aci*-salt by a base. Since the α-azidonitrocarbanion formed from compound **2** is labile, we had to optimize the reaction conditions. The highest yield of 1-azido-1-nitroalkanes **2a,b** (80%) was achieved when the reaction was carried out in the $CH_2Cl_2—H_2O$ two-phase system with the fast acidification of the reaction mixture at the end of the process. The use of $K_3Fe(CN)_6$ as oxidant decreases the yield of product **2a** to 29% at 78% conversion of compound **1a**. 1-Dinitroethane, which is the product of oxidative addition of the nitrite ion generated in α-nitroazide **2a** decomposition to nitroethane (**1a**), is formed (9% yield) along with azido derivative **2a**. The formation of $Me_2C(NO_2)_2$ from Me_2CHNO_2 proceeds similarly.[4,5]

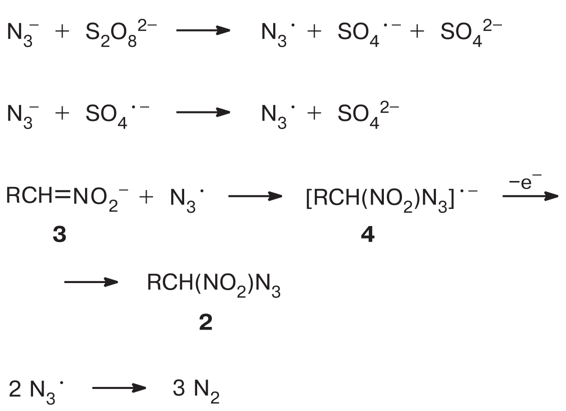
The reaction of 1-nitroalkanes with the $(NH_4)_2S_2O_8—NaN_3$ system starts, most likely, from the oxidation of the azide ion, which has a lower oxidation potential than the 1-*aci*-nitroalkane anions ($E_{1/2}$ = 0.20 [7] and 0.91±0.01 V,[8] respectively), by peroxodisulfate. This assumption is favored by the absence of the product of oxidative dimerization of nitroalkanes $RCH(NO_2)CH(NO_2)R$ in the reaction mixture. The generated azide radical $N_3^{\bullet}$ further adds to the anion of 1-*aci*-nitroalkane **3** to form radical anion **4**, which is oxidized to product **2** by the $S_2O_8^{2-}$ anions or $SO_4^{\bullet -}$ radical anions. Some azide radicals recombine simultaneously to be transformed into molecular nitrogen (Scheme 3).

Unlike 2-azido-2-nitropropane,[4,5] 1-azido-1-nitroalkanes do not undergo further azidation.

1-Azido-1-nitroethane (**2a**) and 1-azido-1-nitrobutane (**2b**) are colorless mobile liquids. Their structures were established from the ^{1}H NMR, IR, and UV spectra and confirmed by elemental analysis data. The UV spec-

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 8, pp. 1354—1355, August, 2002.

Scheme 3



$$N_3^- + S_2O_8^{2-} \longrightarrow N_3^{\bullet} + SO_4^{\bullet -} + SO_4^{2-}$$

$$N_3^- + SO_4^{\bullet -} \longrightarrow N_3^{\bullet} + SO_4^{2-}$$

$$\underset{\mathbf{3}}{RCH{=}NO_2^-} + N_3^{\bullet} \longrightarrow \underset{\mathbf{4}}{[RCH(NO_2)N_3]^{\bullet -}} \xrightarrow{-e^-} \underset{\mathbf{2}}{RCH(NO_2)N_3}$$

$$2\ N_3^{\bullet} \longrightarrow 3\ N_2$$

trum of azidonitroethane **2a** in 0.1 *M* HCl contains an absorption band at λ_{max} = 221 nm and remains unchanged during 1 day. The UV spectrum of anion **2a**$^-$ detected at pH 10 contains an absorption band at λ_{max} = 279 nm, whose intensity decreases exponentially with time (half-life ~10 min), and N_2 is simultaneously evolved. As can be seen, anion **2a**$^-$ absorbs at longer wavelengths than the anions of nitroethane (λ_{max} = 229 nm)[9] and 1-halo-1-nitroethanes (λ_{max} = 230—239 nm [10]).

The signal from the methinic proton in the ^{1}H NMR spectra of compounds **2a,b** exhibits the downfield shift compared to those of initial nitroalkanes (5.7 and 4.5 ppm,[11] respectively) but to a less extent than those in 1-chloro- and 1-bromo-1-nitroethanes (6.15 and 6.25 ppm,[11] respectively).

Thus, oxidative coupling of the azide ion with the 1-nitroalkane anions in the presence of $(NH_4)_2S_2O_8$ is an efficient method for the preparation of 1-azido-1-nitroalkanes.

Experimental

Attention! Azidonitro compounds and by-products, which can be formed during synthesis of the azidonitro compounds, are toxic and dangerously explosive. All procedures with them require the corresponding safeguards.

^{1}H NMR spectra were recorded on a Perkin—Elmer R-12 instrument (60 MHz) in acetone-d$_6$ using HMDS as internal standard. UV spectra were obtained on a Perkin—Elmer 402 spectrophotometer. IR spectra were recorded on a Specord M-80 instrument in thin layer. TLC analysis was carried out on Silufol UV-254 plates (eluent CCl_4 (78%)—Pr^{i}OH (20%)—AcOH (2%)). Solvents and reagents were purified according to standard procedures.

1-Azido-1-nitroethane (2a). Nitroethane (**1a**) (3.0 g, 0.04 mol) was added to a solution of NaOH (1.8 g, 0.045 mol) in water (40 mL) at 0—4 °C with vigorous stirring. After 15 min NaN_3 (7.8 g, 0.12 mol) was added, and 20 mL of CH_2Cl_2 were added after NaN_3 was dissolved. Then a solution of $(NH_4)_2S_2O_8$ (18.3 g, 0.08 mol) in water (50 mL) was added dropwise for 5 min to the mixture at the same temperature. The reaction mixture was acidified by 1 *M* HCl (80 mL) to a weakly acidic reaction. The organic layer was separated, and the aqueous layer was extracted by CH_2Cl_2 (2×20 mL). After the solvent was removed, compound **2a** was obtained in 79.2% yield (2.75 g) with b.p. 41—42 °C (0.80 kPa), d_4^{20} 1.251, n_D^{20} 1.4529, R_f 0.86. Found (%): C, 20.43; H, 3.51; N, 48.46. $C_2H_4N_4O_2$. Calculated (%): C, 20.69; H, 3.47; N, 48.27. UV (0.1 *M* HCl), λ_{max}/nm (logε): 221 (3.22). IR, ν/cm^{-1}: 2136, 1260 (N_3); 1576, 1360 (NO_2). ^{1}H NMR, δ: 5.75 (q, 1 H, CH, *J* = 6.6 Hz); 1.72 (d, 3 H, Me).

1-Azido-1-nitrobutane (2b) was prepared similarly in 82.6% yield with b.p. 37—38 °C (0.53 kPa), d_4^{20} 1.079, n_D^{20} 1.4407, R_f 0.80. Found (%): C, 33.76; H, 5.70; N, 39.29. $C_4H_8N_4O_2$. Calculated (%): C, 33.33; H, 5.59; N, 38.87. IR, ν/cm^{-1}: 2128, 1240 (N_3); 1560, 1352 (NO_2). ^{1}H NMR, δ: 5.73 (t, 1 H, CH, *J* = 6.1 Hz); 0.89—2.07 (m, 7 H, Pr).

References

1. R. B. Kaplan and H. Schechter, *J. Am. Chem. Soc.*, 1961, **83**, 3535.
2. Z. Matacz, H. Piotrowska, and T. Urbanski, *Pol. J. Chem.*, 1979, **53**, 187.
3. N. Kornblum, H. K. Singh, and W. J. Kelly, *J. Org. Chem.*, 1983, **48**, 332.
4. S. I. Al-Khalil and W. R. Bowman, *J. Chem. Soc., Perkin Trans. 1*, 1986, 555.
5. S. I. Al-Khalil and W. R. Bowman, *Tetrahedron Lett.*, 1982, **43**, 4513.
6. G. K. S. Prakash, J. J. Struckhoff, Jr., C. Weber, A. Schreiber, R. Bau, and G. A. Olah, *J. Org. Chem.*, 1997, **62**, 1872.
7. R. Haul and E. Scholz, *Naturwissenschaften*, 1944, **32**, 294.
8. S. Wawszonek and T.-Y. Su, *J. Electrochem. Soc.*, 1973, **120**, 745.
9. I. V. Tselinskii, I. V. Shugalei, and M. B. Shcherbinin, *Fizicheskaya khimiya nitrosoedinenii* [*Physical Chemistry of Nitro Compounds*], Izd-vo LTI im. Lensoveta, Leningrad, 1985, 186 pp. (in Russian).
10. A. G. Bazanov, M. V. Chistyakova, M. F. Kozlova, I. V. Tselinskii, and B. V. Gidaspov, *Reakts. Sposobnost´ Organ. Soedin.* [*Reactivity of Organic Compounds*], 1973, **10**, 807 (in Russian).
11. I. L. Knunyants, L. S. German, and I. N. Rozhkov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1966, 1062 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1966, **15** (Engl. Transl.)].

Received December 25, 2001;
in revised form March 25, 2002