

Fig. 1. Electronic absorption spectra (in the visible region) of solutions of **2a** (1), **2c** (2), **2e** (3), and **2f** (4) in **1a**, **1c**, **1e**, and **1f**, respectively, after contact with O_2 ; **2e** (5) and **2f** (6) in the absence of O_2 .

of compounds **2c** and **2e** isolated in the solid state by hydrochloric acid.

No release of H_2 (~0.4 mL) during interaction of **1a**, **1c**, and **1f** with Fe was observed volumetrically, probably due to dissolution of H_2 in the metal.

The electronic absorption spectra of solutions of **2a, c, e, f** in the starting thiols after the mechanochemical reaction (Fig. 1) were recorded on a Specord M40 spectrophotometer in sealed 0.5-cm cells.

After the mechanochemical interaction with Fe, sulfides Bu_2S and Ph_2S and disulfides Pr_2S_2 , Bu_2S_2 , and Ph_2S_2 gain no color characteristic of IDT, which contradicts the assumption^{2,9,10} about their formation in the reaction with metallic Fe. According to our data, all organic sulfides and disulfides studied form only FeS during the mechanochemical interaction with Fe.

References

1. E. S. Forbes and A. J. D. Reid, *ASLE Trans.*, 1973, **16**, 50.
2. L. A. Hamilton and W. W. Woods, *Ind. Eng. Chem.*, 1950, **42**, 513.
3. P. Claesson, *J. Prakt. Chem.*, [2] 1877, **15**, 193.
4. W. Manchot and H. Gall, *Chem. Ber.*, 1927, **60**, 2318.
5. B. A. Averill, T. Herskovitz, R. H. Holm, and J. A. Ibers, *J. Am. Chem. Soc.*, 1973, **95**, 3523.
6. K. S. Hagen, J. M. Berg, and R. H. Holm, *Inorg. Chim. Acta*, 1980, **45**, L17.
7. K. S. Hagen, J. G. Reynolds, and R. H. Holm, *J. Am. Chem. Soc.*, 1981, **103**, 4054.
8. H. Strasdeit, B. Krebs, and G. Henkel, *Inorg. Chem.*, 1984, **23**, 1816.
9. W. Davey, *Sci. Lubr.*, 1955, **7**, 23.
10. K. G. Allum and E. S. Forbes, *J. Inst. Petrol.*, 1967, **53**, 173.

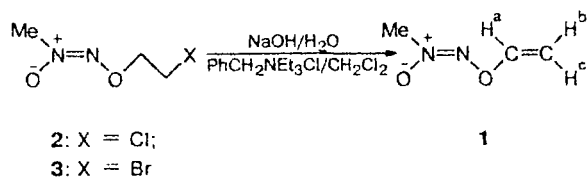
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Synthesis of vinyloxy-NNO-azoxymethane

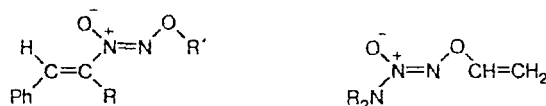
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Previously unknown vinyloxy-NNO-azoxymethane (**1**), the first alkoxy-NNO-azoxyalkane (AAZA) with the double $C=C$ bond at the oxygen atom, was synthesized by the dehydrohalogenation of AAZA **2** and **3**¹ under phase transfer catalysis conditions.



Four AAZA with the double $C=C$ bond at the N atom (**4**–**7**)^{2,3} and two triazenes **8**⁴ and **9**⁵ close in structure to **1** are described in the literature.



4²: R = $N^+(O^-)=\text{NOMe}$; R' = Me

5²: R = COOMe; R' = Me

6^{2,3}: R = H; R' = Me

7^{2,3}: R = H; R' = Et

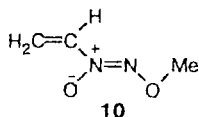
8: R = Et;

9: R₂ = (CH₂)₄

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To monitor the reaction course, compounds **1** and **2** were determined quantitatively by GLC using an LKhM-8MD instrument (columns 15% Carbowax-20M on Chromaton N-AW DMCS, 0.25–0.315 mm, 3 m × 3 mm, N₂ as the carrier gas, 30 mL min⁻¹, temperature of the columns was 140 °C for **1** and 180 °C for **2**, temperature of the evaporator was 200 °C). Methoxy-NNO-azoxyethene (**10**)* (a structural isomer of olefin **1**) was used as the internal standard.



The dehydrohalogenation of chloride **2** results in the formation of olefin **1** in a low yield (5% with Et₄NBr as the catalyst and 25% with PhCH₂NEt₃Cl with an almost complete conversion of **2**). Compound **1** is formed within 2 days in 75% yield (per the reacted starting compound) from the more reactive bromide **3** with PhCH₂NEt₃Cl, and conversion of **3** reaches 69%. Attempts to bring the reaction to the complete consumption of compound **3** resulted in a sharp increase in the amount of by-products with retention times close to that of compound **1**.

Compound **1** is a colorless liquid with a strong odor; it decolorizes rapidly a solution of Br₂ in CCl₄. The greater retention time of **1** as compared to that of **10** during the GLC analysis on the polar liquid phase (7.1 and 6.3 min, respectively) indicates that compound **1** is more polar than **10**. The shift of the band of the π–π* transition in the UV spectrum of **1** with respect to that of allyloxy-NNO-azoxymethane⁶ to the long-wave region (248 and 234 nm, respectively) indicates π–π conjugation between the N₂O₂ group¹ and C=C bond.

Vinyloxy-NNO-azoxymethane (1). A 47% solution of NaOH (75 g, 0.88 mol) was added to a solution of **3** (16.1 g, 0.088 mol) and PhCH₂NEt₃Cl (2.0 g, 0.0088 mol) in CH₂Cl₂ (75 mL). The mixture was stirred at 20 °C for 48 h, the layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (2 × 25 mL). The combined extract was washed with a 10% solution of NaHCO₃ and dried with Na₂SO₄. After the solvent was distilled off, the residue was fractionated *in vacuo*. The yield of **1** was 4.13 g (46% of the theoretical yield), b.p. 66.5–66.8 °C (7 Torr), *n*_D²⁰ 1.4791. IR, ν/cm⁻¹: 3060, 3030, 2975, 2945, 1635 (C=C), 1510 (N₂O₂), 1420 (N₂O₂), 1315 (N₂O₂), 1155, 1130, 1090, 1005, 945, 855, 635. UV (H₂O), λ/nm (ε): λ_{min} 221 (2570), λ_{max} 248 (6980). ¹H NMR (200 MHz, 50% solution in CD₃CN), δ: 3.95 (s, 3 H, CH₃); 4.45 (d.d, 1 H, H_b, J_{ab} = 6.6 Hz, J_{bc} = 2.4 Hz); 4.83 (d.d, 1 H, H_c, J_{ac} = 14.1 Hz); 6.95 (d.d, 1 H, H_a). Unreacted starting compound **3** with b.p. 88–93 °C (~1 Torr) was isolated in 39% yield (6.28 g) by distillation of the bottoms.

References

1. I. N. Zyuzin, G. N. Nechiporenko, N. I. Golovina, R. F. Trofimova, and M. V. Loginova, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 1486 [*Russ. Chem. Bull.*, 1997, **46**, 1421 (Engl. Transl.)].
2. R. B. Woodward and C. Wintner, *Tetrahedron Lett.*, 1969, **32**, 2689.
3. I. N. Zyuzin, *Izv. Akad. Nauk, Ser. Khim.*, 1998, 1263 [*Russ. Chem. Bull.*, 1998, **47**, 1231 (Engl. Transl.)].
4. J. E. Saavedra, T. M. Dumans, J. L. Flippen-Anderson, and L. K. Keefer, *J. Org. Chem.*, 1992, **57**, 6134.
5. J. E. Saavedra, T. R. Billiar, D. L. Williams, Y.-M. Kim, S. C. Watkins, and L. K. Keefer, *J. Med. Chem.*, 1997, **40**, 1947.
6. I. N. Zyuzin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 2626 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 2433 (Engl. Transl.)].

* Synthesis of compound **10** will be described later.