Synthesis of methoxy-*NNO*-azoxyethene

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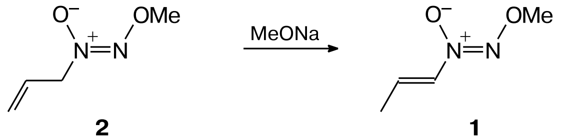
The first representative of the alkoxy-*NNO*-azoxy olefin series, *viz.*, methoxy-*NNO*-azoxyethene, was synthesized by the pyrolysis of 1,1-bis(methoxy-*NNO*-azoxy)ethane.

Key words: alkoxy-*NNO*-azoxy olefins, methoxy-*NNO*-azoxyethene, 1,1-bis(methoxy-*NNO*-azoxy)ethane, pyrolysis, UV spectra.

Five alkoxy-*NNO*-azoxy olefins with the C=C double bond at the *N*-oxide nitrogen atom are known, and four of them are styrene derivatives.[1,2] Only one such azoxy olefin containing no aromatic substituent, *viz.*, 1-(methoxy-*NNO*-azoxy)prop-1-ene (**1**), was synthesized[3] by the isomerization of 3-(methoxy-*NNO*-azoxy)prop-1-ene (**2**) (Scheme 1).

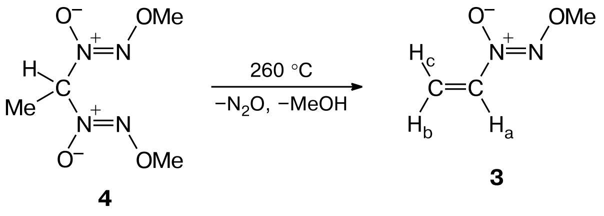
Scheme 1



The simplest azoxy olefin (methoxy-*NNO*-azoxyethene (**3**)) cannot be synthesized by this method. However, it is ethene **3** which is the most interesting as a monomer for the preparation of power-rich polymeric compositions.[4]

The purpose of this work was to study the possibility of synthesis of compound **3** using the vacuum pyrolysis of 1,1-bis(methoxy-*NNO*-azoxy)ethane (**4**)[5] (Scheme 2).

Scheme 2



The formation of β-(methoxy-*NNO*-azoxy)styrene by the pyrolysis of 1,1-bis(methoxy-*NNO*-azoxy)-2-phenylethane[2] and a ~100% yield of isobutylene in the thermal decomposition of 2-methyl-2-(methoxy-*NNO*-azoxy)propane in the gas phase[6] indicated that this reaction is possible in principle.

We found that the thermolysis of compound **4** affords, indeed, azoxy olefin **3**. As can be seen from the data in Table 1, the chromatographic yield of compound **3** in the 220—272 °C temperature interval changes slightly (71—75%). At lower temperatures, the yield decreases due to a low conversion at an appropriate duration of the process. However, the yield based on the decomposed starting compound **4** remains high. At temperatures higher than 272 °C, the yield decreases due to the destruction of product **3**. The chromatographic yield is highest at 260 °C and a duration of the reaction of 20 min (75%). The preparative synthesis of compound **3** in 53% yield was carried out under these conditions.

Compound **3** is a colorless liquid with a strong smell. It is indefinitely soluble in water EtOH, Me_2CO, and Et_2O, is immiscible with hexane, and discolors a solution of Br_2 in $CHCl_3$.

The substantial shift of the band of the π—π*-transition in the UV spectrum of compound **3** (λ_{max} = 250 nm) toward the long-wave region compared to those of

Table 1. Yields of compound **3** under different pyrolysis conditions

T/°C	Duration of reaction	Degree of conversion	Yield*
		%	
168	6.5 h	11	8 (70)
190	10 h	84	53 (70)
220	2.3 h	99	71 (71)
230	1.3 h	100	74 (74)
240	1.0 h	100	74 (74)
250	30 min	100	74 (74)
260	20 min	100	75 (75)
272	13 min	100	72 (72)
285	8 min	100	65 (65)
300	5 min	100	59 (59)

* The yield of compound **3** based on reacted compound **4** is presented in parentheses.

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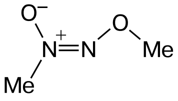
methoxy-*NNO*-azoxymethane (**5**) (λ_{max} = 234 nm)[7] and allyloxy-*NNO*-azoxymethane (**6**) (λ_{max} = 234 nm)[8] indicates the π—π-conjugation between the six-electron π-system of the N_2O_2 group[9] and the C=C bond.



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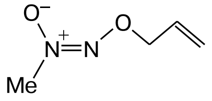

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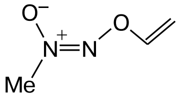

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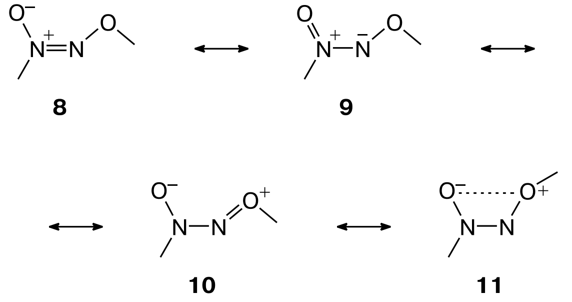
The hydroxydiazeneoxide group can be presented by a set of four resonance forms[9] (Scheme 3). In the resonance form **11**, the O...O bond designates the π-interaction without a σ-bond. Probably, valent forms **8** and **9** contribute mainly to the conjugation with the C=C bond in molecule **3**.

Scheme 3



Almost the same great shift of the band of the π—π*-transition in the UV spectrum was detected for the isomer of compound **3**: vinyloxy-*NNO*-azoxymethane (**7**) (λ_{max} = 248 nm).[10] However, resonance forms **10** and **11** are involved in conjugation with the C=C bond in this case.

The IR spectrum of compound **3** exhibits intense absorption bands at 1290, 1390, and 1480 cm^{-1} characteristic of the N_2O_2 group.[1,3,7—10] The band of stretching vibrations of the C=C bond with a medium intensity lies[11] at 1655 cm^{-1}.

In the ^1H NMR spectrum of compound **3**, the singlet of the methoxy group (δ 4.15) demonstrates a slight downfield shift compared to methoxy-*NNO*-azoxyalkanes (δ 3.89—3.95), whose ^1H NMR spectra were measured under the same conditions.[7] The methoxy-*NNO*-azoxy group in its electron influence resembles much its isoelectronic nitro group. Therefore, these groups should deshield the ethenic protons in a similar manner, despite different conditions of spectra recording. The chemical shifts of the *trans*-, *cis*-, and *gem*-protons of the vinyl group in nitroethene (a 10% solution in CCl_4) are equal[12] to 5.87, 6.55, and 7.12 ppm, whereas those in compound **3** in $CDCl_3$ and in the absence of a solvent are equal to 5.37, 6.25, 6.93 and 5.59, 6.32, 7.31 ppm, respectively. This assignment of the vinylic protons of compound **3** agrees with the spin-spin coupling constants (see Experimental). The spin-spin coupling constant of the atoms in the *trans*-position (15 Hz), as for nitroethene (15.0 Hz),[12] is much lower than that for unsubstituted ethene (19 Hz) due to a decrease in the electron density around the vinylic protons under the effect of the electron-acceptor group.[12]

In the ^{13}C NMR spectrum of compound **3**, the signal of the MeO group at δ 61.5 exists in the region characteristic of several other methoxy-*NNO*-azoxy compounds (δ 60—63 in $CDCl_3$).[13—15] The ^{13}C NMR signals of the vinyl group were assigned by the comparison with the spectroscopic characteristics of nitro olefins.[12]

The ^{14}N NMR spectrum of compound **3** exhibits a relatively narrow ($\Delta\nu_{1/2}$ ~80 Hz) signal at δ –66.8 characteristic of the *N*-oxide nitrogen atom,[13] which was described for several other alkoxy-*NNO*-azoxy compounds (δ = –66—–71, $\Delta\nu_{1/2}$ = 80—220 Hz).[13,14]

In the mass spectrum of compound **3**, the peak of the molecular ion is most intense, and fragmentation agrees with the published data.[1,16] In particular, the most intense peaks of ions in the mass spectrum of β-(ethoxy-*NNO*-azoxy)styrene[1] $[M]^+$, $[M - Et]^+$, $[M - EtNO]^+$, and $[EtNO]^+$ are similar to the most intense peaks in the spectrum of compound **3**.

Thus, the first member of the alkoxy-*NNO*-azoxy olefin series, *viz.*, methoxy-*NNO*-azoxyethene (**3**), was synthesized by the pyrolysis of 1,1-bis(methoxy-*NNO*-azoxy)ethane (**4**) in melt.

Experimental

The IR spectrum was recorded with a Specord IR-75 spectrometer (in thin film). The UV spectrum was recorded with an Specord M-40 spectrometer (solutions in H_2O). ^1H (200.13 MHz), ^{13}C (50.32 MHz), and ^{14}N (21.69 MHz) NMR spectra were obtained on a Bruker AC-200 spectrometer (in $CDCl_3$). Chemical shifts for ^1H and ^{13}C were measured relatively to the solvent signals (7.25 and 77.0 MHz), and those for ^{14}N were measured relatively to the external standard ($MeNO_2$). The ^1H NMR spectrum without a solvent was recorded with an NMR spectrometer (294 MHz) designed and manufactured at the Institute of Problems of Chemical Physics of the Russian Academy of Sciences (IPCP RAS) using Me_4Si as the internal standard (signals of protons were assigned by analogy, see above). The mass spectrum was obtained with an MX-1320 spectrometer (EI, 70 eV).

The yield of compound **3** was studied in sealed ~180-mL glass vessels with a falcate membrane, using a weighed sample of compound **4** of ~150 mg. The reaction course was monitored by a change in the pressure of gaseous products.[6] The temperature in these experiments and during the synthesis of compound **3** was maintained with an accuracy of ±0.2 K using an air thermostat designed and manufactured at the IPCP RAS and measured with a calibrated chromel—copel thermocouple. The yield of compound **3** was determined using GLC with an LKhM-8MD chromatograph (column packed with 15% Carbowax-20M on Chromaton N-AW DMCS, N_2 as the carrier gas, 30 mL min^{-1}, temperature of the column 150 °C, temperature of the evaporator 200 °C), τ_{sp} = 6.6 min, PhCN as the internal standard, τ_{sp} = 5.25 min.

1,1-Bis(methoxy-*NNO*-azoxy)ethane (4) was synthesized according to a modified procedure.[5] Nitrogen oxide[17] was passed through a solution of NaOH (98%, 245 g, 6 mol) and ethyl methyl ketone (400 mL, 322 g, 4.47 mol, 2.23 equiv.) in MeOH (2.5 L) with vigorous stirring and cooling with such a rate that NO was completely absorbed, maintaining the temperature at 20—25 °C. A precipitate began to form after 20 min, and after 2 h the absorption of NO was sharply slowed down. The reaction mixture was additionally stirred in an NO atmosphere for 3 h at ~20 °C and neutralized by phenolphthalein with AcOH (5 mL). The precipitate was filtered off, washed with MeOH (1 L) and Et_2O (1 L), and dried in air at the relative humidity not higher than 60% (the product smeared at the humidity higher than 70%). Thus obtained **1,1-bis(nitrosohydroxylamino)ethane disodium salt** (490 g) was suspended without purification in DMF (1 L), and Na_2CO_3 (53 g, 0.5 mol) was added. Then dimethyl sulfate (560 mL, 5.8 mol) was gradually added with stirring and cooling for 3.5 h, maintaining the temperature at 20—25 °C. Plentiful gas evolution was observed, and the reaction mixture darkened and homogenized, except for a minor precipitate of Na_2CO_3. The mixture was additionally stirred for 0.5 h at 20 °C and for 0.5 h at 50 °C, and the solvent was distilled off on a rotary evaporator at 20—95 °C (8 Torr). In this distillation, the target product was not distilled off (≤ 0.1%). ***Attention! The by-product, cancerogenic N-nitrosodimethylamine, was distilled off along with DMF.*** The residue was dissolved in water (1 L) and extracted with $CHCl_3$ (400 mL) for 15 h in a liquid-liquid extractor for the heavy organic phase. The extract (~0.5 L) was passed through a column packed with silica gel (100—160 μm, 100 g), washed with $CHCl_3$ (250 mL), and evaporated *in vacuo*. The residue was recrystallized from EtOH (200 mL). The yield of the product was 118 g (16% based on ethyl methyl ketone), m.p. 72—74 °C (*cf.* Ref. 5: m.p. 75—75.5 °C). After recrystallization from an H_2O—MeOH mixture, the product (92 g) was obtained with m.p. 75—75.5 °C.

Methoxy-*NNO*-azoxyethene (3). A 4-L glass vessel containing compound **4** (7 g, 68.5 mmol, the maximum amount for which the pressure of the pyrolysis products at 260 °C does not exceed 1.5 atm) was evacuated with an oil pump (~0.1 Torr), sealed off and heated at 260 °C for 20 min, cooled, and opened. The condensate was washed off with $CHCl_3$ (30 mL). The solvent was distilled off from the combined washings of five analogous experiments, and the residue was doubly distilled *in vacuo*. The yield of the product was 10.6 g (53%), b.p. 66—68 °C (8 Torr), n_D^{20} 1.4898, d_4^{20} 1.111. UV, λ_{max}/nm (ε): 250 (11170). IR, ν/cm^{-1}: 665, 745, 960, 1020, 1065, 1080, 1210, 1290 (N_2O_2), 1390 (N_2O_2), 1480 (N_2O_2), 1655 (C=C), 2845, 2960, 3000, 3115, 3140. ^1H NMR (without solvent, δ: 4.15 (s, 3 H, Me); 5.59 (d, 1 H, H_b, $J_{a,b}$ = 7.5 Hz); 6.32 (d, 1 H, H_c, $J_{a,c}$ = 15 Hz); 7.31 (dd, 1 H, H_a, $J_{a,b}$ = 7.5 Hz, $J_{a,c}$ = 15 Hz). ^1H NMR ($CDCl_3$), δ: 4.02 (s, 3 H, Me); 5.37 (d, 1 H, H_b, $J_{a,b}$ = 8 Hz); 6.25 (d, 1 H, H_c, $J_{a,c}$ = 15 Hz); 6.93 (dd, 1 H, H_a, $J_{a,b}$ = 8 Hz, $J_{a,c}$ = 15 Hz). ^{13}C NMR, δ: 61.5 (CH_3O); 113.6 (=CHN); 136.4 (CH_2=). ^{14}N NMR, δ, ($\Delta\nu_{1/2}$/Hz)): −66.8 (~80). MS, m/z (I_{rel} (%)): 102 $[M]^+$ (100), 87 $[M - Me]^+$ (85), 58 (14), 57 $[M - MeNO]^+$ (70), 46 (6), 45 $[MeNO]^+$ (16), 43 (11), 42 (8), 41 (6), 40 (4), 32 (6), 31 (16), 30 (38), 29 (19), 28 (47), 27 (59).

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