insignificantly. An s—p charge transfer is observed for the C(1) carbon atom, which is a central atom in the [C(1)C_4] "microcluster" in the bulk of the superstoichiometric phase.

According to calculations, the charges of the "muffin-tin" sphere of the C(1) atom are 1.35 (C 2s state) and 2.34 *e* (C 2p state), which indicates that new sp^3-like carbon—carbon bonds similar to interatomic bonds in diamond lattice are formed in the bulk of carbon microclusters in β-$SiC_{x>1.0}$.

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Synthesis of 3-nitro-3-azalk-2-yl ethers

A. A. Spiridonov,[a]* *M. S. Fedoseev,*[a] *and A. I. Spiridonov*[b]

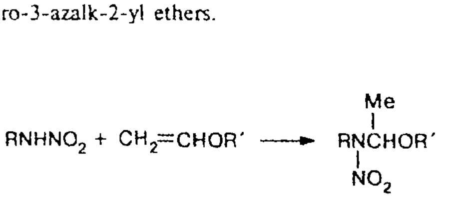
[a]*Institute of Technical Chemistry, Ural Branch of the Russian Academy of Sciences,*
13 ul. Lenina, 614000 Perm, Russian Federation.
Fax: +7 (342 2) 92 4375
[b]*Nizhnekamsk Institute of Chemical Technology,*
47 prosp. Stroitelei, 423550 Nizhnekamsk, Russian Federation.
Fax: +7 (855 5) 31 7549

Primary *N*-nitramines react with vinyl ethers to give 3-nitro-3-azalk-2-yl ethers.

Key words: primary *N*-nitramines, vinyl ethers, 3-nitro-3-azalk-2-yl ethers.

Polar addition of compounds bearing a reactive hydrogen atom to the double bond of vinyl ethers is well known,[1,2] whereas literature data on the reaction of the latter with primary *N*-nitramines are lacking.

We established that this reaction occurs in the presence of a mineral acid (H_3PO_4 or H_2SO_4) as a catalyst to give 3-nitro-3-azalk-2-yl ethers (**1a—c**), which were not found in the literature[3—5] to be synthesized in the common ways.



$$\mathrm{RNHNO_2 + CH_2{=}CHOR' \longrightarrow R\underset{\displaystyle NO_2}{\underset{|}{N}}\overset{\displaystyle Me}{\overset{|}{C}}HOR'}$$

1a—c

R = Me, R′ = Bu (**a**); C_2H_4Cl (**b**); R = Et, R′ = Bu (**c**)

Primary *N*-nitramines react with *n*-butyl vinyl ether even at 30—35 °C to give products **1a** and **1c** in 52.3% and 30.5% yields, respectively. The reaction with vinyl ethers containing an electron-accepting substituent requires heating (60 °C), which decreases the yield of **1b** to 24.5% (converted to vinyl ether) owing to stimulation

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Table 1. Characteristics of 3-nitro-3-azalk-2-yl ethers (**1a—c**)

Compound	B.p./°C (*p*/Torr)	d_4^{20} /g cm^{-3}	n_D^{20}	Found/Calculated (%)			Molecular formula	^{13}C NMR ($CDCl_3$), δ
				C	H	N		
1a	90 (4)	1.0182	1.4460	48.10 47.71	8.79 9.17	16.56 15.90	$C_7H_{16}N_2O_3$	13.3 ($\underline{C}H_3CH_2$); 17.9 ($\underline{C}H_3CH$); 18.8 (CH_2); 29.7 (CH_3N); 31.0 (CH_2); 68.4 (CH_2O); 85.0 (CHO)
1b	66 (2)	1.1597	1.4453	33.08 32.89	6.14 6.08	14.97 15.35	$C_5H_{11}N_2O_3Cl$	18.9 ($\underline{C}H_3CH$); 29.6 (CH_3N); 63.9 (CH_2Cl); 70.6 (CH_2O); 84.6 (CHO)
1c	70 (3)	0.9919	1.4421	50.51 50.50	9.64 9.56	15.44 14.73	$C_8H_{18}N_2O_3$	12.7 ($\underline{C}H_3CH_2N$); 13.5 ($\underline{C}H_3CH_2$); 19.0 ($\underline{C}H_3CH + CH_2$); 31.3 ($CH_2$); 38.8 ($CH_2N$); 68.8 ($CH_2O$); 82.5 (CHO)

of acid-catalyzed decomposition of the primary nitramine, although taken in 50% excess. The equimolar ratio of the initial components affords product **1b** only in 14% yield. The compounds obtained were identified by ^{13}C NMR spectroscopy, elemental analysis (Table 1), and IR spectroscopy. The individuality of the compounds was checked by GLC.

Experimental

The compounds were analyzed using an LKhM-8 MD chromatograph with a flame-ionizing detector (column XE-60, evaporator temperature 200 °C, column temperature 180 °C). ^{13}C NMR spectra were recorded on a Jeol FX-90Q instrument (22.5 MHz) in $CDCl_3$ with Me_4Si as the internal standard. IR spectra were obtained on a UR-20 spectrometer (thin film).

***n*-Butyl 3-nitro-3-azabut-2-yl ether (1a).** A solution of methylnitramine (7.6 g, 0.1 mol), *n*-butyl vinyl ether (10 g, 0.1 mol) in 80 mL of CH_2Cl_2, and conc. H_2SO_4 (0.4 g) was stirred in a flask equipped with a reflux condenser at 30—35 °C for 6 h. Then the reaction mixture was cooled to −20 °C and neutralized with a 5% aqueous solution of $NaHCO_3$. The organic layer was separated, washed with water, and dried with $MgSO_4$. The solvent was removed, and the residue was distilled *in vacuo* to give product **1a** (9.2 g, 52.3%). IR, ν/cm^{-1}: 1540, 1320 ($N-NO_2$); 1130 (C—O—C). The content of the main component **1a** is 95.6 wt.%.

2-Chloroethyl 3-nitro-3-azabut-2-yl ether (1b). A solution of methylnitramine (5.7 g, 0.075 mol), 2-chloroethyl vinyl ether (5.5 g, 0.05 mol), and 85% H_3PO_4 (0.9 g) in 80 mL of $CHCl_3$ was stirred in a flask equipped with a reflux condenser at 60 °C for 12 h. Then the reaction mixture was cooled, and the target product was isolated as described for compound **1a**. Yield 2.3 g (24.5%). IR, ν/cm^{-1}: 670 (C—Cl); 1525, 1310 ($N-NO_2$); 1130 (C—O—C).

***n*-Butyl 3-nitro-3-azapent-2-yl ether (1c).** A solution of ethylnitramine (10.8 g, 0.12 mol), *n*-butyl vinyl ether (10 g, 0.1 mol), and 85% H_3PO_4 (0.6 g) in 80 mL of $CHCl_3$ was stirred in a flask equipped with a reflux condenser at 30—35 °C for 7 h. The product was isolated by analogy with compound **1a**. Yield 5.8 g (30.5%). IR, ν/cm^{-1}: 1525, 1300 ($N-NO_2$); 1129 (C—O—C).

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