## REACTION OF THE DIMETHOXYAMINYL RADICAL WITH TERTIARY NITROSOALKANES AS A METHOD FOR THE PREPARATION OF N-ALKYL-N'-METHOXYDIAZENE N-OXIDES

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The reaction of the dimethoxyaminyl radical with functionally substituted nitrosoalkanes (2) in a 2:1 ratio at  $20^{\circ}C$  gives the corresponding N-alkyl-N'-methoxydiazene N-oxides (3) as a single isomer in preparative yields.

Keywords: dimethoxyaminyl radical, tertiary nitrosoalkanes, N-alkyl-N'-methoxydiazene N-oxides.

We have found that dialkoxyaminyl radicals [1-3] exist in solution in equilibrium with their diamagnetic dimers, tetraalkoxyhydrazines [2, 3] and form adducts with the 2-cyano-2-propyl radical.

In the present work, we studied the reaction of the dimethoxyaminyl radical (DAR) with tertiary nitrosoalkanes, commonly used as traps for various radical types.

DAR was generated from dimethoxyamine by the action of  $PbO_2$  according to our previous procedure [2] and used without isolation and purification in ethereal solution. Functionally substituted tertiary nitrosoalkanes (2a) and (2b) were obtained from the corresponding N-chloro-N-methoxyamines (1). Chloramine 1a is converted to 2a by the action of  $K_2CO_3$  according to our previous procedure [4], while 1b [5] is unaltered under these conditions but is smoothly converted into 2b [6] by the action of SbCl<sub>5</sub>.





The reaction of DAR with nitrosoalkanes 2 taken in a 2:1 ratio is complete in 0.5 h in ethereal solution at ~20°C. When equivalent amounts of the two reagents are taken, half of the nitrosoalkane does not undergo reaction. The structures of the resultant N-alkyl-N'-methoxydiazene N-oxides (3) were supported by spectral methods. The PMR spectra of 3a and 3b correspond to a single form, apparently the Z isomer since this isomer is obtained predominantly even in the case of the simplest derivative, N-methyl-N'-methoxydiazene N-oxide. The Z and E isomers of this compound hardly differ in their PMR spectra [7]. The UV spectra of 3a and 3b have a  $\pi \rightarrow \pi^*$  transition band characteristic for compounds of this class [8, 9]. The mass spectrum of 3b also corresponds to this structure [8, 10, 11].

The formation of products 3a and 3b may be explained as in the scheme shown above by the formation of intermediate dimethoxyaminonitroxyl radical A and its fragmentation with the loss of a methoxyl radical. A two-fold excess of the starting DAR is required for binding the methoxyl radical.

Related thermal and photochemical reactions of  $N_2F_2$  with nitrosoalkanes to give N-alkyl-N'-fluorodiazene N-oxides have been described [12-15]. A complex mechanism has been ascribed for these reactions [13, 14]. Intermediate diffuoroaminonitroxyl radicals similar to A were detected by ESR spectroscopy [15].

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The formation of N-alkyl-N'-methoxydiazene N-oxides 3 is a new method for the preparation of this class of compounds [7-10].

## EXPERIMENTAL

The PMR spectra were taken on a Bruker M-400 spectrometer. The UV spectra were taken on a Specord UV-VIS spectrometer, while the mass spectrum was taken on a Hitachi M-80A mass spectrometer.

An ethereal solution of the dimethoxyaminyl radical was prepared according to our previous procedure [2].

Methyl ester of 3-nitroso-3-methylbutanoic acid (2a) was obtained according to our previous procedure [4] in 91% yield and used without purification.

Methyl ester of 3-(N-chloro-N-methoxyamino)-3-trifluoromethylbutanoic acid (1b) was obtained according to our previous procedure [5] in quantitative yield and used without purification.

Methyl Ester of 3-Nitroso-3-trifluoromethylbutanoic Acid (2b). A solution of  $0.59 \text{ g} (2 \text{ mmoles}) \text{ SbCl}_5$  in 3 ml absolute  $\text{CH}_2\text{Cl}_2$  was added to a solution of 0.49 g (2 mmoles) 1b in 3 ml absolute  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$ . The mixture was brought to  $20^\circ\text{C}$  and subjected to chromatography on a silica gel column using  $\text{CH}_2\text{Cl}_2$  as the eluent to give 0.24 g (61%) 2b. The PMR spectrum of this product was identical to that of an authentic sample of 2b [6].

**N-(1,1-Dimethyl-2-methoxycarbonyl)ethyl-N'-methoxydiazene N-Oxide (3a).** A mixture of the dimethoxyaminyl radical obtained from 3.54 mmoles (MeO)<sub>2</sub>NH and 0.21 g (1.42 mmole) **2a** in 10 ml absolute ether was maintained at 20°C until complete decolorization of the solution (~0.5 h). The solvent was removed in vacuum and the residue was subjected to chromatography on a silica gel column using ether as the eluent to give 0.15 g (56%) **3a.** Found: C, 44.37; H, 7.11; N, 14.91%. Calculated for C<sub>7</sub>H<sub>14</sub>N<sub>2</sub>O<sub>4</sub>: C, 44.20; H, 7.42; N, 14.73%. UV spectrum in heptane ( $\lambda_{max}$ , nm): 238 ( $\varepsilon$  7500). PMR spectrum in C<sub>6</sub>D<sub>6</sub>: 1.40 s (6H, Me<sub>2</sub>C), 2.62 s (2H, CH<sub>2</sub>), 3.22 s (3H, OMe), 3.55 s (3H, OMe).

**N-(1-Methyl-1-trifluoromethyl-2-methoxycarbonyl)ethyl-N'-methoxydiazene** N-Oxide (3b). A mixture of the dimethoxyaminyl radical obtained from 0.9 mmole (MeO)<sub>2</sub>NH and 0.08 g (0.38 mmole) 2b in 10 ml absolute ether was maintained at 20°C until the solution was completely decolorized (0.5 h). The solvent was removed in vacuum and the residue was subjected to chromatography on an alumina column (Brockmann neutral) using ether as the eluent to give 0.69 g (74%) 3b. Found: C, 34.02; H, 4.31; N, 11.59%. Calculated for  $C_7H_{11}F_3N_2O_4$ : C, 34.43; H, 4.54; N, 11.47%. UV spectrum in heptane ( $\lambda_{max}$ , nm): 239 ( $\epsilon$  10,486). PMR spectrum in  $C_6D_6$  ( $\delta$ , ppm, J, Hz): 1.77 q (3H, Me,  ${}^4J_{H,F} = 1.07$ ), 2.20, 3.53 AB (2H, CH<sub>2</sub>,  ${}^2J = -16.9$ ), 3.15 s (3H, OMe), 3.42 s (3H, OMe). Chemical ionization mass spectrum using isobutane at 70 eV, m/z ( $I_{rel}$ , %): 245 [M + H]<sup>+</sup> (3), 244 [M]<sup>+</sup>, (26), 229 [M - Me]<sup>+</sup> (8), 228 [M - O]<sup>+</sup> (2), 214 [M - NO]<sup>+</sup> (1), 213 [M - MeO]<sup>+</sup> (11), 199 [M - NOMe]<sup>+</sup> (5), 184 (6), 169 [M - N<sub>2</sub>O<sub>2</sub>Me]<sup>+</sup> (13), 149 (45), 137 (34), 127 (10), 91 (57), 73 (27), 59 (100), 45 (28).

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