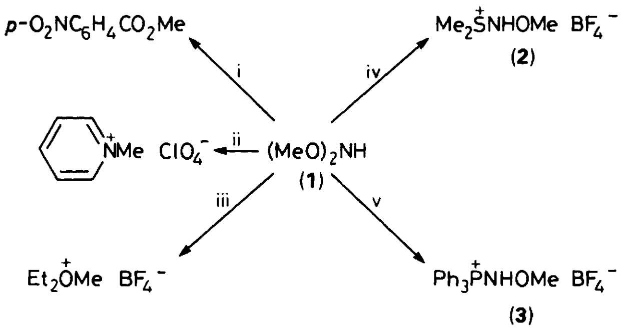
N,N-Dimethoxyamine; a New Methylating, Aminating, and Epiminating Reagent

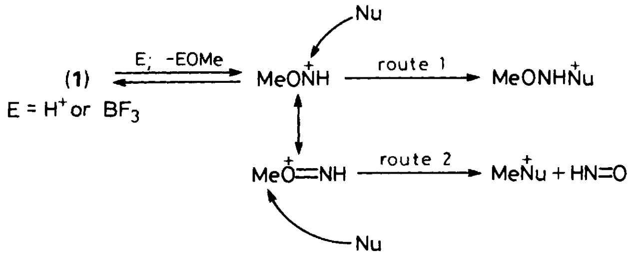
Vladimir F. Rudchenko,* Sergei M. Ignatov, and Remir G. Kostyanovsky
Institute of Chemical Physics, Academy of Sciences of the U.S.S.R., B-334 Moscow, U.S.S.R.

Electrophilically catalysed cleavage of the N–O bond of *N,N*-dimethoxyamine results in the formation of singlet *N*-methoxynitrenium ion, which aminates soft nucleophiles, methylates hard ones, and epiminates alkenes.

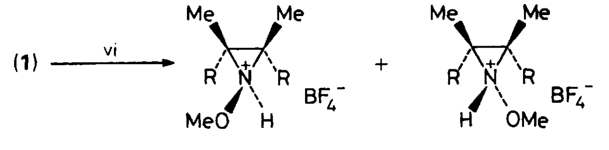
Two electronegative *N*-substituents in *N,N*-dialkoxyamines[1] significantly decrease the p character of the nitrogen lone electron pair. Therefore, these compounds are characterized by a higher pyramidal stability [$\Delta G^{\ddagger}_{\text{inv.}} \simeq 20$ kcal mol^{-1} (1 cal = 4.184 J)][1] and weaker nucleophilicity[1] compared to common amines and *N*-alkoxyamines. However, *N,N*-dialkoxyamines undergo reactions typical for secondary amines; hydroxy- and amino-methylation,[1] acylation and carbamoylation,[2] and *N*-chlorination.[3] They are also easily oxidised forming stable *N,N*-dialkoxyaminyl radicals.[4]



Scheme 1. *Reagents and conditions.* i, p-$O_2NC_6H_4CO_2H$, C_6H_6, boiling, (98%); ii, Py·$HClO_4$ (Py = pyridine), MeCN, room temp., 3 days, (29%); iii, Et_2O, BF_3·Et_2O (1.3 equiv.), 0 °C, 1 h, (23%); iv, Me_2S, BF_3·Et_2O (1.3 equiv.), CH_2Cl_2–CCl_4, 0 °C, 1 h, (99%); v, Ph_3P, BF_3·Et_2O (1.3 equiv.), CH_2Cl_2–CCl_4, 0 °C, 1 h, (81%).



Scheme 2



(4) R = H; **(5)** R = Me

Scheme 3. *Reagents and conditions*: vi, tetramethylethylene or *cis*-but-2-ene (3—4 equiv.), BF_3·Et_2O (1.3 equiv.), Et_2O, 1 h at −78 °C and 1 h at 0 °C, yields **(4)** and **(5)** in 95 and 31% yields, respectively, *anti*-**(4)**/*syn*-**(4)** ≃1.2.

We report here a new type of *N,N*-dialkoxyamine transformation; mild electrophilically initiated cleavage of the N–O bond, which previously was found for other systems containing the -O–N–O- fragment (*N*-alkyl-*N,N*-dialkoxy-[5] and *N,N,N*-trialkoxy-amines[3]). Thus, the formation of products of nucleophilic methylation and methoxyamination in reactions of *N,N*-dimethoxyamine **(1)** (Scheme 1) can be explained by suggesting generation of an intermediate *N*-methoxynitrenium ion which, similarly to *N,N*-dialkoxynitrenium ions,[3] possesses the properties of an ambident cation (Scheme 2).

According to Klopman's generalized perturbation equation[6] and MNDO calculations on the model *N*-hydroxy nitrenium ion,[7] which predict the greatest positive charge for the H atom of the hydroxylic group and the maximal LUMO coefficient for the N atom, reactions of the *N*-methoxynitrenium ion with soft nucleophiles (route 1, Scheme 2) are orbital controlled, while those with hard nucleophiles (route 2) are controlled by the charge.

The *N*-methoxynitrenium ion readily undergoes cycloaddition to alkenes forming 1-methoxyaziridinium tetrafluoroborates[†] (Scheme 3, anion BF_4^- is produced *via* disproportionation of the initially formed anion BF_3OMe^- with excess BF_3[8]).

The stereospecific cycloaddition of *N*-methoxynitrenium ion to *cis*-but-2-ene indicates its singlet ground electronic state. This corresponds to the calculation results,[7,9] predicting the preference of the singlet state for nitrenium ions containing the electron-donating *N*-substituents.

Thus, a new source[3,5,7,10] of *N*-alkoxynitrenium ions has been found, and the wide synthetic potential of the latter shown.

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[†] All new compounds gave satisfactory spectral and analytical data. *Selected spectroscopic data* for **(2)**: ^1H NMR (CD_3CN) δ 3.02 (6H, s), 3.78 (3H, s), 8.23 (1H, s). For **(3)**: ^1H NMR (CD_3CN) δ 3.55 (3H, s), 7.94—7.76 (15H, m), 9.02 (1H, d, J_{PH} 12.5 Hz). For *syn*-**(4)**: ^1H NMR (CD_3CN) δ 1.49 (6H, m, $^3J_{HMe}$ 6.3 Hz, $^4J_{HMe}$ −0.15 Hz), 3.86 (3H, s), 3.45 (2H, m, ^3J 9.2 Hz), 9.12 (1H, s). For *anti*-**(4)**: ^1H NMR (CD_3CN) δ 1.44 (6H, m, $^3J_{HMe}$ 6.5 Hz, $^4J_{HMe}$ −0.28 Hz), 3.90 (3H, s), 3.62 (2H, m, ^3J 9.8 Hz), 9.12 (1H, s). For **(5)**: ^1H NMR (CD_3CN) δ 1.53 (6H, s), 1.58 (6H, s), 3.91 (3H, s).