

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

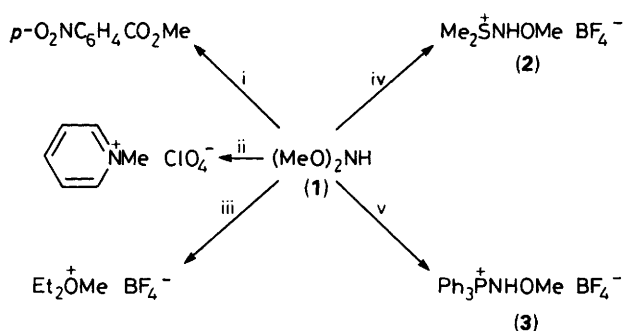
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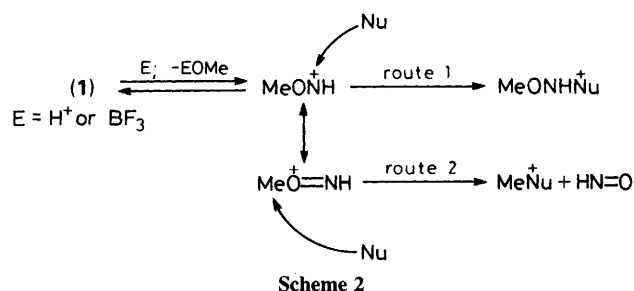
Electrophilically catalysed cleavage of the N–O bond of *N,N*-dimethoxyamine results in the formation of singlet *N*-methoxynitrenium ion, which aminates soft nucleophiles, methylates hard ones, and epiminates alkenes.

Two electronegative *N*-substituents in *N,N*-dialkoxyamines¹ significantly decrease the p character of the nitrogen lone electron pair. Therefore, these compounds are characterized by a higher pyramidal stability [$\Delta G_{\text{inv}}^{\ddagger} \approx 20 \text{ kcal mol}^{-1}$ (1 cal = 4.184 J)]¹ and weaker nucleophilicity¹ compared to common

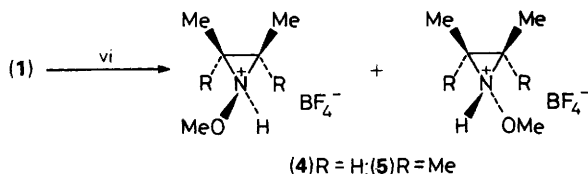
amines and *N*-alkoxyamines. However, *N,N*-dialkoxyamines undergo reactions typical for secondary amines; hydroxy- and amino-methylation,¹ acylation and carbamoylation,² and *N*-chlorination.³ They are also easily oxidised forming stable *N,N*-dialkoxyaminyl radicals.⁴



Scheme 1. Reagents and conditions. i, $p\text{-O}_2\text{NC}_6\text{H}_4\text{CO}_2\text{H}$, C_6H_6 , boiling, (98%); ii, $\text{Py} \cdot \text{HClO}_4$ (Py = pyridine), MeCN, room temp., 3 days, (29%); iii, Et_2O , $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.3 equiv.), 0°C , 1 h, (23%); iv, Me_2S , $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.3 equiv.), $\text{CH}_2\text{Cl}_2\text{-CCl}_4$, 0°C , 1 h, (99%); v, Ph_3P , $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1.3 equiv.), $\text{CH}_2\text{Cl}_2\text{-CCl}_4$, 0°C , 1 h, (81%).



Scheme 2



Scheme 3. Reagents and conditions: vi, tetramethylethylene or *cis*-but-2-ene (3–4 equiv.), $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (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-³amines). 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*-dialkoxy-nitrenium ions,³ possesses the properties of an ambident cation (Scheme 2).

According to Klopman's generalized perturbation equation⁶ 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, $^3J_{\text{HMe}}$ 6.3 Hz, $^4J_{\text{HMe}}$ -0.15 Hz), 3.86 (3H, s), 3.45 (2H, m, $^3J_{\text{HMe}}$ 9.2 Hz), 9.12 (1H, s). For *anti*-(4): ^1H NMR (CD_3CN) δ 1.44 (6H, m, $^3J_{\text{HMe}}$ 6.5 Hz, $^4J_{\text{HMe}}$ -0.28 Hz), 3.90 (3H, s), 3.62 (2H, m, $^3J_{\text{HMe}}$ 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).