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Synthesis and Properties of 2,3-Dimethoxy-1,4,2,3-dioxadiazinane and Dialkoxydiazene Oxides

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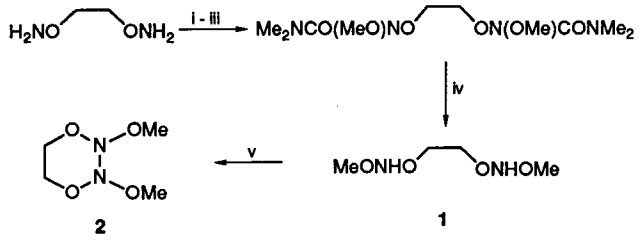
The oxidation of 1,2-bis(methoxyaminooxy)ethane **1** with PbO_2 results in the formation of 2,3-dimethoxy-1,4,2,3-dioxadiazinane **2** as a mixture of *trans*- and *cis*-isomers (55:45), the regio- and stereo-specific reaction of which with *p*-nitrobenzoic acid gives (*E*)-dialkoxydiazene oxide **3** and methyl *p*-nitrobenzoate.

Dialkoxyaminyl radicals $(RO)_2\dot{N}$ are a new class of persistent radicals. A theoretical prediction of the possibility of their existence[1] and their actual discovery[2] were made independently and almost simultaneously. In solution they exist in equilibrium with their diamagnetic tetraalkoxyhydrazine dimers, which can be isolated in a pure state.[2,3] It has been shown[4] that the only known aminyl diradicals $Ar\dot{N}SArS\dot{N}Ar$ undergo recombination to form the macrocyclic polyhydrazines. Therefore, both intra- and inter-molecular recombination for diradicals such as $RO\dot{N}O(CH_2)_nO\dot{N}OR$ are expected. We surmised that an 'enthropic preference' exists for the intramolecular cyclization of these radicals where $n = 2$. In order to verify this idea 1,2-bis(methoxyaminooxy)ethane **1** was obtained by the general method for dialkoxyamine synthesis[5] (Scheme 1). It was found that oxidation of **1** with PbO_2 did indeed give the six-membered compound **2**,† the first cyclic tetraalkoxyhydrazine. Previously, only 2,3-dicarbalkoxy derivatives of this heterocycle have been described[6] and an attempt to obtain its 2,3-dialkyl derivatives failed.[7] The synthesis and properties of mono- and di-alkoxyhydrazines have been described.[8]

There is no paramagnetic broadening of the NMR signals of compound **2** at room temperature. This proves that the equilibrium diradical $\rightleftharpoons$**2** is almost completely shifted towards



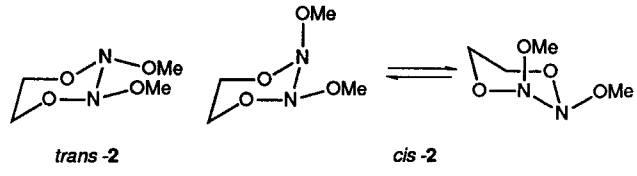
Scheme 1 *Reagents and conditions*: i, Me_2NCOCl–Et_3N, MeCN, 20 °C, 5 days, reflux, 3.5 h (95%, oil); ii, Bu^tOCl–CH_2Cl_2, – 78 °C (100%, oil); iii, MeONa–MeOH, – 8 °C, 1 h (75%, oil); iv, KOH–H_2O, 20 °C, 2 days (56%, b.p. 80–81 °C/1.5 Torr); v, PbO_2–Et_2O, 20 °C, 3 h (95%, oil)

† All new compounds gave satisfactory spectroscopic and analytical data. *Selected spectroscopic data* for **1**: ^{1}H NMR (C_6D_6) δ 3.41 (3H, s, MeO), 3.86, 3.92 (4H, AA′BB′, CH_2CH_2), 7.73 (1H, s, NH), 7.74 (1H, s, NH); CIMS (*iso*-C_4H_{10}), *m/z* 210 (71%, M + C_4H_{10}), 153(23, M + H), 152(2, M^+), 103(100).

For *trans*-**2**: ^{1}H NMR ($C_6D_5CD_3$, 27 and – 50 °C, LAOCN3-type analysis of the AA′BB′ spectrum for the CH_2CH_2 fragment) δ 2.94 (2H, m, H_e, ^2J – 11.8, $^3J_{ee}$ 2.1 Hz), 3.49 (6H, s, MeO), 4.39 (2H, m, H_a, $^3J_{aa}$ 10.5, $^3J_{ae}$ 3.5 Hz); ^{13}C NMR ($C_6D_5CD_3$, 27 °C) δ 56.39 (CH_2, ^1J 148.4 Hz), 58.81 (MeO, ^1J 144.3 Hz).

For *cis*-**2**: ^{1}H NMR ($C_6D_5CD_3$, 27 °C) δ 3.41 (2H, br m, H_e), 3.55 (6H, s, MeO), 3.80 (2H, br m, H_a); ^{1}H NMR ($C_6D_5CD_3$, – 50 °C) δ 2.75, 3.48 (2H, m, H_e, ^2J – 11.1, $^3J_{ee}$ 0.8 Hz), 3.49 (3H, s, MeO), 3.64 (3H, s, MeO), 4.24, 4.32 (2H, m, H_a, $^3J_{aa}$ 11.9 Hz, $^3J_{ae}$ 3.1 Hz); ^{13}C NMR ($C_6D_5CD_3$, 27 °C) δ 57.20 (br), 68.90 (br, CH_2), 60.03 (MeO, ^1J 144.9 Hz); ^{13}C NMR ($C_6D_5CD_3$, – 50 °C) δ 56.22 (CH_2, ^1J 148.1 Hz), 59.61, 60.22 (MeO, ^1J 145.0 Hz), 68.64 (CH_2, ^1J 146.3 Hz).

For **3**: ^{1}H NMR (CD_3CN): δ 3.12 (1H, t, OH, ^3J 5.5 Hz), 3.71 (2H, BB′ part of the AA′BB′C spectrum, CH_2OH), 3.95 (3H, s, MeO), 4.36 (2H, AA′ part of the AA′BB′C spectrum, CH_2ON); IR (neat) ν_{max}/cm^{-1} 940, 1030, 1075, 1225, 1480, 1580, 3400; UV (heptane) λ_{max} 232 nm (ε 2760); CIMS, *m/z* 137(99, M + H), 136(2, M^+), 75(100).



Scheme 2

compound **2**. The signals in this spectrum were assigned to the *trans*- and *cis*-isomers of **2** in the ratio 55:44 (Scheme 2) on the basis of variable temperature NMR spectra and literature data on the conformation of hexahydropyridazines,[9] tetrahydro-1,2-oxazines[10] and tetramethoxyhydrazine.[3] The parameters for the interconversion of the *cis*-isomer (Scheme 2) were determined by ^{13}C NMR spectroscopy, from the coalescence temperature of the MeO-group signals: T_c = 238 K, $\Delta\nu$ = 85 Hz, k = 188.7 s^{-1}, $\Delta G^{\neq}$ = 47.3 kJ mol^{-1}.

Compound **2** is relatively unstable. Decomposition takes place during short-term heating in toluene, on dissolution in MeOH and on chromatography (Al_2O_3 or SiO_2). The reaction of compound **2** with *p*-nitrobenzoic acid gave methyl *p*-nitrobenzoate and dialkoxydiazene oxide **3** in the form of one isomer (Scheme 3). The latter is the first representative of this type of compound. Compound **3** is the diester of the hypothetical hyponitric acid ($H_2N_2O_3$), salts of which are well known,[11] for example, the Angeli salt.[12] The 1-alkyl-2-alkoxydiazene 1-oxides have also been described.[13]

Compound **3** does not change during distillation, chromatography (Al_2O_3), or under the action of *p*-nitrobenzoic acid and aqueous Na_2CO_3 solution. An (*E*)-configuration for **3** was determined by X-ray analysis[14] of its derivative **4** (Scheme 3). The regio- and stereo-specificity of the acidic decomposition of **2** proves that this reaction proceeds *via* a synchronous mechanism under stereoelectronic control[14,15] (Scheme 3).

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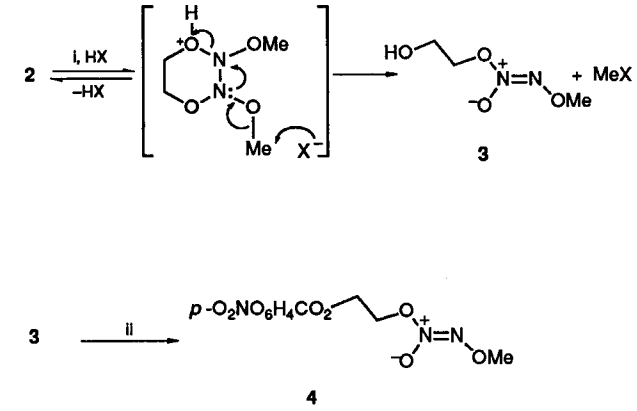

Scheme 3 *Reagents and conditions*: i, HX = *p*-$O_2NC_6H_4CO_2H$, Et_2O, 20 °C, 2 days, (yields **3** in 40% yield, oil); ii, *p*-$O_2NC_6H_4COCl$–Et_3N, C_6H_6, 20 °C, 3 days (93%, m.p. 85 °C)

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