Di(methyl-*NON*-azoxy)formal as the first example of azoxyformals

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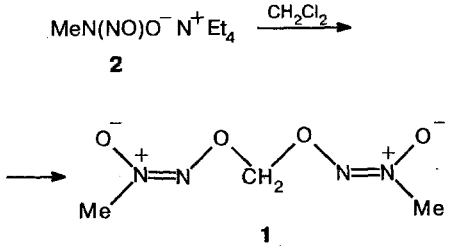
Di(alkoxy-*NNO*-azoxy)methanes have long been known and well studied in the series of alkoxy-*NNO*-azoxy compounds.[1] However, their structural isomers di(alkyl-*NON*-azoxy)formals are not described in the literature. The first representative of this class, di(methyl-*NON*-azoxy)formal (**1**), has unexpectedly been obtained upon refluxing a solution of methylnitrosohydroxylamine tetraethylammonium salt (**2**)[2] in methylene chloride.



When an excess of CH_2Cl_2 used as solvent is replaced with MeCN, the yield of **1** increased from 20 to 35 %.

A solution of 0.1 mol of salt **2** and 0.07 mol of CH_2Cl_2 in 40 mL of anhydrous MeCN was refluxed for 1 h and kept for 1 day at ~20 °C. Colorless needles of **1** were separated, washed with water on a filter, and dried in air. Yield 35 %, m.p. 194–198 °C, after double recrystallization from DMF–MeCN m.p. 199–200 °C. Found (%): C, 21.70; H, 4.95; N, 33.70. $C_3H_8N_4O_4$. Calculated (%): C, 22.22; H, 4.97; N, 34.56. UV (water), λ_{max}/nm: 229 (ε 17800). IR (mull with CCl_4), ν/cm^{-1}: 3050; 3000; 2975; 2845 (C–H); 1535; 1400–1450 (N_2O_2); 1335; 1310; 1185; 1110; 1075; 1030; 945. ^1H NMR (MeCN, δ): 3.87 (s, 6 H, Me); 5.80 (s, 2 H, CH_2). Mass spectrum (EI, 70 eV), m/z (I_{rel} (%)): 164 $[M]^+$ (2), 149 $[M-Me]^+$ (11), 134 $[M-2Me]^+$ (8), 89 $[M-MeN_2O_2]^+$ (66), 59 $[MeN_2O]^+$ (100).

X-ray diffraction analysis of **1** was performed (DAR-UM, Cu-Kα irradiation, λ = 1.5418 Å, R = 0.045, 1071 independent reflections $C_3H_8N_4O_4$). Crystals of **1** are monoclinic: a = 9.980(1), b = 8.365(1), c = 8.584(1) Å, γ = 90.62(2)°, V = 716.56 Å^3, d_{calc} = 1.521 g cm^{-3}, Z = 4, space group $P2_1/b$. A molecule in the crystal is located in the usual position and has a *Z,Z*-configuration.

Nonhydrogen atoms of both halves of the molecule of **1** lie in their planes, which pass through the central C atom, and the angle between the planes is 75.5°. The coordinates of atoms and a model of the molecule of **1** will be published in detail elsewhere.

References

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Synthesis of polyfluoroalkyl-containing 2-oxo-1,1a,2,3-tetrahydroazirino[1,2-*a*]quinoxalines

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1-Polyfluoroalkyl-2-oxo-1,1a,2,3-tetrahydroazirino[1,2-*a*]quinoxalines have been obtained for the first time by the reactions between ethyl α,β-dibromo-α-fluoroalkylcarboxylates (synthesized by the known procedure[1] and used without purification) and *o*-phenylenediamine in the presence of triethylamine.

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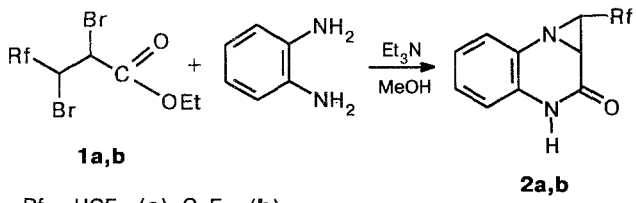

1a,b **2a,b**

Rf = HCF_2 (**a**), C_6F_{13} (**b**)

All compounds **2** have a *trans*-configuration of the aziridine cycle ($J_{H(1)-H(2)}$ = 2.5 Hz, protons are numerated from C=O).

General procedure for preparation of 2. Et_3N (2 molar eq.) and *o*-phenylenediamine (1 molar eq.) were added to a solution of dibromoester **1** (1 molar eq.) in MeOH. The mixture was refluxed for 3 h and left to stand for 1 day. Then the mixture was poured into water and extracted with ether. Extracts were dried over $MgSO_4$, the ether was distilled off, and the residue was recrystallized from hexane.

1-Difluoromethyl-2-oxo-1,1a,2,3-tetrahydroazirino[1,2-*a*]quinoxaline (2a). M.p. 207—208 °C. IR (ν/cm^{-1}): 1689 (C=O). ^{1}H NMR ($CDCl_3$, δ): 2.51—2.73 (m, 1 H, H(2)); 3.16 (d, 1 H, H(1), J = 2.56 Hz); 5.73 (td, 1 H, HCF_2); 6.69—7.44 (m, 4 H, Ar); 8.29 (s, 1 H, NH).

1-Perfluorohexyl-2-oxo-1,1a,2,3-tetrahydroazirino[1,2-*a*]quinoxaline (2b). M.p. 183—184 °C. IR (ν/cm^{-1}): 1690 (C=O). ^{1}H NMR ($CDCl_3$, δ): 2.56—2.74 (m, 1 H, H(2)); 3.22 (d, 1 H, H(1), J = 2.53 Hz); 6.72—7.48 (m, 4 H, Ar); 8.35 (s, 1 H, NH).

References

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