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Synthesis of 3,4-Dihydro-1,2-diazete 1,2-Dioxides based on 1,2-Bishydroxylamines and 1,2-Nitroso Oxime

Dmitrii G. Mazhukin, Leonid B. Volodarskii,* Lidiya A. Tikhonova and Aleksei Ya. Tikhonov

Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russia. Fax: + 7 383 235 4752

Oxidation of 1,2-bishydroxylamines having one or two hydroxylamino groups at a secondary carbon atom(s), by sodium hypobromite, leads to 3,4-dihydro-1,2-diazete 1,2-dioxides; treatment of 1,2-nitroso oxime with nitric acid or N_2O_4 gives 3,4-dihydro-3-nitro-1,2-diazete 1,2-dioxide.

Oxidation of 1,2-bishydroxylamines containing hydroxylamino groups at tertiary carbon atoms is known to lead to tetra-substituted 3,4-dihydro-1,2-diazete 1,2-dioxides.[1,2] 3,4-Dihydro-3,3,4,4-tetramethyl-1,2-diazete 1,2-dioxide is of interest as a triplet quencher.[1] 3-Bromo-3,4-dihydro-1,2-diazete 1,2-dioxides have been obtained by oxidation of 1,2-hydroxylamino oximes containing a hydroxylamino group at a tertiary carbon atom.[3] The oxidation of both 1,2-bishydroxylamines[4] and 1,2-hydroxylamino oximes[3] is thought to form vicinal dinitroso compounds in which intramolecular interaction of the nitroso groups leads to 3,4-dihydro-1,2-diazete 1,2-dioxides. Oxidation of 1,2-hydroxylamino oximes with the hydroxylamino group at a secondary carbon atom gives furazan 2-oxides.[3]

In the present communication we describe the synthesis of 3,4-dihydro-1,2-diazete 1,2-dioxides **1a, b** and **2** containing hydrogen atoms at the 3- and 4-positions of the heterocycle, and the synthesis of 3,4-dihydro-3-nitro-1,2-diazete 1,2-dioxide **3**. Oxidation of 1,2-bishydroxylamines† where one hydroxylamino group of **4a, b** or both hydroxylamino groups of **5** are at secondary carbon atoms, by sodium hypobromite, leads to 3,4-dihydro-1,2-diazete 1,2-dioxides **1a, b** and **2** in 80–95% yields (Scheme 1).‡ 3-Bromo-3,4-dihydro-1,2-diazete 1,2-dioxides or furoxane[3] are possibly formed under these conditions in trace amounts (TLC). Hence, intramolecular interaction of the nitroso groups to form the 3,4-dihydro-1,2-diazete 1,2-dioxides proceeds faster than isomerization of the nitroso group(s) to oxime group(s).[5]

The following general procedure was used. An aqueous solution of **4a, b** or **5** (10 mmol in 15 ml of water) was added

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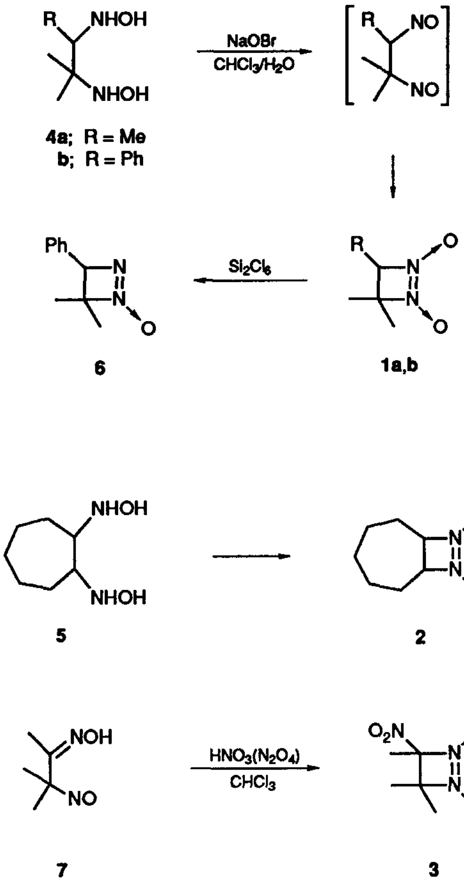
† 1,2-Bishydroxylamines were obtained by the hydrolysis of 1,2-dihydroxyimidazolidines. Their synthesis will be reported elsewhere.

‡ Satisfactory elemental analyses were obtained for all new compounds. **1a:** m.p. 96–97 °C; IR ν_{max}/cm^{-1} (KBr) 1445, 1480, 1565; UV λ_{max}/nm (EtOH) 259 (lg ϵ 4.25); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.53 (3H,s), 1.55 (3H, d, *J* 7.5 Hz), 1.67 (3H, s), 4.48 (1H, q, *J* 7.5 Hz). **1b**: m.p. 112–114 °C; IR ν_{max}/cm^{-1} (KBr) 1440, 1460, 1480, 1575; UV λ_{max}/nm (EtOH) 260 (lg ϵ 4.00); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.19 (3H, s), 1.81 (3H, s), 5.56 (1H, s), 7.3–7.5 (5H, m). **2**: m.p. 145–147 °C; IR ν_{max}/cm^{-1} (KBr) 1445, 1470, 1555; UV λ_{max}/nm (EtOH) 259 nm (lg ϵ 4.02); ^{13}C NMR (50.3 MHz, [$^2H_6$] Me_2SO), δ 24.04 (t), 25.29 (t), 29.78 (t), 73.92 (d). **6**: m.p. 50–52 °C; IR (KBr) 1455, 1560; UV λ_{max}/nm (EtOH) 215 (lg ϵ 4.19); ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.08 (3H, s), 1.72 (3H, s), 4.80 (1H, s), 7.3–7.5 (5H, m).



Scheme 1

dropwise to a vigorously stirred mixture of 15% aqueous NaBrO (40 mmol) and 30 ml $CHCl_3$ at −5→3 °C over 15 min. The phases were separated, and the aqueous phase was extracted with $CHCl_3$ (2×15 cm^3). The combined $CHCl_3$ portion was dried over $MgSO_4$, filtered and evaporated. The resulting solid was treated with hexane to give the crude product **1a**, **b** or **2** which was purified by recrystallisation from ethanol.

Deoxygenation of 3,4-dihydro-3,3-dimethyl-4-phenyl-1,2-diazete 1,2-dioxide **1b** with hexachlorodisilane leads to 3,4-dihydro-4,4-dimethyl-3-phenyl-1,2-diazete 1-oxide **6**.‡ Treatment of 1,2-nitroso oxime **7**[3] with nitric acid or nitrogen tetraoxide affords 3,4-dihydro-3-nitro-3,4,4-trimethyl-1,2-diazete 1,2-dioxide **3** in ~10% yield.§

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§ **3**: m.p. 111–113 °C; IR ν_{max}/cm^{-1} (KBr) 1445, 1500, 1575; UV λ_{max}/nm (EtOH) 248 (lg ε 3.90); ^1H NMR (60 MHz, CD_3OD) δ 1.41 (3H, s), 1.61 (3H, s), 2.10 (3H, s).