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ATTEMPTED FORMATION OF THE UNKNOWN TETRAMETHYLAZIRIDINYL-1-OXYL BY PHOTOLYSIS AND THERMOLYSIS OF DIAZETIDINE-1,2-DIOXIDE

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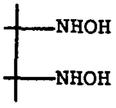
We have for some time been investigating the reactions of 2,3-dimethylbutane-2,3-bis-hydroxylamine 1[1] with regard to its tendency to form nitronylnitroxides 2 from aldehydes.[2] A recent report[3] describing the spontaneous decomposition of 1 to the theoretically interesting tetramethylaziridinyl-1-oxyl 3 compels us to describe observations based on our experience with 1 which raise serious doubts as to the validity of the authors' claim.



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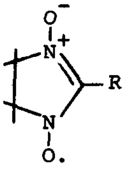

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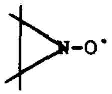

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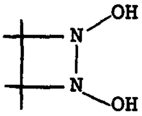
Like Luckhurst and Sundholm[3] we find that the bis-hydroxylamine 1 undergoes spontaneous decomposition at room temperature with formation of a nitroxide radical. This process proceeds most readily in a closed container and is apparently self-catalyzed by one or more volatile products. The major product 4 is a volatile crystalline compound, m.p. 59-61° the same as given by the previous authors for 3; m/e 112(M^+-H_2O-O),[4] 97 (M^+-H_2O-O-CH_3), 73(M^+/2). Although it is accompanied by traces of a nitroxide radical, it is diamagnetic and shows nmr ($CDCl_3$) signals at δ1.94(4 CH_3) and 9.14(2 OH, exchangeable). This compound was further characterized[5] by conversion with oxalylchloride and with phosgene to the cyclic derivatives 5, m.p. 68-69°,[5] and 6, m.p. 75-76°,[5] respectively, both of which show two closely spaced (0.01-0.02 Hz) methyl singlets in the nmr that coalesce on addition of a trace of acid due to the acceleration of the rate of nitrogen inversion. Both of these compounds could be hydrolytically reconverted to the diol 4. The diol was independently prepared in 60% yield by treatment of a hot aqueous solution of the bis-hydroxylamine 1 with excess manganese dioxide. Other oxidants such as aqueous bromine or sodium periodate caused further oxidation of 4 to give primarily the diazetidine dioxide 7,[5] m.p. 190-192°(d); nmr ($CDCl_3$), δ1.64 (s); λ_{max}(CH_3CN), 254 mμ (ϵ 10,500); ν_{max}($CHCl_3$) 1555 (N-O); m/e 144 (M^+), 114 (M^+-NO), and 84 (M^+-2NO); mol. wt. (osmometry) 145.



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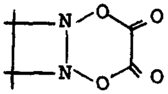

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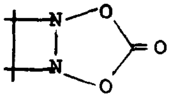

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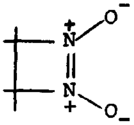

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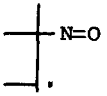

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Attempts to synthesize the aziridinyl-1-oxyl 3 by elimination of nitric oxide from the dioxide 7 have proved unsuccessful. Vapor phase pyrolysis (0.01 mm Hg) at 250° led principally to 2,3-dimethyl-2-butene and nitric oxide. No esr signal attributable to 3 could be detected from the products. Photolysis of 7 in acetonitrile with 2537-Å light proceeded efficiently ($\Phi = 0.43$) and led to the same two products together with the liquid 2,3-dimethyl-3-nitro-1-butene; m/e 129 (M^+), 114 (M^+-CH_3), 83 (M^+-NO_2); nmr (CCl_4), δ1.72 (2 CH_3), 1.80 (d of d, $J_1=J_2=0.7$ Hz, $=CCH_3$), and 5.1-5.2 (m, $C=CH_2$). The latter product was derived from a secondary thermal reaction of the other products and thus the compound was not formed when the nitric oxide was swept out of the solution with a stream of nitrogen during the photolysis. Although the photochemical reaction proceeded smoothly even at 77°K in an ethanol-ether glass, no esr signal corresponding to 3 or its open chain analog 8 could be observed at either temperature. Direct photoexcitation of 7 may, therefore, lead to concerted decomposition, possibly with initial formation of N_2O_2. An attempt to cause a step-wise decomposition through sensitization of 7 with benzene or acetophenone failed to produce any reaction.

Our failure to detect the aziridinyl-1-oxyl 3 in the above experiments together with the apparent identity of diol 4 with the species reported as 3 by the previous authors leads us to conclude that three-membered ring nitroxyl radicals still remain an unknown class of compound. The reported structure proof of this compound[3] by lithium aluminum hydride reduction to give 2,3-dimethyl-2-butylamine clearly is incorrect. The only identification offered for this product was a mass spectrum which was inconsistent with this structure [m/e predicted:[6] 101, 85, 58; found: 101, 98, 59].

References:

1. M. Lamchen and T. W. Mittag, J. Chem. Soc., Sect. C, 2300 (1966).
2. E. F. Ullman, L. Call, and J. Osiecki, J. Org. Chem., 35, 3623 (1970) and references cited therein.
3. G. R. Luckhurst and F. Sundholm, Tetrahedron Letters, 675 (1971).
4. The tetramethyldiazetidine mono-oxide expected upon loss of water from 3 also shows this fragment and displays no molecular ion; unpublished observation, L. Call and E. F. Ullman.
5. Satisfactory elemental analyses were obtained for all the new compounds.
6. H. Budzikiewics, C. Djerassi, and D. H. Williams "Mass Spectrometry of Organic Compounds," Holden-Day, Inc., San Francisco, pp. 297-304.