DICYANOFUROXAN AND HYDRAZINE OR HYDROXYLAMINE

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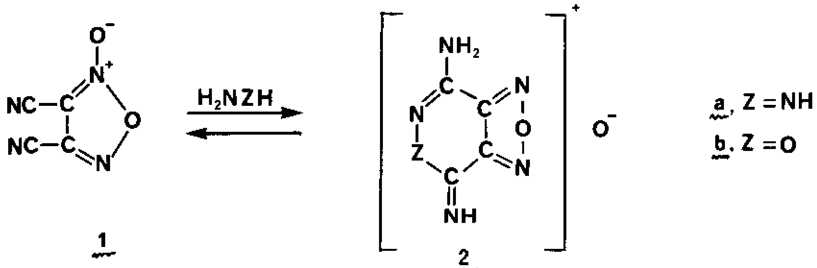
Abstract - Dicyanofuroxan combined with hydrazine to produce 1,4-diamino[4,5-c]pyridazinofuroxan (or an imine tautomer 2a) and with hydroxylamine to produce the imine 2b of 1-oxo-4-amino[4,5-c]oxazinofuroxan; mild thermolysis of the latter adduct gave 3(4)-cyano-4(3)-carbamoylfuroxan 8.

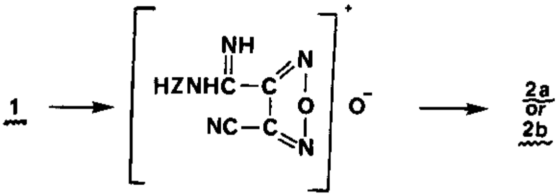
The explosive nature of a mixture[1] of dicyanofuroxan (DCF) 1 and hydrazine may have precluded further investigations on the chemical properties of the system. A reaction, not necessarily important in the explosion process, has been found to occur near 0°C and to provide an efficient preparation of 1,4-diamino[4,5-c]pyridazinofuroxan 2a.[2,3] A similar reaction with hydroxylamine gave the imine 2b of 1-oxo-4-amino[4,5-c]oxazinofuroxan, also in good yield.[3,4]



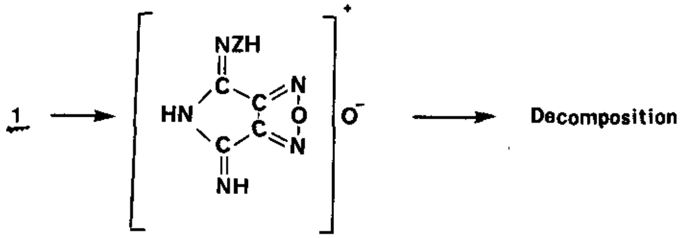
1

2

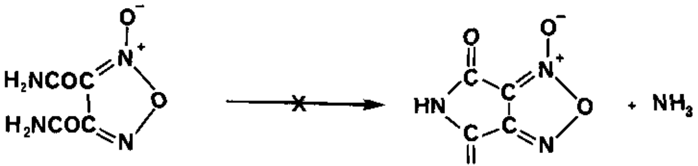
An amidrazone 3a and an amidoxime 3b were assumed but undetected initial intermediates capable of cyclizing directly into the appropriate product 2a,b. There was no evidence for an alternative cyclization into a pyrrolinofuroxan 4,[5] a molecule subject to the characteristic strain of a 5-5-bicyclic system fused through planar (sp^2) atoms.[6,7] This factor presumably accounted for the failure to obtain a bicyclic imide 6 on heating the diamide 5 of furoxandicarboxylic acid.



3a,Z=NH
3b,Z=O



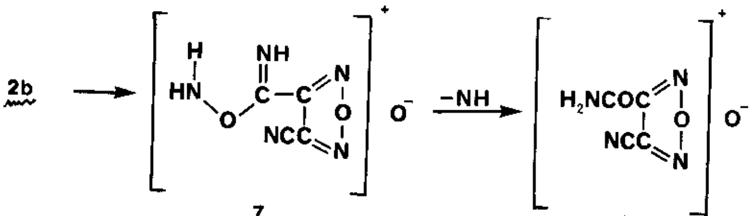
4a, Z=NH
4b, Z=O



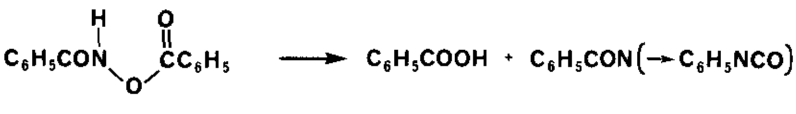
5 6

A preference shown by each reagent to react at cyano substituents rather than at dipole centers in the furoxan rings in compounds 1, 2, and 3 is consistent with the inability of other monocyclic furoxans to be reactive toward hydrazines and hydroxylamines. In contrast benzofuroxans have been reduced to dioximes of *o*-benzoquinones by substituted hydrazines[8] and by hydroxylamine,[9] and to give *o*-nitroaryl hydrazines on treatment with certain amines.[10]

Moderate heat transformed the oxazinofuroxan 2b into 4(5)-cyano-5(4)-carbamoylfuroxan 8. This rearrangement and elimination can be attributed to an initial tautomerization of 2b into an O-imidoylhydroxylamine 7 a rarely encountered type of molecule. Its ability to undergo thermal elimination of imidogen parallels the loss of benzoyl nitrene from O,N-dibenzoylhydroxylamine.[11]



7 8



$$C_6H_5CON(H)OC(O)C_6H_5 \longrightarrow C_6H_5COOH + C_6H_5CON(\rightarrow C_6H_5NCO)$$

EXPERIMENTAL

To dicyanofuroxan[12] **1** (1.0 g, 8.0 mmole) in dimethylformamide (DMF) (30 ml) at 0°C 85% hydrazine hydrate (0.8 g, 16 mmole) in DMF (5 ml) was added dropwise over 0.5 h with stirring which was then continued for 2 h. Crushed ice was added, the aqueous solution was extracted with ether (200 ml) and the organic layer was washed with cold water (3 x 100 ml). The residue after removal of the ether recrystallized from a mixture of ethyl acetate and hexane as the furoxan **2a**, a yellow solid, (67% yield), mp 118-119°C (dec); calc'd for $C_4H_4N_6O_2$:C, 28.57; H, 2.38; N, 50.00; found: C, 28.44; H, 2.43; N, 50.27; ir(KBr): 3460 (m), 3370 (m) and 1600 cm^{-1}(s); nmr($(CD_3)_1CO$): δ6.4 (broad singlet, *exchanged with* (D_2O); *m/e (70 eV)(%):* 168(100) M^+, 152(5), 151(5), 139(70), 138(15) and 108(90); ^{13}C nmr (DMSO-d_6): 96.64, 107.33, 132.35 and 151.42 ppm.[13]

The substitution of a molar equivalent of hydroxylamine for hydrazine, and methylene chloride for ether in extraction afforded the furoxan **2b** as a colorless solid (78% yield), mp 143-144°C (dec); calc'd for $C_4H_3N_5O_3$:C, 28.40; H, 1.77; N, 41.42; found: C, 28.58; H, 1.58; N, 40.30; ir(KBr): 3470 (m), 3360 (m) and 1610 cm^{-1}(s); nmr ($(CD_3)_2CO$):δ5.9 (exchangeable with D_2O); m/e (70 eV)(%): 169(5) M^+, 168(100), 153(5), 138(10), 109(90); ^{13}C nmr (DMSO-d_6): 96.60, 107.00, 142.22 and 150.53 ppm.[13]

Heating in a mixture of ethyl acetate and hexane brought about the change **2b** → **8**. The amide **8** was obtained as a colorless solid, mp 178-179°C (dec);[16] ir(KBr): 3390 (m), *3300 (w), 3220 (m), 2250 (s), 1700 (s), 1620 (s), 1600 (s),* 1485 (m), 1375 (m), 1065 (m), 1030 (m) and 840 cm^{-1} (m); nmr ((CD_3CO): δ7.85 (broad, exchangeable with D_2O; m/e (70 eV)(%): 154(100) M^+, 139(5), 124(50), 112(50), 111(90), 109(30), 95(5) and 92(5); calc'd for $C_4H_2N_4O_3$:C, 31.17; H, 1.30; N, 36.36; found: C, 31.28; H, 1.39: N, 36.54.

ACKNOWLEDGMENT. Financial support was received from the Office of Naval Research.

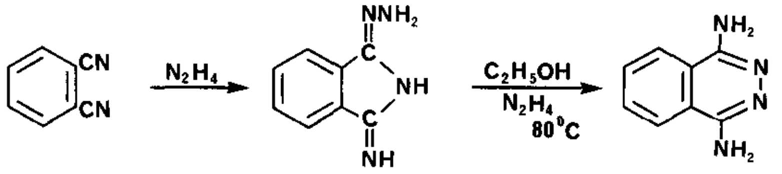
REFERENCES AND FOOTNOTES.

1. R. H. Homewood, V. J. Krukonis and R. C. Loszewski, U. S. 3,832,249 (*Chem. Abstr.*, 1975, **82**, 113795z) described DCF as an explosive comparable to trinitrotoluene. D. D. Denson and F. M. Van Meter, U. S. 3,740,947 (*Chem. Abstr.*, 1973, **79**, 94195y) described a mixture of DCF and hydrazine as a hypergolic propellant for rockets.
2. 1,4-Diaminophthalazine was obtained from phthalonitrile and hydrazine: L. Di Stefano and R. D. Castle, *J. Heterocyclic Chem.*, 1968, **5**, 111.

3. Tautomeric imine structures are available to the aminopyridazine **2a** and amino-oxazine **2b**.

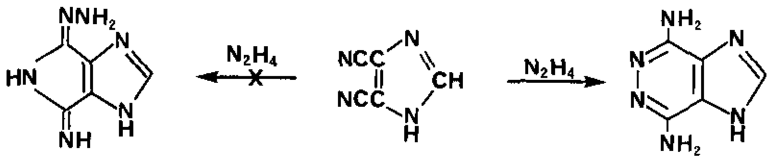
4. A comparable preparation of a 3,6-dioxoperhydro-1,2-oxazine from cyclohexen-4,5-dicarboxylic acid anhydride and N-cyclohexylhydroxylamine was reported by P. Gygax and A. Eschenmoser, *Helv. Chim. Acta*, 1977, **60**, 507.

5. J. A. Elvidge and A. P. Redman (*J. Chem. Soc. Perkin I*, 1972, 2820) reported the isolated intermediacy of 3-hydrazono-1-iminoisoindoline in the production of 1,4-diaminophthalazine from phthalonitrile and hydrazine:



6. J. F. Barnes, M. J. Barrow, M. M. Harding, R. M. Paton, P. L. Ashcroft, J. Crosby and C. J. Joyce [*J. Chem. Research* (*M*) 1979, 3601] described trimethyleneturoxan as stable at 25°C and decomposing explosively at 150°C at atmospheric pressure. Other attempts to fuse a five membered ring onto a furoxan ring were unsuccessful (J. H. Boyer and J. A. Hernandez, unpublished results, cf., R. C. Elderfield, Heterocyclic Compounds, Vol 7, J. Wiley, New York, 1961, p 471; J. Ackrell, M. Altaf-ur-Rahman, A. J. Boulton and R. C. Brown, *J. Chem. Soc. Perkin I*, 1972, 1587.

7. K. Mitsuhashi, N. Katou, N. Kembou and T. Suzuki [*Seikei Daigaku Kagakubu Kogaku Hokoku* 1976, **21**, 1519 (*Chem. Abstr.*, 1976, **84**, 180170w)] treated 4,5-imidazoledicarbonitrile with hydrazine to produce a diaminopyridazinoimidazole apparently without the intervention of a pyrrolinoimidazole.



8. M. M. El-Abadelah, Z. H. Khan and A. A. Anani, *Synthesis*, 1980, 146.

9. J. H. Boyer and W. Schoen, *J. Amer. Chem. Soc.*, 1956, **78**, 423.

10. D. W. S. Latham, O. Meth-Cohn and H. Suschitzky, *J. Chem. Soc. Perkin I*, 1976, 2216.

11. C. Walling and A. N. Naglieri, *J. Amer. Chem. Soc.*, 1960, **82**, 1820.

12. C. O. Parker, W. D. Emmons, H. A. Rolewicz and K. S. McCallum, *Tetrahedron*, 1962, **17**, 79.

13. ^{13}C-Chemical shifts (ppm) of 107.33 and 107.00 were assigned to the furoxan carbon atom closer to the exocyclic oxygen atom and 151.42 and 150.53 to the other furoxan carbon atom in compounds **2a** and **2b**.[14] Specific assignments for the position of the exocyclic oxygen atom and for the non-furoxan ^{13}C-chemical shifts in compounds **2a**,**b** cannot be made at this time.

14. ^{13}C-Chemical shift ranges (ppm) of 102 to 118 and 141 to 167 with an average difference of 42 have been assigned to furoxan carbon atoms. The more upfield value described the furoxan carbon atom closer to the exocyclic oxygen atom.[6,15]

15. (a) F. A. L. Anet and I. Yavari, *Org. Magn. Res.*, 1976, **8**, 158. (b) L. Stefaniak, M. Witanowski and G. Webb, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, 1978, **26**, 281 (*Chem. Abstr.*, 1978, **89**, 128704n). (c) T. Osawa, Y. Kito, M. Nawiki and K. Tsuji, *Tetrahedron Lett.*, 1979, 4399.

16. C. Grundmann, G. W. Nickel and R. Bansal (*Liebig's Ann. Chem.*, 1975, 1029) reported mp 182-184°C (dec.).

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