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2*H*-PYRROLE-1-OXIDES BY SELENIUM DIOXIDE DEHYDROGENATION OF PYRROLINE-1-OXIDES(1)

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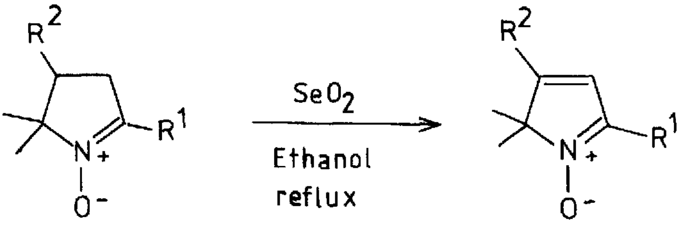
Summary: Five different 2*H*-pyrrole-1-oxides have been prepared by dehydrogenation of their corresponding pyrroline-1-oxide presursors and characterized by 1,3-dipolar cycloadditions with dimethyl ethyne dicarboxylate and/or N-phenyl maleic imide.

2*H*-Pyrrole-1-oxides(2,3), a class of interesting unsaturated five-membered cyclic imine-N-oxides, have received current attention(3). Aimed at the preparation of a line of 2*H*-pyrrole-1-oxides (2a-d), we used 1.2 molar amounts of selenium dioxide(4) in ethanol at reflux temperature(5) as a dehydrogenating agent on the pyrroline-1-oxides 1a(6) and 1b-d(7) with varied success. From 1c, in addition to a 15% yield of 2c, up to 40% of 2e are obtained by secondary oxidation of the 3-CH_3-group(8).



1a-d

2a-e

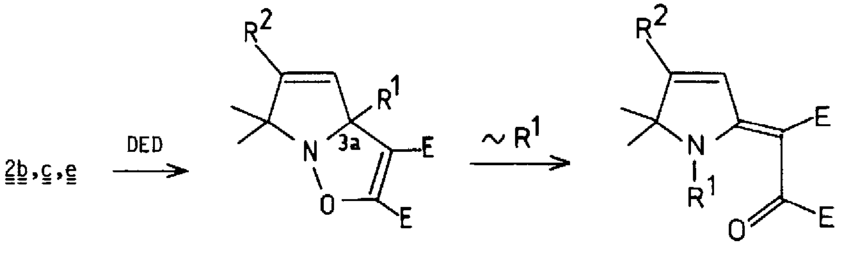
1, 2	R^1	R^2	Yield of 2(%)
a	H	H	≤ 30
b	H	C_6H_5	60
c	C_6H_5	CH_3	15
d	C_6H_5	C_6H_5	75
2e	C_6H_5	CHO	≤ 40

Spectral characterization of 2a-e: All compounds show intense M^+-, $(M-15)^+$-, $(M-16)^+$- and $(M-17)^+$ - peaks in their 70 eV mass spectra. ^{1}H-NMR(9): 2a (unstable oil): δ 1.39 (s, 6 H), ABX [$\delta_A \approx 6.35$, $\delta_B \approx 6.49$, $\delta_X \approx 7.24$ (unresolved), J_{AB} = 5.6 Hz, J_{AX} = 1.2 Hz, J_{BX} = 1 Hz].- 2b (m.p. 108-109°C): δ 1.60 (s, 6 H), 6.70 (d, J = 1 Hz, 1 H), 7.35 (m, 6 H). - 2c (m.p. 124°C): δ 1.41 (s, 6 H), 2.03 (d, J = 1.4 Hz, 3 H), 6.58 (m, 1 H), 7.45 (m, 3 H), 8.42

(m, 2 H). - 2d (m.p. 76°C[10]): δ 1.69 (s, 6 H), 7.20 (s, 1 H), 7.43 (m, 8 H), 8.44 (m, 2 H). - 2e (m.p. 105°C): δ 1.60 (s, 6 H), 7.50 (m, 3 H), 7.80 (s, 1 H), 8.31 (m, 2 H), 9.70 (s, 1 H).

For further characterization, exploratory 1,3-dipolar cycloadditions[11] with dimethyl ethyne dicarboxylate (DED) and N-phenylmaleic imide (NPM) have been carried out.

All 2H-pyrrole-1-oxides 2a-e seem to by highly reactive towards DED. However, only the secondary ring-opened product 4a [m.p. 185°C (dec.), IR (KBr): 3245 cm^{-1} (NH), 1735 and 1683 cm^{-1} (C=O)] was obtained from 2b via 3a. This reflects the high migratory aptitude of the 3a-hydrogen in the primary cycloadduct 3a[11a]. Similarly, products 4b (oil) and 4c (m.p. 204°C), resulting from 3b,c by phenyl migration, were obtained in addition to the primary adducts 3b (oil) and 3c (m.p. 73°C)[8].



3a-c

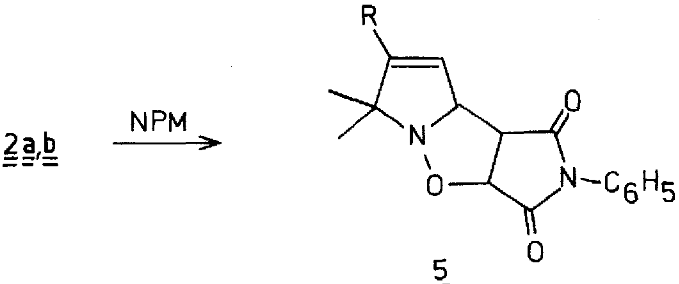
4a-c

3,4	R^1	R^2
a	H	C_6H_5
b	C_6H_5	CHO
c	C_6H_5	C_6H_5

E = $COOCH_3$

^{1}H-NMR[9]: 4a: δ 1.62 (s, 6 H), 3.75 (s, 3 H), 3.85 (s, 3 H), 7.50 (m, 6 H), 11.44 (broad, 1 H). - 3b: Four s (3 H each) at δ 1.30, 1.57, 3.65 and 3.92, δ 7.40 (m, 6 H), 9.95 (s, 1 H).- 4b: δ 1.50 (s. 6 H), 3.21 (s, 3 H), 3.74 (s, 3 H), 8.29 (s, 1 H), 10.02 (s, 1 H). - 3c: Four s (3 H each) at δ 1.24, 1.50, 3.60, 3.90, δ 6.40 (s, 1 H), 7.40 (m, 8 H), 7.58 (m, 2 H). - 4c: δ 1.53 (s, 6 H), 3.20 (s, 3 H), 3.74 (s, 3 H), 7.2 - 7.6 (m, 10 H), 7.70 (s, 1 H).

Among the 2H-pyrrole-1-oxides prepared in this study, only the two aldonitrones 2a,b were found to react with NPM to give a quantitative yield of adducts 5a,b (one single stereoisomer in each case)[8].



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5	R	m.p. (°C)
a	H	147
b	C_6H_5	160

^{1}H-NMR[9]: **5a**: δ 1.10 (s, 3 H), 1.43 (s, 3 H), 3.70 (dd, J_1 = 8 Hz, $J_2 \approx$ 1 Hz, 1 H), 4.70 (m, 1 H), 4.88 (d, J = 8 Hz, 1 H), AB portion of an ABX (approximately) with δ_A = 5.81, δ_B 5.59 (broadened), $J_A \approx$ 5.5 Hz, $J_{AX} \approx$ 2.4 Hz (J_{BX} not determined but very small), 7.40 (m, 5 H). - **5b**: δ 1.33 (s, 3 H), 1.50 (s, 3 H), 3.78 (dd, J_1 = 7.5 Hz, $J_2 \approx$ 1.2 Hz, 1 H), 4.78 (unresolved m, 1 H), 4.91 (d, J = 7.5 Hz), 5.70 (d, J $\approx$ 1.2 Hz, 1 H), 7.36 (m, 10 H).

More results of 1,3-dipolar cycloadditions of 2*H*-pyrrole-1-oxides to various dipolarophiles and various other aspects of the chemistry of 2*H*-pyrrole-1-oxides will be reported in a forthcoming paper.

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References and Notes

[1] Taken in part from the planned doctorate thesis of Herbert Bender, University of Duisburg.

[2] Earlier examples: A. H. Blatt, J. Amer. Chem. Soc. **56**, 2774 (1934); R. A. Abramovitch and B. W. Cue, Heterocycles **2**, 287 (1974).

[3] a) D. St. C. Black, N. A. Blackman and R. F. C. Brown, Tetrahedron Lett. **1975**, 3423; Aust. J. Chem. **32**, 1785-1794 (1979). b) D. St. C. Black and N. A. Blackman, Aust. J. Chem. **32**, 1795-1803 (1979). c) D. St. Black, N. A. Blackman and L. M. Johnstone, ibidem 2025.

[4] N. Rabjohn, Org. React. **24**, 261 (1976).

[5] The choice of solvent and conditions seems to be crucial for the reaction to be proceed to the desired products. More details will be reported elsewhere.

[6] R. Bonnett, R. F. C. Brown, V. M. Clark, I. O. Sutherland and Sir A. Todd, J. Chem. Soc. **1959**, 2094.

[7] J. B. Bapat and D. St. C. Black, Aust. J. Chem. **21**, 2483 (1968).

[8] All stable compounds reported in this letter gave satisfactory elemental analyses and show spectral characteristics in accord with the proposed structures.

[9] 90-MHz-^{1}H-NMR-spectra were recorded using $CDCl_3$ as a solvent and tetramethylsilane as an internal standard.

[10] Compound **2d** has been reported by D. St. C. Black et. al. [3b] to be a pale yellow viscous oil. Our compound of m.p. 76°C shows a ^{1}H-NMR-spectrum identical to that reported for the oily compound[3b].

[11] a) For review on 1,3-dipolar cycloadditions of nitrones and the stability of the resulting cycloadducts see D. St. C. Black, R. F. Crozier and V. C. Davies, Synthesis **1975**, 205 and refs. cited therein. b) R. Huisgen, J. Org. Chemistry **41**, 403 (1976) and references cited therein.

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