

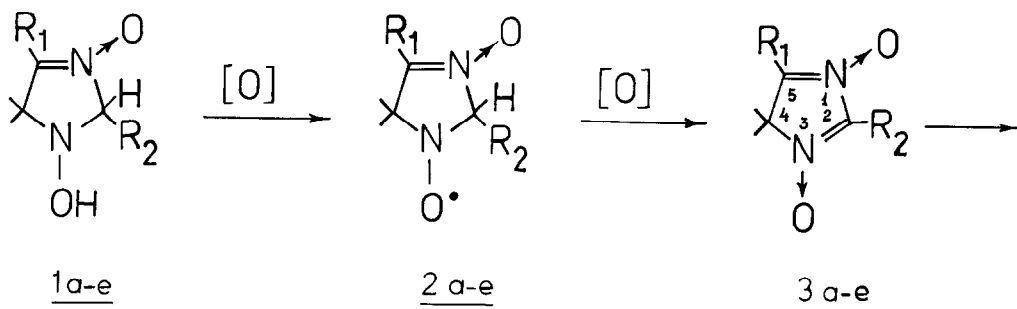
ROUTE TO STABLE NITROXIDES WITH ALKOXY GROUPS  
 AT  $\alpha$ - CARBON - THE DERIVATIVES OF 2- AND 3-IMIDAZOLINES

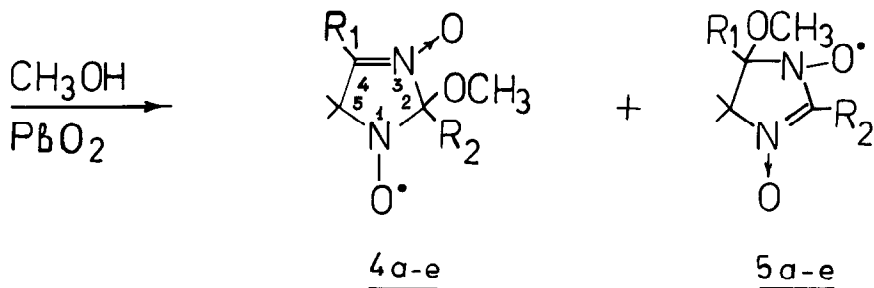
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**Summary:** Oxidation of 1-hydroxy-5,5-dimethyl-3-imidazoline-3-oxides containing one or two hydrogen atoms in position 2 of the heterocycle with lead dioxide in alcohol leads to stable nitroxides with alkoxy groups at  $\alpha$ -carbon, the derivatives of 2- and 3-imidazolines, via the intermediate formation of 4H-imidazol-1,3-dioxides.

The majority of stable nitroxides bear alkyl groups at carbons attached to the nitroxyl nitrogen, i.e., at the  $\alpha$ -carbon atoms<sup>1,2</sup>. The nitroxides where groups other than alkyls are present at the  $\alpha$ -carbon atoms may display new spectral and physico-chemical properties.

Oxidation of 1-hydroxy-5,5-dimethyl-3-imidazoline-3-oxides (1a-e)<sup>3,4</sup> with an excess of lead dioxide in methanol during 20 hours gave stable nitroxides 4a-e and nitronyl nitroxides 5a-e<sup>5</sup>.





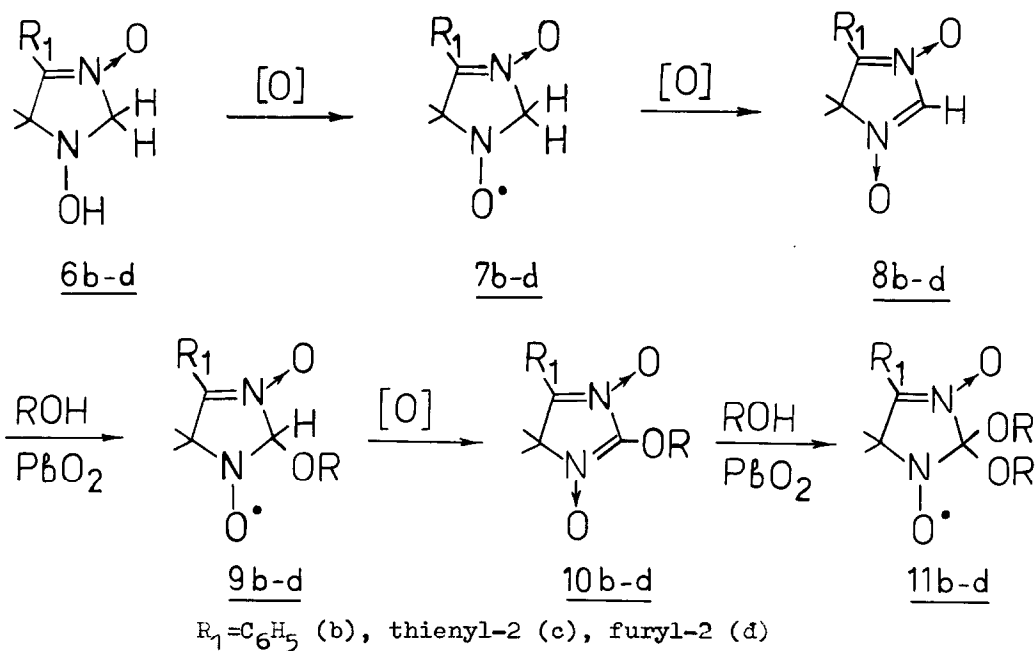
	1			4			5		
index	R <sub>1</sub>	R <sub>2</sub>	Yield,%	M.p.,°C	a <sub>N</sub> ,G triplet	Yield,%	M.p.,°C	a <sub>N</sub> ,G quintet	
a	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	25	135-136	13.50	15	oil	*	
b	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	32	123-125	13.20	65	160-161	7.61	
c	thienyl-2	C <sub>6</sub> H <sub>5</sub>	70	180-182	13.22	6	117-118	7.60	
d	furyl-2	C <sub>6</sub> H <sub>5</sub>	52	117-118	13.27	23	94-96	7.60	
e	C <sub>6</sub> H <sub>5</sub>	furyl-2	13	145-146	13.02	62	144-146	**	

\* a<sub>N-1</sub> = 7.52, a<sub>N-3</sub> = 7.68, a<sub>H</sub> = 1.80 quart (2-CH<sub>3</sub>) and 0.60 quart (4-OCH<sub>3</sub>)

\*\* a<sub>N-1</sub> = 7.51, a<sub>N-3</sub> = 7.83, a<sub>H</sub> = 0.63 quart (4-CH<sub>3</sub>)

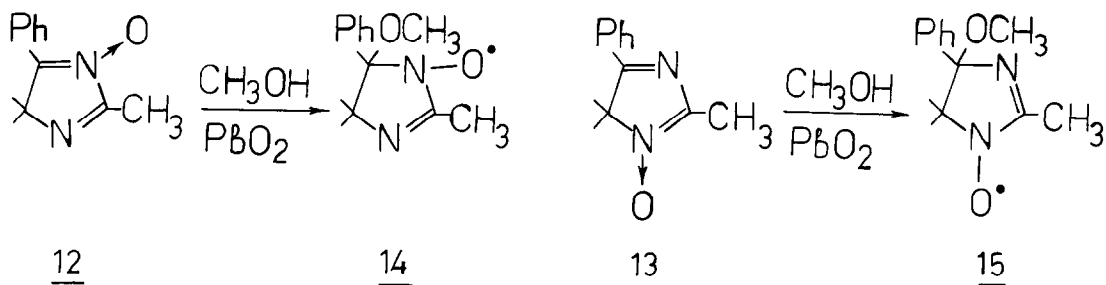
The ESR spectra of the initially formed radicals 2a-e showed the hyperfine interaction (hfi) constants a<sub>N</sub> = 15.0-15.5G and a<sub>H</sub> = 19-20G. The formation of 4H-imidazol-1,3-dioxides 3a-e was detected by TLC and in some cases these compounds (3a-b) were isolated from the reaction mixture and had characteristics similar to those reported in <sup>6</sup>. Treatment of 3a,b with PbO<sub>2</sub> in methanol yielded radicals 4a,b and 5a,b.

Oxidation of 6b-d<sup>7</sup> with an excess of PbO<sub>2</sub> in methanol during 3 hours gave stable nitroxides 11b-e (R=CH<sub>3</sub>): 11b 35% (m.p. 113-114°C, a<sub>N</sub>=12.50G)<sup>8</sup>; 11c 62% (m.p. 181-182°C, a<sub>N</sub>=12.52G); 11d 60% (m.p. 159°C, decompn., a<sub>N</sub> = 12.45G). Upon treatment of 6b with PbO<sub>2</sub> in ethanol and isopropanol the reaction proceeds much more slowly (20 and 80 hours respectively); 11b (R=C<sub>2</sub>H<sub>5</sub>) 50% (m.p. 77-79°C, a<sub>N</sub> = 12.69G), 11b (R=iso-C<sub>3</sub>H<sub>7</sub>) 10% (m.p. 87-90°C, a<sub>N</sub> = 12.91G). In these cases nitronyl nitroxides were less stable and were only detected in the reaction mixture by ESR (quintet a<sub>N</sub>=5.7 G).



The intermediate formation of radicals 7 and 9 in these reactions was confirmed by ESR: 7b  $a_{\text{N}}=15.50$ ,  $a_{\text{H}}=20.15\text{G}$ ; 9b ( $\text{R}=\text{C}_2\text{H}_5$ )  $a_{\text{N}}=13.33$ ,  $a_{\text{H}}=14.0\text{G}$ . Compound 8b was isolated in pure form<sup>9</sup>. Transformations of 4H-imidazol-1,3-dioxides to radicals may proceed by the two most possible mechanisms: a) oxidation of 3, 8 or 10 to radical cation with subsequent quick reaction with alcohol<sup>10</sup>; b) the interaction of 3, 8 or 10 as a spin trap with the alkoxy radical formed in oxidation of alcohol with  $\text{Pb(IV)}$ <sup>11</sup>.

This reaction applies in general to compounds containing the nitrono group in the conjugated system with nitrogen atoms in positions 1,3. This may be illustrated by the formation of the imino nitroxides 14 and 15<sup>12</sup> upon treatment of 4H-imidazol-1- and -3-oxides 12 and 13<sup>6</sup> with  $\text{PbO}_2$  in methanol.



All the compounds obtained have corrected elemental analysis data. Most of the radicals are stable upon long storage at room temperature.

## REFERENCES AND NOTES

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2. H.C.Aurich, in: The Chemistry of Amino, Nitroso and Nitro Compounds and Their Derivatives. Supplement F, Part 1/Ed.S.Patai, Chichester-New York-Brisbane-Toronto-Singapore: Intersci, 1982, p.565.
3. 1a,b are reported in <sup>4</sup>; 1c-e were obtained as in <sup>4</sup>, by interaction of the respective  $\alpha$ -hydroxylaminooximes<sup>13</sup> with benzaldehyde (1c,d) and furfural (1e): 1c - m.p.188-189°C, 1d - m.p.180-182°C, 1e - m.p.192°C (decompn.).
4. L.B.Volodarsky, V.S.Kobrin, Yu.G.Putsykin, Khim.Get.Soedin., 1972, 1241.
5. The ESR spectra were recorded in water, the hfi constants were obtained by simulation of spectra, accuracy  $\pm 0.05\text{G}$ , g-factors of 4 and 5 are equal to  $2.0060 \pm 0.0002$ . The IR spectra of all the radicals show a  $\nu \text{OCH}_3$  band at  $2840\text{--}2850 \text{ cm}^{-1}$ . The UV spectra of 3-imidazoline-3-oxide nitroxides contain an absorption band of  $\alpha$ -arylnitron group at  $290\text{--}320 \text{ nm}$  ( $\lg \epsilon \gg 4.2$ ). The UV spectra of 5 are typical of nitronyl nitroxides<sup>14</sup>; e.g.: 58  $\lambda \text{ nm}$  ( $\lg \epsilon$ ): 238 (3.94), 268 (4.15), 350 (3.94), 366 (4.08), 628 (2.95).
6. I.K.Korobeinicheva, M.M.Mitasov, V.S.Kobrin, L.B.Volodarsky, Izv.Sib.Otd. Akad.Nauk SSSR, Ser.Khim.Nauk, No.2, v.1, 96 (1976).
7. 6b was reported in <sup>6</sup>, 6c (m.p.188-189°C) and 6d (m.p.120-122°C) were obtained by interaction of  $\alpha$ -hydroxylaminooximes<sup>13</sup> with formaldehyde<sup>6</sup>.
8. PMR (DMSO-d<sub>6</sub>,  $\delta$  ppm) of 11bH (R=CH<sub>3</sub>) obtained by the reduction of 11b (R=CH<sub>3</sub>) by zink in alcohol in the presence of NH<sub>4</sub>Cl: 1.46 (6H, 2CH<sub>3</sub>), 3.48 (6H, 2OCH<sub>3</sub>), 7.45m(2H, meta), 7.47m(1H, para), 8.20m(2H, ortho), 8.30(1H, OH).
9. 8b: m.p.155°C decompn., UV  $\lambda \text{ nm}$  ( $\lg \epsilon$ ): 249(4.00), 277(3.72), 356(4.03). PMR (acetone-d<sub>6</sub>,  $\delta$  ppm): 1.83(6H, 2CH<sub>3</sub>), 7.4-7.7m(3H, meta and para), 8.5-8.7m (2H, ortho), 8.24(1H, 2-H).
10. I.A.Grigor'ev, G.I.Shchukin, V.V.Khramtsov, L.M.Weiner, V.F.Starichenko, L.B.Volodarsky, Izv.Akad.Nauk SSSR, Ser.Khim., 1985 (in press).
11. P.Brun, B.Waegell, in: Reactive Intermediates./Ed. R.A.Abramovitch, N.Y.-L., Plenum-Press, 1983, v.3, p.367.
12. 14 (70%, oil) and 15 (60%, m.p.40-42°C) have complex ESR spectra because of splitting on two magnetically non-equivalent nitrogen atoms ( $a_{\text{N-1}} > 2a_{\text{N-3}}$ ) and protons of 2-CH<sub>3</sub>. In the PMR spectra of concentrated CCl<sub>4</sub> solutions of these radicals, the main difference is in the shift of broad signals of gem-CH<sub>3</sub> groups: downfield (19 and 21 ppm) for 14 and upfield (-11 and -16ppm) for 15.
13. L.B.Volodarsky, I.A.Grigor'ev, L.N.Grigor'eva, I.A.Kirilyuk, S.A.Amitina, Zh.Org.Khim., 21, 443 (1985).
14. E.F.Ullman, J.H.Osiecky, D.G.B.Boocock, R.Darcy, J.Am.Chem.Soc., 94, 7049 (1972).