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OXIDATION OF NITROXIDES by m-CHLOROPERBENZOIC ACID

by

James A. Cella*, James A. Kelley and Edward F. Kenehan

Division of Biochemistry
Walter Reed Army Institute of Research
Washington, D.C. 20012

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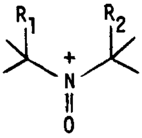
Nitroxides react with a variety of oxidizing agents including the halogens[1], silver oxide[2], $SbCl_4$[3], nitrogen dioxide[4] and mineral acids[5] to produce brightly colored oxoammonium ions, 1, which can be isolated as stable salts or further transformed under the reaction conditions.



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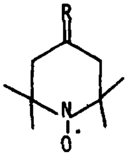
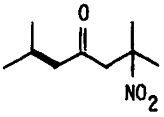
This report describes the oxidation of nitroxides by m-chloroperbenzoic acid (MCPA) and discusses the chemistry of the oxoammonium ions produced by this process.

Nitroxides of the piperidine series, 2, or their amine precursors, when added to MCPA in methylene chloride produce brightly colored solutions whose properties suggest the presence of oxoammonium ions. For example, oxoammonium ions oxidize alcohols to their respective carbonyl compounds[6]. While neither nitroxides nor peracids alone react appreciably with alcohols, a mixture of the two oxidizes alcohols readily[7,8]. Additional evidence for the generation of oxoammonium ions in the peracid-nitroxide system is derived from the chemistry of keto-nitroxide, 2a. Treatment of 2a with excess MCPA in methylene chloride produces the nitro compound, 3. [3: mp 41-42^{o}; ir 5.92(νC=O) and 7.40μ(νNO_2); nmr ($CDCl_3$) δ6.00(m,1,vinyl C-H)$_a$, 3 10(s,2,$COCH_2$)$_b$, 2.09(d,3,vinyl-CH_3,$J_{a,c}$= 1.2 Hz)$_c$, 1.85(d,3,vinyl-CH_3,$J_{a,d}$=1.2 Hz)$_d$ and 1.65 ppm(s,6,gem diMe), mass spectrum m/e 185(M^+,0.4%), 138(M-HNO_2,1.4%), 123(1.5%), 110(2.8%), 83(100%), 82(19%), 55(29%), 39(14.5%); Anal., Calcd. for $C_9H_{15}NO_3$: C,58.4%; H, 8.2%; N, 7.6%; Found: C, 58.1%; H, 7.9%; N, 7.6%].

Cleavage of the piperidine ring in this reaction parallels the production of nitroso compound 4, from the reaction of 2a with silver oxide[2]. Presumably, this cleavage proceeds *via* the intermediacy of ion 5. In the peracid system,



2a, R=O
2b, R=H_2



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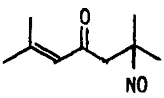

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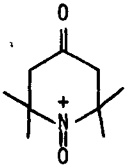

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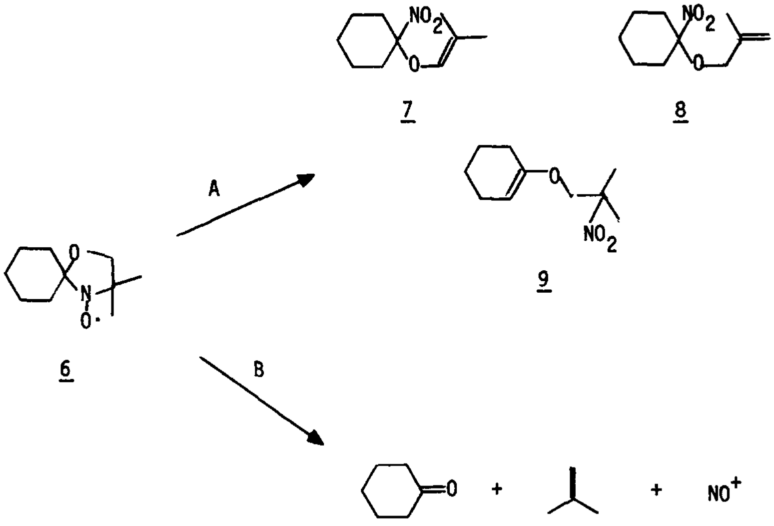
the nitroso compound is rapidly oxidized to 3. The unsubstituted nitroxide, 2b, is recovered unchanged after brief treatment with MCPA although alcohols added to these brightly colored solutions are oxidized[8].

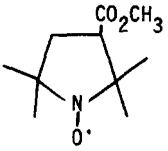
Cleavage of the oxoammonium ion therefore requires a substituent to activate the β-hydrogens and/or stabilize the double bond produced by this cleavage. In this regard it was interesting to see whether an oxoammonium ion derived from a doxyl[9] nitroxide such as 6 would undergo an analogous cleavage. In this case, two modes of cleavage are possible; loss of a proton from a β-carbon to produce unsaturated nitro compounds 7,8 or 9 (Path A), or ring cleavage with extrusion of NO^+, isobutylene and cyclohexanone (Path B). Doxyl 6 reacts with nitrogen dioxide *via* path B to afford cyclohexanone as the only detectable product[4]. On treatment of 6 with chlorine, a small amount of a chlorinated nitroso compound was produced (presumably *via* a path analogous to path A), however this process is complicated by concomitant chlorination[4].

Treatment of 6 with excess MCPA in methylene chloride at room temperature produces, after quenching with aqueous sodium carbonate, cyclohexanone and isobutylene oxide as the only detectable products. The oxoammonium ion derived from 6 therefore undergoes cleavage *via* Path B as in the reaction of 6 with



nitrogen dioxide[4]. In this case the isobutylene produced is trapped as the epoxide. This facile cleavage of doxyls may be responsible for the low yields often obtained in the preparation of these radicals by the peracid oxidation of oxazolidines.

In contrast to the rapid reaction of the piperidine and doxyl radicals with MCPA, pyrrolidine radicals 10 and 11 and pyrroline radical 12 are recovered unchanged after treatment with excess peracid in methylene chloride at room temperature. Moreover, these radicals do not catalyze the oxidation of alcohols by MCPA[8]. Solutions of 10, 11, and 12 with MCPA are not intensly colored as are the corresponding piperidine and doxyl nitroxide solutions. These data suggest that oxoammonium ions derived from 10, 11 and 12 are not generated by the action of MCPA on these radicals.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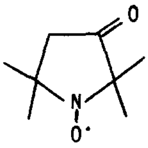
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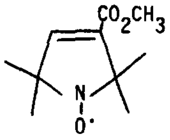
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