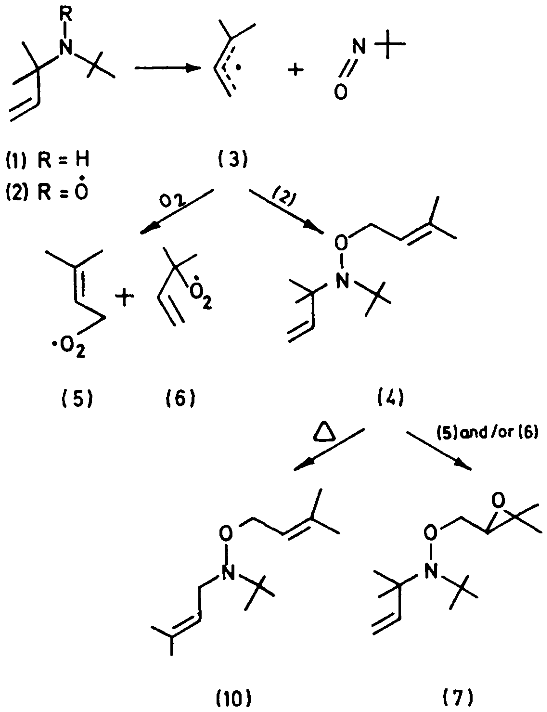
Decomposition of an Allyl-substituted Nitroxide Radical

By R. L. Craig and J. S. Roberts*
(*Department of Chemistry, University of Stirling, Stirling*)

Summary Decomposition of *N*-(1,1-dimethylallyl)-*N*-t-butylaminoxyl (**2**) gives Bu^{t}NO, *N*-(1,1-dimethylallyl)-*O*-(3,3-dimethylallyl)-*N*-t-butylhydroxylamine (**4**), and the corresponding epoxide (**7**), the latter being obtained only under aerobic conditions; the hydroxylamine (**4**) is thermally labile and rearranges to *NO*-di-(3,3-dimethylallyl)-*N*-t-butylhydroxylamine (**10**) at 140°.

In general dialkyl nitroxide radicals are stable compounds if the carbon atoms adjoining the nitroxide are fully substituted.[1] However, we now report such a compound which is relatively unstable.[2] Oxidation of (**1**)[3] with either *m*-chloroperbenzoic acid or hydrogen peroxide–sodium tungstate yielded the expected nitroxide (**2**), a_N (CCl$_4$) 15·4 Oe, *g* 2·0070, as a dark red oil.† Decomposition of this compound, either in solution or as a neat liquid, occurred readily at 25° with a first-order rate constant of $4{\cdot}18 \times 10^{-5}$ s^{-1}, $t_{\frac{1}{2}}$ 276 min (measured in CCl$_4$ solution). T.l.c. examination of the resultant greenish-blue solution showed two major products in addition to a small amount of (**2**). Bu^{t}NO was shown to be responsible for the coloration of the decomposition mixture by its ready removal by sublimation on to a cold-finger condenser and identification by n.m.r. and m.p. (dimer). Separation of the two less volatile compounds was achieved by preparative t.l.c. and these were characterised by n.m.r. and m.s. as the trialkylhydroxylamine (**4**), and the epoxide (**7**). Under completely anaerobic conditions the decomposition of (**2**) only yielded Bu^{t}NO and (**4**).



Scheme 1.

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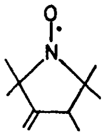
† Purification of (**2**) could only be effected by column chromatography at −40°.

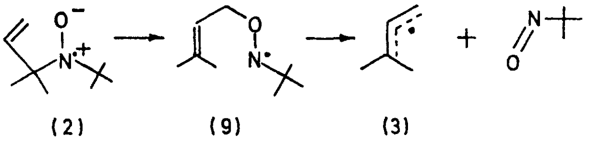
From a mechanistic standpoint, this decomposition can be rationalised in terms of homolytic fission of the allylic C–N bond, thus generating the dimethylallyl radical (**3**) and Bu^{t}NO and subsequent combination of (**2**) and (**3**) in the more sterically favoured sense.[4] Under aerobic conditions (**3**) could combine with molecular oxygen to form the peroxy-radicals (**5**) and/or (**6**) which, by analogy with previous work,[5] could effect epoxidation of the more substituted double bond of (**4**) as shown in Scheme 1.

This result is in contrast to the thermal stability of the similarly substituted cyclic nitroxide (**8**) which is stable in toluene under reflux over a period of 17 h.[6] In addition to the entropy factor a plausible interpretation of this difference of reactivity is the favourable alignment (*i.e.* coplanarity) of the π orbital with respect to the allylic C–N bond which is possible in the case of (2) as a consequence of free rotation but quite impossible in the case of (8) in which the π system is orthogonal to the C–N bond. An alternative explanation is a [2,3] sigmatropic shift[7] in the case of (**2**) and subsequent homolytic fragmentation of the resultant hydroxylamino-radical (**9**)[8] as shown in Scheme 2.



(8)

During the initial course of this work we attempted to purify (**2**) by distillation which, as is shown by the above report, resulted in its rapid decomposition. T.l.c. and n.m.r. examination of the products revealed the presence of another hydroxylamine (**10**) in addition to those products already mentioned. This compound, however, is not a primary decomposition product of (**2**) but is derived from (**4**). Thus, heating a neat sample of (**4**) at 140° effected complete isomerisation to (**10**) $t_{\frac{1}{2}}$ 6 min. Although inversion of a substituted allyl group is well known[9] we are not aware of this occurring with hydroxylamines. One possible mechanism for this rearrangement is homolytic fission of the allylic C–N bond followed by recombination. To test this possibility we have attempted to observe a CIDNP effect during isomerisation at 140°, but without success. This negative result, however, does not necessarily invalidate the homolysis mechanism and we are studying this rearrangement.



Scheme 2.

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