Decomposition of a Prop-2-ynyl-substituted Nitroxide Radical: *X*-Ray Crystal Structure of the Product

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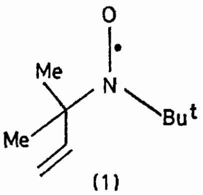
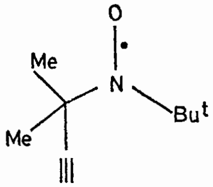
Summary Thermal decomposition of *N*-(1,1-dimethylprop-2-ynyl)-*N*-t-butylaminoxyl (**2**) gives 9-isopropylidene-3,3-dimethyl-5,8-di-t-butyl-5,8-diaza-4,7-dioxabicyclo[4,2,1]-nonan-2-one (**3**) as the major product whose molecular structure was determined by *X*-ray crystallography.

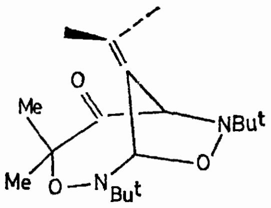
In view of the ready decomposition of the nitroxide radical (**1**) into dimethylallyl radicals[1] and the general interest in prop-2-ynyl/allenyl radicals,[2] we have examined the thermal behaviour of the nitroxide (**2**).[3,4] Heating a dry benzene solution of (**2**) at 80° for *ca.* 5 min either in the presence or absence of oxygen results in the formation of a mixture of products from which the major component (*ca.* 40%) can be isolated by preparative t.l.c. This compound, m.p. 62°, analyses for $C_{18}H_{32}N_2O_3$ by high resolution m.s. and is devoid of hydroxy, acetylenic, and allenic groups as deduced from its i.r. spectrum, which, however, exhibits a strong carbonyl band at 1713 cm^{-1}. The n.m.r. spectrum ($CDCl_3$) is deceptively simple with singlet peaks at τ 4·31 (1H), 5·82(1H), 8·22(3H), 8·31(3H), 8·62(3H), 8·66(3H), 8·80(9H), and 8·96(9H). These data together with the incorporation of a third oxygen atom signalled a totally unexpected decomposition product. Since chemical means of structural elucidation proved unrewarding, single crystals were submitted to *X*-ray analysis.



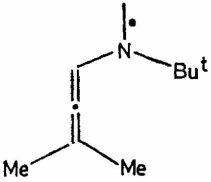
(1)



(2)

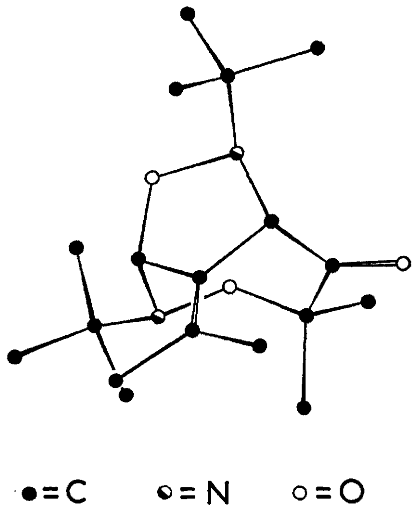


(3)



(4)

Crystal data: colourless orthorhombic crystals, space group $Pna2_1$ (No. 33); $a = 1813(2)$, $b = 1156(2)$, $c = 945(2)$ pm; $U = 1980 \times 10^6$ pm^3; D_m (flotation) = 1·09 g cm^{-3}, $Z = 4$, D_c = 1·09 g cm^{-3}.



FIGURE

Data were collected on a Hilger-Watts linear diffractometer. The structure was solved by direct methods and all the non-hydrogen atoms were identified. Refinement by full-matrix least-squares with anisotropic temperature factors but not hydrogen atoms gave an *R* factor of 0·089. The molecule is shown in the Figure, and the bond distances and angles agree well with the formulation (**3**).

A number of mechanisms can be envisaged for this rearrangement all of which appear to require the initial generation of dimethylprop-2-ynyl/allenyl radicals and t-nitrosobutane (as evidenced by a blue coloration during the thermolysis). The gross structure of (**3**) can then be accommodated by a subsequent recombination to the allenyl nitroxide (**4**) or a derivative thereof,† and work is in progress to unravel the steps in this rearrangement.

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† Delocalisation of the unpaired electron in (**4**) would result in spin density at the central carbon atom of the allenyl group thus providing a possible means of incorporation of the ketonic oxygen atom (from t-nitrosobutane or another nitroxide radical?).

[1] R. L. Craig and J. S. Roberts, *J.C.S. Chem. Comm.*, 1972, 1142.

[2] J. K. Kochi and P. J. Krusic, *J. Amer. Chem. Soc.*, 1970, **92**, 4110; R. M. Fantazier and M. L. Poutsma, *ibid.*, 1968, **90**, 5490; P. S. Engel and D. J. Bishop, *ibid.*, 1972, **94**, 2148.

[3] E. G. Rozantsev and R. S. Burmistrova, *Doklady Akad. Nauk S.S.S.R.*, 1966, **166**, 129.

[4] As a result of preliminary competitive studies, it is known that compound (**2**) is more stable than (**1**), R. L. Craig and J. S. Roberts, unpublished results.