An E.S.R. Study of the Ring Opening of 2-Methylaziridine-boryl Radicals

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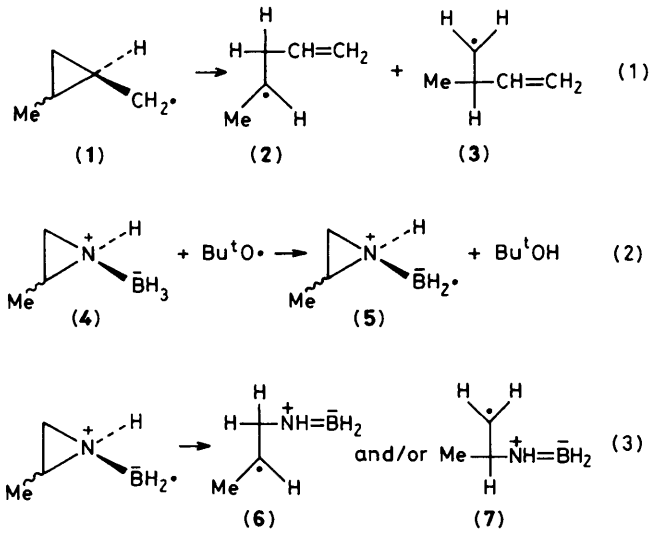
The *cis*-isomer of the 2-methylaziridine-boryl radical undergoes ring opening with C–N cleavage to give mainly the secondary alkyl radical, while the *trans*-isomer gives mainly the less stable primary alkyl radical.

The ring-opening rearrangement of cyclopropylalkyl radicals has been investigated extensively.[1] An intriguing example of this rearrangement is provided by the (2-methylcyclopropyl)methyl radical (**1**) which exhibits very different behaviour depending on whether the ring substituents are *cis* or *trans*. Thus, the *cis*-isomer yields mainly the secondary alkenyl radical (**2**), whilst the *trans*-isomer gives predominantly the less stable primary radical (**3**).[2,3]

We have reported recently[4] that the aziridine-boryl radical, which is isoelectronic with the cyclopropylmethyl radical, undergoes an analogous type of rearrangement and it was thus important to discover whether ring-opening of the



2-methylaziridine-boryl radical (**5**) exhibits the same interesting regiochemistry as its isoelectronic carbocyclic analogue (**1**).

2-Methylaziridine-borane (**4**) was prepared by the reaction of 2-methylaziridine with diborane in tetrahydrofuran at 0 °C. Evaporation of the solvent left a colourless oil which was shown by ^{11}B, ^{13}C, and ^{1}H n.m.r. spectroscopy to consist of a mixture of the *cis*- and *trans*-isomers. The ^{11}B n.m.r. spectrum in C_6D_6 showed two binomial quartets at δ −15.5 ($^{1}J_{B-H}$ 97 Hz) and −19.9 p.p.m. ($^{1}J_{B-H}$ 96 Hz) upfield from $Et_2O{\cdot}BF_3$, and integration of the proton-decoupled spectra gave the relative intensities as 1.4:1, respectively. When a benzene solution of this mixture (with or without an added molar equivalent of 2-methylaziridine) was heated for 3 h at 100 °C, the intensity of the lower-field resonance increased at the expense of the other peak such that the final relative integrals were 4.5:1 (measured at 20 °C). We attribute these changes to conversion of *cis*-(**4**) into the more stable *trans*-(**4**), since it is very likely that the relative stabilities of the *cis*- and *trans*-isomers of (**4**) are similar to those of the isoelectronic 1,2-dimethylcyclopropane.[5]† The geometrical isomers of (**4**) could be separated completely by h.p.l.c. on silica gel, although subsequent distillation of the *trans*-isomer (b.p. 64—65 °C at 0.05 Torr) was accompanied by *ca.* 6% conversion into the *cis*-isomer.

The corresponding amine-boryl radicals *cis*-(**5**) and *trans*-(**5**) were generated by u.v. photolysis of solutions containing *cis*-(**4**) or *trans*-(**4**), respectively, (*ca.* 1.7 M) and di-t-butyl peroxide (*ca.* 15% v/v) in cyclopropane–oxirane (2:1 v/v) or cyclopropane–t-pentyl alcohol (3:1 v/v), while the samples were in the cavity of an e.s.r. spectrometer. Although no e.s.r. spectra attributable to (**5**) were detected, even at the lowest accessible temperature, strong spectra of the carbon-centred radicals (**6**) and (**7**) formed by ring opening were observed during continuous u.v. photolysis between 151 and 235 K. The spectra obtained at 152 K from *cis*-(**4**) and *trans*-(**4**) are shown in Figure 1 along with computer simulations of the spectra of (**6**) and (**7**), and the e.s.r. parameters are given in Table 1. It is immediately apparent that *cis*-(**5**) gives mainly the *secondary* radical (**6**), whilst *trans*-(**5**) gives mainly the *primary* radical (**7**) which is presumably the less stable isomer. The values of [(**6**)]:[(**7**)], obtained by double integration of appropriate lines, were 96:4 and 34:66 at 151 K when the radicals were derived from *cis*-(**4**) and *trans*-(**4**), respectively; values at other temperatures are given in Table 1. The relative concentrations of (**6**) and (**7**) did not depend on the extent of sample photolysis, indicating that *cis*-(**4**) and *trans*-(**4**) do not interconvert under the experimental conditions.

Table 1. E.s.r. parameters and relative concentrations of the radicals (**6**) and (**7**) obtained from ring opening of *cis*-(**5**) and *trans*-(**5**) in cyclopropane–oxirane (2:1 v/v).

Source of radicals	T/K	[(6)]:[(7)][a]	Hyperfine splittings (in G)[b] for the major product radical.[c] $a(H_\alpha)$[d]	$a(H_\beta)$[d]	a(1N)
cis-(**4**)	151	96:4	21.6 (1)	28.0 (2) 24.9 (3)	3.2
	196	*ca.* 97:3	21.6 (1)	26.1 (2) 25.0 (3)	3.5
	235	95:5[e]	21.6 (1)	25.7 (2) 25.0 (3)	3.7
trans-(**4**)	151	34:66	22.1 (2)	34.0 (1)	3.4
	196	31:69	22.1 (2)	32.4 (1)	3.7
	235	31:69[e]	22.1 (2)	31.4 (1)	3.9

[a] Any differences in activation energies for the formation of (**6**) and (**7**) from either *cis*-(**5**) or *trans*-(**5**) are too small to measure reliably. [b] 1 G = 10^{-4} T. [c] The *g*-values of (**6**) and (**7**) were both 2.0029 at 151 K. [d] Numbers of equivalent nuclei shown in parentheses. [e] In cyclopropane–t-pentyl alcohol (3:1 v/v) solvent.

The kinetically-controlled regioselectivities observed for the ring opening of *cis*-(**5**) and *trans*-(**5**) can be understood on the basis of simple frontier molecular orbital (FMO) theory and the expected conformational preferences of these radicals as determined by steric effects. The regioselective ring openings of *cis*-(**1**) and *trans*-(**1**) have been interpreted in a similar fashion.[3,7]

Because of the considerable angle strain present in (**5**), the transition state for ring opening is likely to occur early along the reaction co-ordinate and the rate of cleavage should be strongly influenced by orbital interactions in the cyclic reactants and less dependent on the relative stabilities of the ultimate products. In terms of localised C–N σ bonds and an unpaired electron in a localised sp-hybrid orbital[4] on boron, the key FMO interaction which leads to ring opening should be between the SOMO and an unoccupied σ* C–N orbital. In (**5**) the C–N σ* orbital associated with the unsubstituted carbon will be lower in energy (and hence closer in energy to that of the SOMO) than that associated with the carbon which bears the electron donating methyl group and thus, in the absence of stereoelectronic effects, the primary radical (**7**) should be formed preferentially. However, the extent of overlap between the SOMO and the C–N σ* orbital is also important in determining the rate of C–N cleavage and the most favourable arrangement will be when the axis of the SOMO eclipses the C–N bond in question. The four transition states having this optimum geometry are shown in (**8**)—(**11**).

For the *trans*-isomer there is no steric barrier to adoption of either transition state structure (**8**) or (**9**) and thus the primary

† The ^{13}C chemical shifts for *trans*-1,2-dimethylcyclopropane are all greater than those of the corresponding carbons in the *cis*-isomer (ref. 6). The ^{13}C [15.8 (q), 34.9 (t), 37.4 (d) p.p.m. downfield from Me_4Si in C_6D_6] and ^{11}B chemical shifts for the isomer of (**4**) assigned the *trans*-structure are also all greater (less negative for ^{11}B) than those [11.2 (q), 33.8 (t), 32.5 (d) p.p.m. for ^{13}C] assigned to corresponding nuclei in the *cis*-isomer. These differences between *cis*- and *trans*-isomers are similar in magnitude for the cyclopropane and the amine-borane, thus providing further support for our structural assignments.

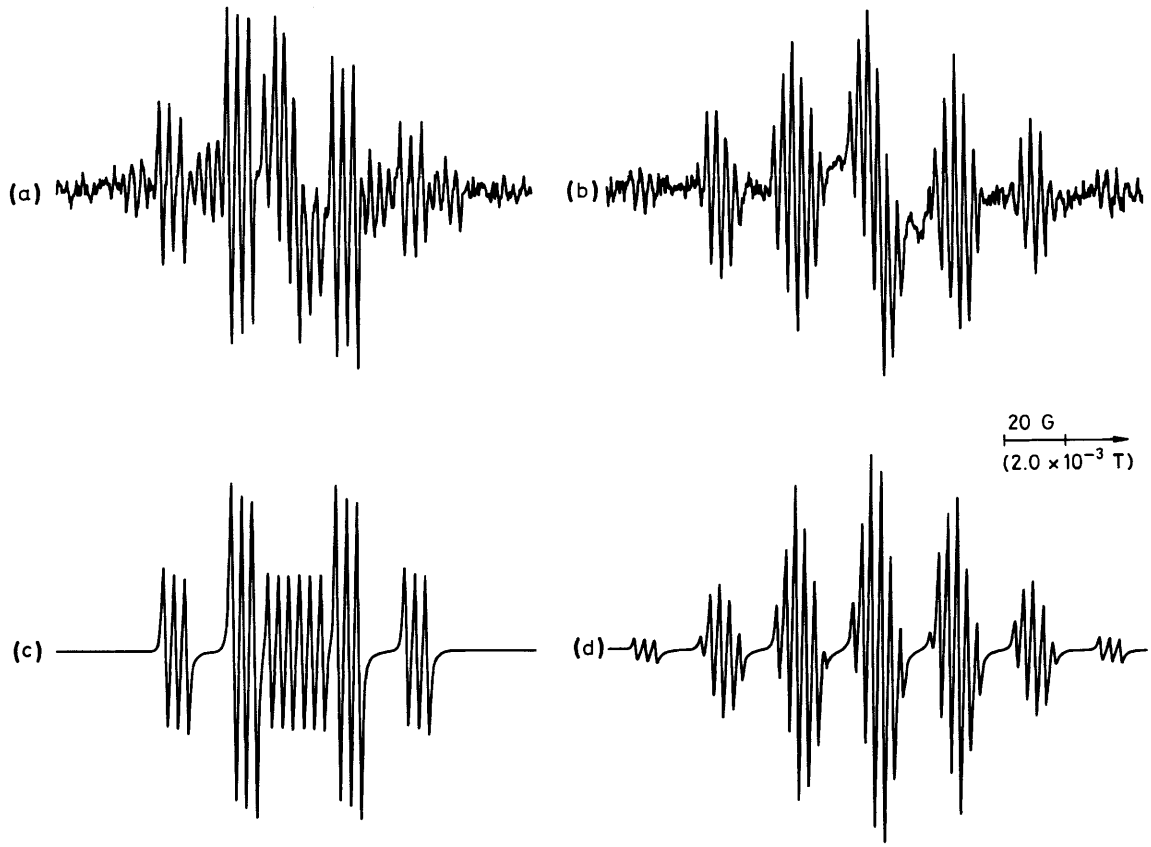
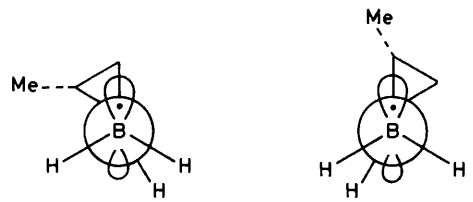
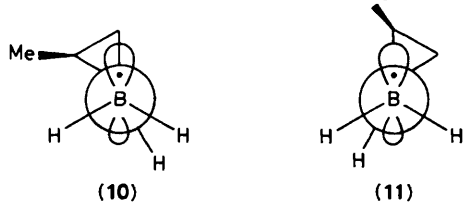


Figure 1. E.s.r. spectra of (**6**) and (**7**) obtained from (a) *trans*-2-methylaziridine-borane, *trans*-(**4**), and (b) *cis*-2-methylaziridine-borane, *cis*-(**4**), in cyclopropane–oxirane (2:1 v/v) solvent at 152 K. (c) Computer simulation of the spectrum of the primary radical (**7**). (d) Computer simulation of the spectrum of the secondary radical (**6**).



(**8**)

(**9**)



(**10**)

(**11**)

radical (**7**) will be formed preferentially. However, for the *cis*-isomer attainment of (**10**) will be impeded by non-bonded interactions between the methyl group and the nearer hydrogen attached to the boron radical centre, whilst no such destabilising interaction is present in (**11**). Evidently, for *cis*-(**5**) the ready attainment of maximum overlap between the SOMO and the MeC–N σ* orbital more than compensates for the poorer energetic matching between these two orbitals and the secondary radical (**6**) is the major cleavage product.

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