Electron Spin Resonance Study of Inversion Isomers of 1-Fluorocyclopropyl Radicals

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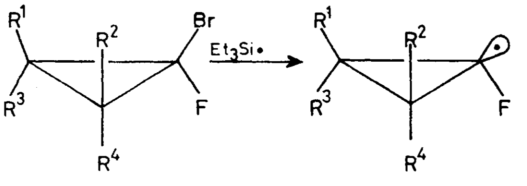
Summary Inversion isomers of 1-fluoro-2,3-*cis*-dimethylcyclopropyl radicals have been observed separately by e.s.r. spectroscopy; the hyperfine splitting constant (h.f.s.c.) of the β-proton *cis* to the odd electron orbital is far larger than that of the *trans* β-proton.

WE here report an e.s.r. study of 1-fluorocyclopropyl radicals which do not invert about the pyramidal carbon radical-centre during their life-time.

Photolysis of a cyclopropane solution of di-t-butyl peroxide, triethylsilane, and (Ia) at −108 °C gave an e.s.r. spectrum consisting of double (7·48 mT) triplets (0·553 mT) with $g = 2{\cdot}0040$ (Scheme 1). The radical generated by homolytic abstraction of bromine from (Ib) at −108 °C showed a spectrum consisting of a doublet (7·76 mT), a triplet (1·56 mT), and a septet (0·243 mT) with a g factor of 2·0040. We attribute the former radical to (IIa) and the latter to (IIb), based on studies by Ando and his co-workers[1] which showed that the stereochemistry of the fluorine atom is retained during homolytic reduction of *gem*-halogenofluorocyclopropanes. The spectrum of (IIa) only was observed during photolysis of the reaction mixture containing (Ia) and only (IIb) could be detected from (Ib). The doublet splittings of 7·4—7·8 mT in these species are reasonable for h.f.s.c.s of fluorine nuclei bonded to pyramidal carbon radicals.[2] The h.f.s.c.s are assigned as shown in Scheme 2.

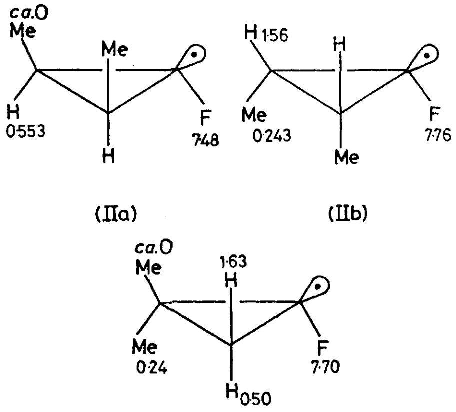


(I) (II)

a; $R^1 = R^2 = Me, R^3 = R^4 = H$
b; $R^1 = R^2 = H, R^3 = R^4 = Me$
c; $R^1 = R^3 = Me, R^2 = R^4 = H$

Scheme 1

The spectrum of (IIc) was observed during photolysis of a cyclopropane solution of a mixture of di-t-butyl peroxide, triethylsilane, and (Ic) at −108 °C. The spectrum consisted of three sets of doublets with splittings of 7·70, 1·63, and 0·50 mT, and a 1 : 3 : 3 : 1 quartet with a splitting of 0·24 mT. The g factor was 2·0039. These h.f.s.c.s were assigned as shown in Scheme 2 by reference to the h.f.s.c.s of (IIa) and (IIb).



(IIa) (IIb)

(IIc)

Scheme 2

The h.f.s.c. of the methyl proton *trans* to the odd electron orbital is *ca.* 0·24 mT, whereas that of the *cis* methyl group is too small to be resolved. This is consistent with the W-plan rule for γ-proton h.f.s.c.s.[3] In the present study the h.f.s.c. of the β-proton *trans* to the odd electron orbital is far smaller than that of the *cis* β-proton, in contrast to vinyl and related σ electron radicals, where *trans* β-proton h.f.s.c.s are larger than those of *cis* β-protons.[4]

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