

## Peroxide-initiated Cyclodimerisation of 3,3,4,4-Tetrafluoro-4-iodobut-1-ene

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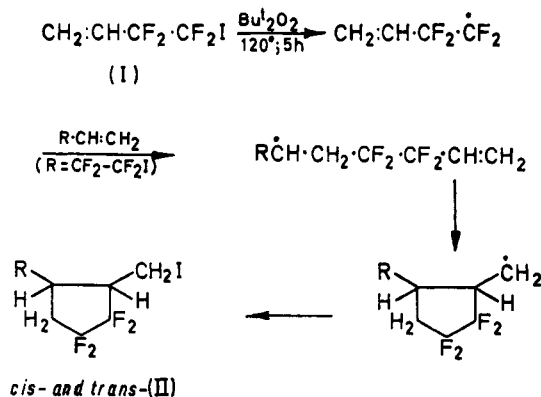
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**Summary** Peroxide-initiated dimerisation of 3,3,4,4-tetrafluoro-4-iodobut-1-ene gives the geometrical isomers of 1,1,2,2-tetrafluoro-3-iodomethyl-4-(tetrafluoro-2-iodoethyl)cyclopentane.

INTRAMOLECULAR cyclisation of hex-5-enyl radicals has been proposed in various reduction of alkyl halides,<sup>1</sup> thermal decomposition reactions,<sup>2</sup> and free-radical-induced additions<sup>3</sup> to hepta-1,6-diene derivatives. The radical intermediate, formed by the peroxide-initiated dimerisation of 3,3,4,4-tetrafluoro-4-iodobut-1-ene (I) has been found to follow the same cyclisation route as that of the simple hex-5-enyl radical which cyclises almost exclusively to the cyclopentylmethyl radical. The olefin (I), b.p. 90.5 at 748 mmHg, was obtained by dehydroiodination of 1,1,2,2-tetrafluoro-1,4-di-iodobutane.<sup>4</sup> The free-radical chain reaction of (I) initiated by 1% wt. of di-*t*-butyl peroxide gave (5 h, 120°) the geometric isomers of the cyclopentane (II; R = CF<sub>2</sub>·CF<sub>2</sub>I) (29%) as the major product. A little telomeric residue (<1%) was also obtained, but no vinylic isomer of (II).

The n.m.r. spectrum of the isomeric mixture of (II) [isomer ratio *ca* 1:1 (g.l.c.); b.p. 77–78° at 0.7 mmHg] showed resonances at  $\tau$  6.75 (d, *J ca.* 6 Hz, CH<sub>2</sub>I), 7.57br (*t*, *J ca.* 11 Hz) and 6.8–7.3 (complex m). The absence of any vinyl hydrogen peak as well as the absence of the  $\tau$  5.50 proton resonance typical of the CHI group, indicates that no significant amounts of its open-chain vinyl or six-membered ring isomers are present. The peak at  $\tau$  7.57 confirms that the CH<sub>2</sub> group is near a ring difluoromethylene group. The <sup>19</sup>F n.m.r. spectrum (94.1 MHz) of the *cis*-isomer (separated by g.l.c.) relative to internal CFCl<sub>3</sub>, showed a band at  $\phi$  59.7 (*t*, *J* 5 Hz, CF<sub>2</sub>I), and 3 AB-patterns spectra: two had  $|J_{AB}|$  values typical of geminal F–F coupling constants for five-membered-ring compounds

( $|J_{2,2}|$  241 Hz;  $|J_{1,1}|$  242 Hz) whereas the other (*J* 266 Hz) was assigned to the exocyclic CF<sub>2</sub>·CH group. Chemical shift values were:  $\phi$  113.3 and 132.2, 117.2 and 119.8 [non-equivalent C(2)- and C(1)-F], and 106.6 and 115.5 (exocyclic CF<sub>2</sub>). The *trans*-isomer showed <sup>19</sup>F n.m.r. bands at  $\phi$  59.1 (CF<sub>2</sub>I), 115.45 [strongly overlapped resonances from C(1)-F<sub>2</sub> (*gem*)], 100.0 and 111.7 (AB  $|J_{AB}|$  261 Hz, exocyclic CF<sub>2</sub>), and 119.7 and 126.6 [AB  $|J_{AB}|$  243 Hz, C(2)-CF<sub>2</sub>]. The <sup>19</sup>F n.m.r. assignments as well as the *cis*- or *trans*-arrangement are based on the consideration that the two geminal fluorine atoms of the CF<sub>2</sub> ring group near the



asymmetric carbon centre will give the largest internal chemical shift and that the *cis*-isomer will show greatest non-equivalence of the ring-CF<sub>2</sub> fluorine atoms since in this isomer the electric-field effect of the substituents R and CH<sub>2</sub>I is additive on the same geminal fluorine nucleus, whereas in the *trans*-isomer this effect becomes partially compensated.

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<sup>3</sup> N. O. Brace, *J. Org. Chem.*, 1969, **34**, 2441 and references cited therein.

<sup>4</sup> N. O. Brace, U.S.P. 3,016,407/1962.