Photochemical Isomerisation of Perfluoroalkyl Olefins[1]

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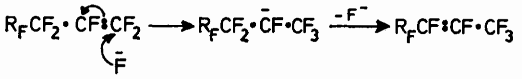
Summary Intense u.v. irradiation causes rearrangement of tetra- and tri-(perfluoroalkyl)ethylenes to less substituted ethylenes including the terminal olefins; migration of allylic fluorine and allylic perfluoroalkyl groups can occur.

Isomerisation of perfluoro-olefins in the presence of catalysts such as fluoride ion is well known, and leads to thermodynamically stable internal olefins *via* the more stable perfluorocarbanion, *e.g.* reaction (1). Photochemical isomerisation of perfluorocyclohexene in the presence of air leads to ring shrinkage and formation of perfluoromethylenecyclopentane (30%) and perfluoro(1-methylcyclopent-



$$R_FCF_2\cdot CF{:}\underset{\bar{F}}{CF_2} \longrightarrow R_FCF_2\cdot\bar{C}F\cdot CF_3 \xrightarrow{-F^-} R_FCF{:}CF\cdot CF_3 \qquad (1)$$

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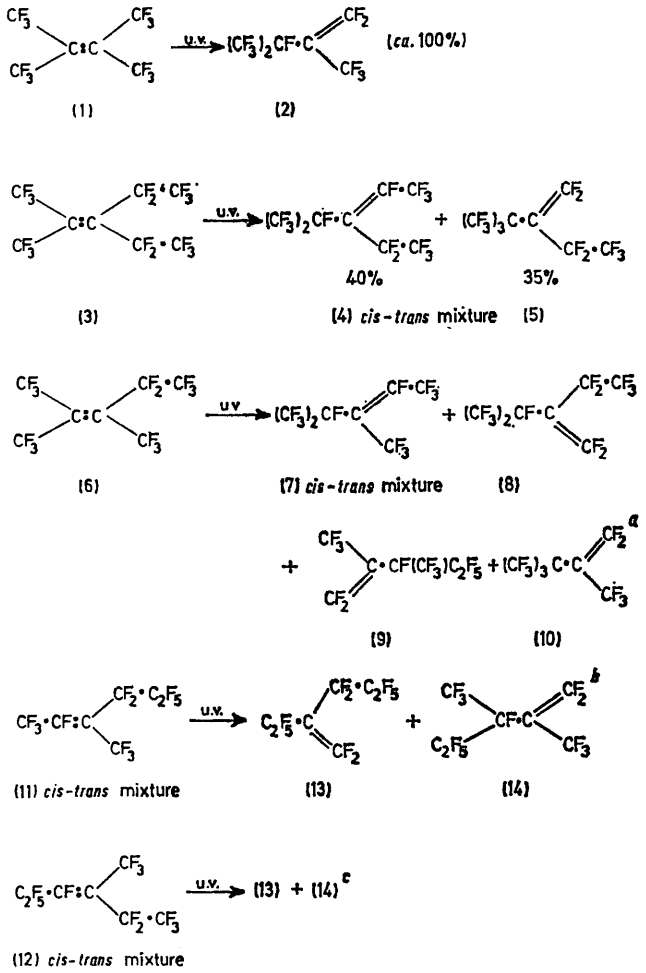
ene) (6%), together with some 30% of high-boiling products.[2]



Scheme

[a] Ratio (**7**) : (**8**) : (**9**) : (**10**) = 2 : 1 : 1 : 2 with new lamp. [b] Ratio (**13**) : (**14**) = 3 : 2. [c] Ratio (**13**) : (**14**) = 5 : 1.

We now report that u.v. irradiation of some perfluoro-olefins provides an efficient synthesis of the reactive terminal olefins. Thus when perfluoro-2,3-dimethylbut-2-ene (**1**) was exposed in the mixed vapour and liquid phases to unfiltered radiation from a 500 W medium-pressure mercury arc placed *ca.* 2 cm from the silica reaction tube, fluorine migration occurred and perfluoro-2,3-dimethylbut-1-ene (**2**) was produced quantitatively in *ca.* 7 days (see Scheme).

Perfluoro-3-ethyl-2-methylpent-2-ene (**3**) underwent a similar photochemical rearrangement to give a high yield of a mixture of *cis*- and *trans*-perfluoro-3-ethyl-4-methylpent-2-ene (**4**) by migration of an allylic fluorine from a C_2F_5 group, and perfluoro-2-ethyl-3,3-dimethylbut-1-ene (**5**) by a concurrent migration of an allylic CF_3 group. Migration of allylic fluorine from a CF_3 group gave perfluoro-3-ethyl-2-methylpent-1-ene (10%).[3] Irradiation of (**4**) did not produce (**5**). Perfluoro-2,3-dimethylpent-2-ene (**6**) also showed allylic fluorine migration to give (**7**), (**8**), and (**9**), and allylic CF_3 group migration to give the terminal olefin (**10**) in comparable yields. The ratio (**7**) : (**8**) : (**9**) : (**10**) depends on the precise irradiation conditions [*e.g.*, a new lamp apparently favours (**10**)].

Replacement of one CF_3 group of (**1**) by fluorine greatly reduced the rate of reaction, but perfluoro-2-methylbut-2-ene slowly gave perfluoro-2-methylbut-1-ene in high yield by migration of allylic fluorine to carbon carrying vinylic fluorine.[3] Prolonged irradiation of perfluoro-2-methylpent-2-ene also gave the terminal olefin $CF_2{:}C(CF_3){\cdot}CF_2{\cdot}CF_2{\cdot}CF_3$ in high yield by allylic fluorine migration to the $CF{\cdot}R_F$ group. Perfluoro-3-methylhex-2-ene (**11**) and perfluoro-3-methylhex-3-ene (**12**) both underwent *cis–trans* isomerisation under mild irradiation, frustrating attempts to investigate the stereochemical requirements for the migration, and both gave mixtures of perfluoro-2-ethylpent-1-ene (**13**) (by fluorine migration) and perfluoro-2,3-dimethylpent-1-ene (**14**) [by C_2F_5 group migration in (**11**) and CF_3 group migration in (**12**)] under more vigorous conditions. In parallel experiments, rearrangement of (**11**) was slightly faster than that of (**12**).

Perfluorobut-2-ene undergoes only geometrical isomerisation at an appreciable rate under these conditions, and the trend in the rates of isomerisation is thus tetra-substituted > tri-substituted > di-substituted ethylenes. The mechanism of the migration is uncertain, but it does not appear to be influenced by the presence of benzophenone or isobutane, and (**1**) did not rearrange detectably in the dark at temperatures up to 300 °C, suggesting the possibility of a suprafacial 1,3-sigmatropic shift which would be symmetry-allowed for the photochemically excited state.[4]

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[1] Presented in part at the 5th European Fluorine Symposium, Aviemore, Scotland, September 1974.

[2] G. Camaggi and F. Gozzo, *J. Chem. Soc.* (*C*), 1971, 925.

[3] R. Fields, R. N. Haszeldine, D. Moran, and J. P. Tomlinson, unpublished results.

[4] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.