Fluoro-olefin Chemistry. Part 13.¹ A Further Route to Perfluoro-2,3dimethylbut-2-ene and the Photochemical Rearrangement of Some Perfluoro-alkyl Olefins

By A. Nicholas Bell, Roy Fields,* Robert N. Haszeldine,* and (in part) Daniel Moran, Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1 QD

Perfluoro-2,3-dimethylbut-2-ene is conveniently prepared from perfluoro-(2,2,4,4-tetramethyldithietan) at 325 °C. Under u.v. irradiation it is efficiently isomerised to perfluoro-2,3-dimethylbut-1-ene. Perfluoro-2-methylbut-2-ene and perfluoro-3-methylpent-2-ene are also isomerised photochemically, but more slowly, migration of fluorine being exclusively to the R_FCF : group. In the presence of fluoride ion the internal olefins are reformed quantitatively.

PERFLUORO-2,3-DIMETHYLBUT-2-ENE (1) has previously been prepared by the low-temperature reaction of fluorine with 2-chloropentafluoropropene and dechlorination of the dimer so formed,² by desulphurisation of tetrakis(trifluoromethyl)thiiran,³ and by the reaction at high temperature and pressure of an excess of trifluoroiodomethane with perfluorobut-2-yne.⁴ Of these, the first requires elemental fluorine, and the second involves a three-stage preparation of the thiiran; the third method was therefore used to prepare (1) for use in a number of reactions.^{4,5} Although the yield of (1)is good at 350 °C, the reaction temperature is critical. Too low a temperature gives mainly 2-iodo-3-trifluoromethylbut-2-ene,⁴ and further work now shows that too high a temperature leads to the formation of small amounts of perfluoro-2,3-dimethylbuta-1,3-diene (2), which are difficult to separate from (1) by distillation,

$$CF_{3}CCI: CF_{2} \longrightarrow (CF_{3})_{2}CCI: CCI(CF_{3})_{2}$$

$$CF_{3}I + CF_{3}C:CCF_{3} \longrightarrow (CF_{3})_{2}C:C(CF_{3})_{2}$$

$$(1)$$

$$(CF_{3})_{2}C \xrightarrow{S} C(CF_{3})_{2}$$

$$(CF_{3})_{2}C \xrightarrow{S} C(CF_{3})_{2}$$

$$(CF_{3})_{2}C \xrightarrow{S} C(CF_{3})_{2}$$

$$(CF_{3})_{2}C \xrightarrow{S} C(CF_{3})_{2}$$

although the diene can be removed effectively by treatment with methanol. The diene apparently arises by defluorination of the initially formed (1), since it is also formed in low yield from (1) at 375 °C in the presence of iron wire or more rapidly at 325 °C with copper. We now report a further route to (1) which avoids these disadvantages.

Pyrolysis of tetrakis(trifluoromethyl)dithietan, readily obtainable in one step from hexafluoropropene, potassium fluoride, and sulphur,⁶ results in a simple desulphurisation, and the butene (1) is produced in 96% yield at 325 °C. If the decomposition is carried out in a glass tube at high pressure (10 atm), some defluorination to the diene (2) is observed, but this does not occur when the reaction is carried out at lower pressure (3.5 atm). This procedure is considerably more convenient than those previously reported, particularly when only small amounts of (1) are required. On a larger scale the reaction may be carried out in a steel autoclave, giving (1) almost quantitatively without detectable impurity. A superficially similar reaction, pyrolysis of the dithietan (3) to give perfluorotetramethylallene (4) has previously been reported,⁷ but in this case carbon disulphide is eliminated rather than sulphur.

$$(CF_3)_2C:C(CF_3)_2 \xrightarrow{heat} (CF_3)_2C:C:C(CF_3)_2 + CS_2$$

(3) (4)

Photochemical Isomerization.⁸—On u.v. irradiation, tetrakistrifluoromethylthiiran lost sulphur quantitatively, but the organic product was a mixture of the expected but-2-ene and an isomer, readily recognized by the perfluoroisopropyl group, vinylic trifluoromethyl group, and almost uncoupled terminal difluoromethylene fluorines in its ¹⁹F n.m.r. spectrum, as perfluoro-2,3dimethylbut-1-ene (5). A separate experiment showed that when (1) was irradiated (medium pressure mercury arc lamp) it was converted quantitatively to the but-1ene in 2—20 days, depending on the efficiency of the lamp and the distance of the sample from it.

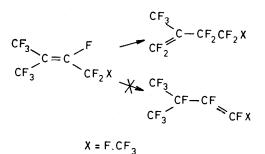
$$F_{2}C \xrightarrow{CF_{3}}{F_{2}C} \xrightarrow{CF_{3}}{F_{2}C} \xrightarrow{hv}{F_{2}C} \xrightarrow{CF_{3}}{F_{2}C} \xrightarrow{CF_{3}}{C-CF(CF_{3})_{2}}$$
(5) 100%

Isomerisation of perfluorocyclohexene by irradiation (185 nm) of mixtures of air and the olefin has previously been reported to give perfluoromethylenecyclopentane (30%), perfluoro-1-methylcyclopentene (6%), and highboiling material (*ca.* 30%); ⁹ the photochemical isomerisation of (1) to (5) however, was unaffected by the presence of benzene, benzophenone, or 2-methylpropane except that the reaction was slower in the presence of a large quantity of benzene, presumably because it absorbed most of the light. There was no detectable isomerisation at 300 °C in the dark.

488

The but-1-ene (5) reacted more readily than (1) with chlorine [reaction complete after 1 day, cf. 10% of (1) recovered after 4 days ⁴], giving 1,2-dichloro-2,3-dimethylbutane quantitatively. Potassium fluoride regenerated (1) from (5), in accord with the well-known rearrangement of terminal fluoro-olefins.¹⁰

Similar, but considerably slower, rearrangements were observed when perfluoro-2-methylbut-2-ene or perfluoro-2-methylpent-2-ene were irradiated, to give after 8—16 weeks irradiation, perfluoro-2-methylbut-1-ene and perfluoro-2-methylpent-1-ene respectively as sole products, formed essentially quantitatively by migration of fluorine to the :CFR_F group from either of the (CF₃)₂C: trifluoromethyl groups. This rearrangement is evidently preferred to migration of fluorine to the (CF₃)₂C: group, which would have given perfluoro-3-methylbut-1-ene and perfluoro-4-methylpent-2-ene respectively; these olefins were not detectable in the reaction mixtures.



U.v. irradiation of perfluorobut-2-ene (a mixture of *cis*- and *trans*-isomers) did not result in any detectable formation of the but-1-ene.

No isomerisation of perfluoro-2-methylbut-1-ene by caesium fluoride was detected by n.m.r. as the reactants warmed from -196 to -25 °C, but by the time the sample had warmed to 55 °C, the but-2-ene was detectable and the reaction then proceeded readily. In the presence of dry diglyme and caesium fluoride, formation of the but-2-ene was complete after 6 h at 34 °C, the only other product being 2H-2-trifluoromethyloctafluorobutane (*ca.* 5%) presumably formed by reaction of the carbanion $C_2F_5\overline{C}(CF_3)_2$ with traces of moisture.

The u.v.-initiated rearrangement of the internal olefins can be represented as a suprafacial [1,3] sigmatropic shift of fluorine, which would be expected to be photochemically allowed,¹¹ but the driving force for the reaction, apart from a possible relief of steric strain in the internal olefin, which would be in accord with the observed reactivity order $(R_F)_2C=C(R_F)_2 > (R_F)_2C=CFR_F > R_FCF=CFR_F$, is not yet known.

EXPERIMENTAL

I.r. spectra were recorded on Perkin-Elmer 257 or 621 spectrophotometers, mass spectra on an A.E.I. MS902 spectrometer, and ¹⁹F n.m.r. spectra on Perkin-Elmer R10 (56.46 MHz) or Varian HA100 (94.1 MHz) instruments. Chemical shifts have positive values to low field of external trifluoroacetic acid. ¹⁹F N.m.r. parameters are available as Supplementary Publication No. SUP 22663 (3 pp).* Irradiations were with a Hanovia 500 medium pressure arc lamp with the reactants sealed *in vacuo* in silica tubes.

The Reaction of Trifluoroiodomethane with Hexafluorobut-2-yne.-Trifluoroiodomethane (162 g, 0.83 mol) and hexafluorobut-2-yne (66.6 g, 0.41 mol) were kept at 350 °C (indicated temperature) (4 days) in a Hastelloy-lined autoclave (250 ml) to give a fraction (60 g) shown by its i.r. spectrum (strong C:C at \tilde{v}_{max} , 1730 and 1748 cm⁻¹) to contain impurities as well as perfluoro-2,3-dimethylbut-2ene. Distillation (Haage spinning-band column, 1 m) gave a series of fractions, b.p. 48.3—53.5 °C, containing varying proportions of perfluoro-2,3-dimethylbut-2-ene and perfluoro-2,3-dimethylbuta-1,3-diene, which were finally separated by g.l.c. (2 m silicone elastomer 30, room temp.) and identified spectroscopically (cf. ref. 12). In another experiment, a fraction (34.5 g), b.p. 54-56 °C, shown by g.l.c. to contain ca. 5% of the diene, was shaken $(4\frac{1}{2} \text{ days}, 80 \text{ °C})$ in vacuo with methanol (30 ml). After addition of water (50 ml) the lower layer was dried and distilled to give pure (1) (30 g).

Dehalogenation of Perfluoro-2,3-dimethylbut-2-ene.—(a) With iron. The olefin (12.7 g, 42.3 mmol) was kept in vacuo at 375 °C in a Hastelloy autoclave (50 ml) packed with iron wool (6 days) to give as volatile products (11.54 g) the original olefin contaminated by perfluoro-2,3-dimethylbuta-1,3-diene (ca. 1%).

(b) With copper. Freshly prepared dry copper powder (2.4 g) and the olefin (0.30 g, 1.0 mmol) were kept in vacuo (40 ml tube) at $325 \,^{\circ}\text{C}$ (62 h) to give silicon tetrafluoride (0.23 mmol) and a mixture of the original olefin (0.16 g, 53%) and perfluoro-2,3-dimethylbuta-1,3-diene (0.11 g, 40%).

Pyrolysis of Tetrakis(trifluoromethyl)dithietan.—(a) In glass. The dithietan (1.84 g, 5.0 mmol), prepared in 94% yield by the reaction of hexafluoropropene with sulphur and potassium fluoride in dry nitrobenzene in a Magnadrive stirred autoclave (cf. ref. 6), was kept at 325 °C (4 days) in a 70 ml Pyrex tube to give perfluoro-2,3-dimethylbut-2-ene (1.44 g, 96\%) and sulphur.

(b) In steel. The dithietan (90.8 g, 0.25 mol) was kept at 300-325 °C (25 h) in a stainless steel autoclave (500 ml) to give perfluoro-2,3-dimethylbut-2-ene (67.1 g, 90%) and sulphur. A coating, presumed to be ferric sulphide, on the surface of the autoclave was readily removed.

Photochemical Reaction of Tetrakis(trifluoromethyl)thiiran. —Tetrakis(trifluoromethyl)thiiran (3.15 g, 9.5 mmol), prepared from the dithietan by oxidation and thermal elimination of sulphur dioxide (cf. ref. 3), was irradiated (6 days) to give perfluoro-2,3-dimethylbut-2-ene (0.43 g, 15%), perfluoro-2,3-dimethylbut-1-ene (2.42 g, 85%) (Found: C, 23.7; H, 0.1%; M^+ , 300. C_6F_{12} requires C, 24.0; H, 0.0%; M, 300), b.p. 54.8—55.0 °C; $\tilde{\nu}_{max}$.1 730 cm⁻¹ (C.C), characterised by its n.m.r. spectrum, and sulphur (0.30 g, 100%).

Photochemical Isomerisation of Perfluoro-2,3-dimethyl but-2-ene.—Perfluoro-2,3-dimethylbut-2-ene (2.50 g, 8.3 mmol) was sealed in vacuo in a 240 ml silica tube, and the combined liquid and vapour phases were irradiated (17 days, 5 cm from the lamp) to give perfluoro-2,3-dimethylbut-1-ene (2.47 g, 99%).

Reaction of Perfluoro-2,3-dimethylbut-1-ene with Chlorine. —The olefin (1.50 g, 5.0 mmol) and chlorine (0.57 g, 8.0 mmol) were irradiated (12 in, 25 h) to give, after removal of the excess of chlorine (Hg), 1,2-dichloroperfluoro-2,3-dimethyl-

* For details of Supplementary Publications see Notice to Authors No. 7 in J.C.S. Perkin I, 1979, Index issue.

butane (1.82 g, 98%) (Found: C, 19.0; H, 0.1. C₆F₁₂Cl₂ requires C, 19.4; H, 0.0%), b.p. (isoteniscope) 119 °C.

Reaction of Perfluoro-2,3-dimethylbut-1-ene with Potassium Fluoride.—The olefin (0.10 g) and dry potassium fluoride (ca. 0.1 g) were kept in vacuo in a Pyrex tube (ca. 5 ml) at 130 °C (3 days) to give perfluoro-2,3-dimethylbut-2-ene quantitatively.

Action of Heat on Perfluoro-2,3-dimethylbut-1-ene.-The olefin (1,26 g, 4.2 mmol) was recovered unchanged after being kept in vacuo (70 ml tube) at 260 °C (18 h).

Photochemical Reactions of Perfluoro-2,3-dimethylbut-2ene.-(a) With 2-methylpropane. Irradiation of the olefin (0.54 g, 1.8 mmol) and 2-methylpropane (0.21 g, 3.6 mmol) in vacuo (5 cm, 325 ml tube, 6 days) gave perfluoro-2,3dimethylbut-1-ene (0.54 g, 100%), 2-methylpropane (0.21 g, 100%), and two very small impurities detected by g.l.c. (each $\leq 0.5\%$).

(b) With benzophenone. The olefin (0.60 g, 2.0 mmol) and benzophenone (1.0 g, 5.5 mmol), irradiated (3 cm. 7 days, 40 ml tube) in vacuo, gave a mixture of the but-1-ene (0.56 g, 94%) and the original olefin (0.04 g, 6%) as the only volatile products.

(c) With benzene. The olefin (1.53 g, 5.1 mmol) and benzene (0.60 g, 7.7 mmol), irradiated (3 cm, 6 days, 40 ml tube) in vacuo, gave a mixture (1.48 g, 97%) of the original olefin (98%) and the but-1-ene (2%).

Action of Heat on Perfluoro-2,3-dimethylbut-2-ene.-After 33 days in vacuo at 300 °C (70 ml tube), the olefin (0.58 g, 1.9 mmol) was recovered essentially quantitatively. Traces (<0.1 mmol) of silicon tetrafluoride and perfluoro-2,3dimethylbuta-1,3-diene were detected, but the but-1-ene was absent.

Photochemical Rearrangement of Perfluoro-2-methylbut-2ene.-Perfluoro-2-methylbut-2-ene (0.35 g, 1.4 mmol), containing perfluoro-2-methylbut-1-ene (4%), was irradiated in a 2 mm i.d. silica n.m.r. tube (3 cm). N.m.r. spectra showed the following concentrations of the original but-2-ene, with corresponding increases in the but-1-ene concentration: 1 day, 91%; 10 days, 45%; 26 days, 16%; 60 days, 3%; 72 days, undetectable. The tube was then opened to give perfluoro-2-methylbut-1-ene (0.34 g, 99%) (Found: C, 24.3; H, 0.3%; M, 250. C₅F₁₀ requires C, 24.0; H, 0.0%; M, 250), \tilde{v}_{max} . 1 756vs (C:C), characterised by its n.m.r. spectrum.

Reaction of Perfluoro-2-methylbut-1-ene with Caesium Fuoride.—(a) Without solvent. The olefin (0.35 g, 1.4 mmol) and dry caesium fluoride (0.050 g, 0.33 mmol) were sealed in vacuo in a 2 mm i.d. n.m.r. tube and warmed to -25 °C, then slowly (6 h) to 55 °C. After $2\frac{1}{2}$ days at 55 °C, the product was perfluoro-2-methylbut-2-ene (>99%), and the original olefin was undetected.

(b) In diglyme. Perfluoro-2-methylbut-1-ene (0.035 g, 0.14 mmol), anhydrous caesium fluoride (0.005 g, 0.03 mmol), and sodium-dried diglyme (0.3 ml) were kept at 34 °C as above to give, after 6 h, perfluoro-2-methylbut-2-ene (96%) and 2H-2-trifluoromethyloctafluorobutane (5%), identified by its n.m.r. spectrum and subsequently prepared unambiguously.13

Photochemical Rearrangement of Perfluoro-2-methylpent-2ene.—The olefin (0.90 g, 3.0 mmol) was irradiated (6 cm) in a silica n.m.r. tube to give perfluoro-2-methylpent-1-ene, in the following concentrations: 1 month, 12%; 2 months, 50%; 4 months, 90%, the remainder being starting material. G.l.c. separation (7.5 m Kel-F 10, 30 °C) gave pure perfluoro-2-methylpent-1-ene (0.51 g, 57%) $\tilde{\nu}_{max}$ 1 742 cm⁻¹ (C:C), characterised by its n.m.r. spectrum.

We thank Dr. G. R. Sparkes for assistance with the experiment with perfluoro-2-methylpent-2-ene.

[9/684 Received, 2nd May, 1979]

REFERENCES

¹ Part 12, M. G. Barlow, M. W. Crawley, and R. N. Haszeldine, J.C.S. Perkin I, 1980, 122.

² W. T. Miller, R. L. Ehrenfeld, J. M. Phelan, M. Prober, and S. K. Reed Ind. Engl Chem., 1947, 39, 401; W. T. Miller, ' Preparation, Properties, and Technology of Fluorine and Organic Fluoro Compounds,' eds. C. Slesser and S. R. Schramm, McGraw-Hill, 1951, p. 567.

⁸ D. M. Gale, W. J. Middleton, and C. G. Krespan, J. Amer. Chem. Soc., 1966, 88, 3617.

⁴ H. H. Evans, R. Fields, R. N. Haszeldine, and M. Illingworth, J.C.S. Perkin I, 1973, 649.

⁵ R. Fields, G. L. Godwin, and R. N. Haszeldine, J. Organo-metallic Chem., 1971, **26**, C70; J.C.S. Dalton, 1975, 1867; D. A. Ball, R. Fields, R. N. Haszeldine, and D. Moran, unpublished results.

⁶ S. R. Sterlin, B. I. D'yatkin, and I. L. Knunyants, Izv. Akad. Nauk S.S.S.R., Ser. Khim., 1967, 2583 (Chem. Abs., 1968, **69**, 52044); B. L. D'yatkin, S. R. Sterlin, L. G. Zhuravkova. and I. L. Knunyants, *Doklady Akad. Nauk S.S.S.R.*, 1968, **183**, 598.

M. S. Raasch, J. Org. Chem., 1970, 35, 3470. ⁸ Preliminary communication, A. N. Bell, R. Fields, R. N. Haszeldine, and I. Kumadaki, J.C.S. Chem. Comm., 1975, 866.

⁹ G. Camaggi and F. Gozzo, J. Chem. Soc. (C), 1971, 925
 ¹⁰ W. T. Miller, J. H. Fried, and H. Goldwhite, J. Amer. Chem.

Soc., 1960, **82**, 3091. ¹¹ R. B. Woodward and R. Hoffmann, Angew. Chem. Internat.

Edn., 1969, 8, 781. ¹² W. Mahler, J. Amer. Chem. Soc., 1962, 84, 4600.

¹³ R. N. Haszeldine, I. Mir, and A. E. Tipping, J.C.S. Perkin I, 1979, 565.