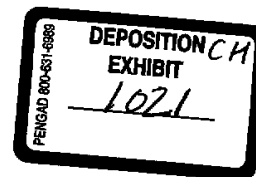


**\*Fluoroolefins - Note I. Cis and trans 1,2,3,3,3-pentafluoropropylene  
(Dario SIANESI and Renzo FONTANELLI)**

**Abstract** - Dehydrofluorination of  $\text{CF}_3\text{-CFH-CF}_2\text{H}$ , prepared by catalytic hydrogenation of perfluoropropene, yielded two isomeric olefins  $\text{C}_3\text{F}_5\text{H}$ . On the basis of oxidation, hydrogenation and bromination reactions, these two olefins have been demonstrated to be the cis, trans isomers of  $\text{CF}_3\text{-CF=CFH}$ ; their absolute configuration has been assigned by NMR.

The isomerization equilibrium in the temperature range 300-550°C can be expressed by the equation:

$$\log \frac{[\text{cis}]_{\text{eq}}}{[\text{trans}]_{\text{eq}}} = -0.34 + \frac{870}{T}$$



Accordingly, for the trans  $\rightarrow$  cis isomerization,  $\Delta H = +3.9$  Kcal/mole,  $\Delta S_{400} = -1.45$  cal/mole °K.

Studies conducted in this laboratory on the synthesis of novel fluorinated polymers have revealed the favourable possibilities offered in this field by certain propylenes substituted with several fluorine atoms.

Among these, pentafluorinated isomers in which the hydrogen atom residue is in the vinyl position, and especially 1'1,2,3,3,3-pentafluoropropylene,  $\text{CF}_3\text{-CF=CFH}$ , referred to for the sake of brevity hereinbelow as 1-hydropentafluoropropylene, appeared to be of particular interest. This compound was described by R. N. Haszeldine and B. R. Steele, who achieved synthesis thereof via a particularly laborious method<sup>1</sup>.

Taking into account the importance that the olefin might have as a monomer and comonomer in polymerizations, we proposed to research and develop methods that would allow easier synthesis thereof. In addition, since this olefin can obviously be in two different geometrical configurations, we proposed to identify the two possible cis-trans isomers and to determine the relative stabilities of the two structures.

We took into consideration a possible synthetic process, already indicated in its general lines by other workers<sup>2</sup>, which consists in replacing a fluorine atom with a hydrogen atom in perfluoropropylene, via hydrogenation of the latter to  $\text{C}_3\text{F}_6\text{H}_2$  and subsequent dehydrofluorination to  $\text{C}_3\text{F}_5\text{H}$ . Obviously, this last reaction can give all the isomers of pentafluoropropylene, i.e. 3-hydro-, 2-hydro- and 1-hydro-pentafluoropropylene, the latter isomer in turn being in two possible geometrical isomers. It was therefore foreseeable that, by

<sup>1</sup> J. Chem. Soc., 1592 (1953)

<sup>2</sup> I. L. KNUNYANTS, M. P. KRAUSUSKAYA and E. I. MYSOV, Izvest. Akad. Nauk SSSR, Otdel Khim. Nauk, 903 (1958) (C.A. 53, 1102); *ibid.*, 1412 (1960) (C.A. 55, 349).

seeking suitable dehydrofluorination conditions, it would be preferentially possible to direct the reaction toward one or other of the isomers.

*Hydrogenation of  $C_3F_6$ .* - According to the literature information, the hydrogenation of a perfluorinated olefin may be readily performed, working in the gaseous phase, with the aid of palladium-based catalyst<sup>2</sup>.

We have effectively found, after a number of guide experiments, that the use of palladium-on-alumina (0.5-2% of Pd) as catalyst allows rapid and quantitative hydrogenation of perfluoropropylene at atmospheric pressure in the gaseous phase, even at temperatures only slightly above 50°C.

The reaction is appreciably exothermic and it is necessary to ensure the dispersion of the heat of reaction such that the temperature of the gases in the reaction zone does not exceed 200-250°. Specifically, above this temperature, hydrogenolysis side reactions readily take place, which not only lower the reaction yield, but also inactivate the catalyst within a short time. Working at temperatures of between 100 and 150°C with a slight excess of hydrogen however, we obtained a virtually quantitative transformation of perfluoropropylene into 1,2-dihydrohexafluoropropane.

*Dehydrofluorination of  $C_3F_6H_2$ .* - The removal of HF from a molecule of a highly fluorinated compound may be a non-trivial operation and may require the use of drastic methods. In particular, the most common processes are pyrolysis or treatment at high temperatures with concentrated alkalis. Both these methods were adapted by us to the case of dehydrohexafluoropropane.

*a) Pyrolytic dehydrofluorination.* - Attempts to remove a molecule of HF by heating  $CF_3-CFH-CF_2H$  to relatively high temperatures did not give positive results. When subjected to the action of high temperatures, 700-850°, this molecule in fact demonstrated very high thermal stability, ending by giving under the limit conditions a complex mixture of scission products. These tests were performed by sending a gaseous stream of the product into externally heated steel, nickel or monel tubular reactors.

Similarly negative results were obtained from a number of attempts to dehydrofluorinate  $C_3F_6H_2$  at lower temperatures, 600-700°, either working under reduced pressure or in the presence of possible catalysts, such as alumina or salts of various metals deposited on active charcoal. However, we obtained better results by performing the pyrolysis in the presence of substances having a certain basic nature, with respect to hydrofluoric acid, such as NaF and, especially, KCl. We in fact observed that by sending  $C_3F_6H_2$  into a tubular reactor filled with KCl and heated to a temperature in the region of 700°, contact times of a few seconds are sufficient to bring about high conversion of the product into a mixture of  $C_3F_5H$  isomers. By gas chromatography analysis, this mixture proved to be constituted essentially of three components, present, respectively, in proportions of 30%, 53% and 17%. This relative

composition, always working at about 700°, is found to be roughly independent of the degree of conversion that may be obtained in the dehydrofluorination.

The isomer present in a proportion of 30%, separated in pure form by fractional distillation, is found to be 2-hydropentafluoropropylene,  $\text{CF}_3\text{-CH=CF}_2$ .

The other two reaction products, I and II, are  $\text{C}_3\text{F}_5\text{H}$  isomers that are very difficult to separate by distillation: b.p. -18, -18.5°C.

Since, for 3-hydropentafluoropropylene, a boiling point of +1.8°C has been reported<sup>3</sup>, it appeared logical to assign to I and II the constitution of geometrical isomers of 1-hydropentafluoropropylene. Furthermore, we obtained a first confirmation of this hypothesis by oxidizing a mixture of these compounds with permanganate in acetone and detecting only the formation of trifluoroacetic acid.

The conclusion that may be drawn from these experiments is that the pyrolytic dehydrofluorination of 1,2-dihydrohexafluoropropane, which moreover appears to be achievable only in the presence of suitable catalysts, is a reaction that does not lend itself to the proposed purposes. In point of fact, it is too sparingly specific with respect to the synthesis of one or other of the  $\text{C}_3\text{F}_5\text{H}$  isomers; this is, for that matter, understandable, given the need to perform this reaction at excessively high temperatures.

*b) Dehydrofluorination with basic agents.* - The most immediate method for the dehydrofluorination of  $\text{C}_3\text{F}_6\text{H}_2$  is found to be simple passage of the compound in gaseous form through a liquid phase constituted of an aqueous solution of KOH with a high titre (70-80%), maintained at a temperature of about 150°. This operation in point of fact gave a virtually quantitative dehydrofluorination: the reaction product is only 1-hydropentafluoropropylene, constituted mainly of isomer I, with minor contents, about 5%, of isomer II.

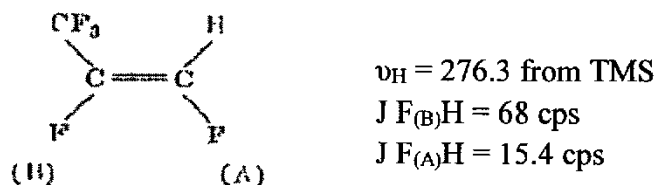
This total specificity in the position and direction of the elimination of HF by means of a basic agent, is obviously attributable to the strong electron-withdrawing effect of the trifluoromethyl group which activates the proton on the adjacent carbon atom, promoting attack by the base.

*Cis 1-hydropentafluoropropylene.* - With an accurate rectification by fractional distillation, we were able to separate out a pure sample of I from the mixture of isomers. This sample was examined by nuclear magnetic resonance, for the determination of its configuration.

The spectra of the compound, both for fluorine and for hydrogen, were acquired at 40 MHz, in 10%  $\text{CCl}_4$  solution. For hydrogen, we used tetramethylsilane (TMS) as internal reference, and for fluorine we used trifluoroacetic anhydride. The "chemical shifts" and the coupling constants were measured via the usual technique of side bands, taking the average of

<sup>3</sup> A. H. FAINBERG and W. T. MILLER, J. Amer. Chem. Soc., 79, 4170 (1957).

ten spectra. The values reported below for the coupling constants, compared with the literature data<sup>4</sup>, indicate the *cis* configuration for this isomer.



$\nu_{F(A)}$	= 3240 cps from $(CF_3CO)_2O$
$\nu_{F(B)}$	= 3270 cps from $(CF_3CO)_2O$
$\nu_{CF_3}$	= -115 cps from $(CF_3CO)_2O$
$J_{H,CF_3}$	$\cong 0$ ; $J_{F(A), CF_3} = 13.5$ cps; $J_{F(B), CF_3} = 6.4$ cps
$J_{F(A), F(B)}$	= not determined; of the order of magnitude of $J_{F(B), CF_3}$

*Cis and trans 1-hydropentafluoropropylene.* - We performed tests for the purpose of establishing beyond doubt that the olefin II is effectively a geometrical isomer of 1-hydropentafluoropropylene, and precisely that it is the *trans* isomer.

Firstly, we wanted to demonstrate that a single compound may be obtained by hydrogenation of the two isomers; to this end, we subjected to hydrogenation in the gaseous phase, over palladium-on-alumina, a mixture constituted of 60% of I and 40% of II. A compound of formula  $C_3F_5H_3$  which is found to be constituted solely of 1,1,1,2,3-pentafluoropropane is derived therefrom, along with a small amount of a hydrogenolysis by-product, identified as 1,1,1,2-tetrafluoropropane.

Next, we treated with bromine, in a closed container exposed to light at room temperature, a sample of pure I: this quantitatively gave a dibromo derivative,  $C_3F_5Br_2H$ , which, by gas chromatography, is found to be constituted of two compounds, III and IV, in respective proportions of about 70% and 30%. They were not able to be separated by distillation and are presumably the two diastereoisomers of



This dibromo derivative, quantitatively dehalogenated with zinc, gave both the olefins I and II, in respective proportions once again equal to about 70% and 30%. By brominating a 60:40 mixture of I and II, we once again obtained the two dibromo derivatives III and IV, again in proportions of about 70% and 30%.

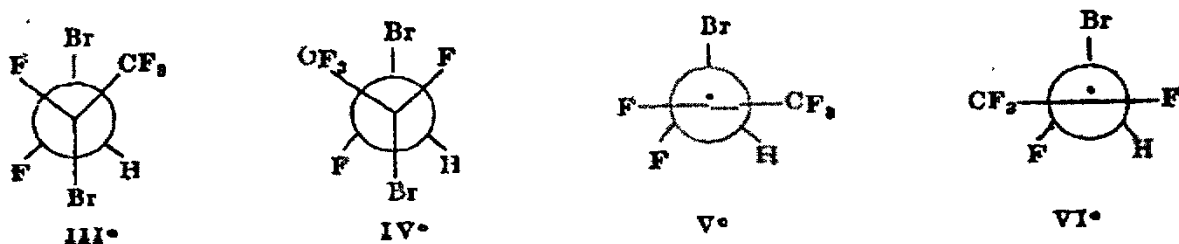
These results may be interpreted by taking into account the fact that the elimination with Zn of two adjacent Br atoms is a reaction which proceeds via a *trans*-stereo specific mechanism ( $E_2$ )<sup>5</sup>: the *threo*-dibromo derivative III consequently gives *cis*-1-

<sup>4</sup> E. G. BRAME, Anal. Chem., 34, 591 (1962), Beaudet Boldeschwieler, J. Mol. Spectros., 9, 30 (1962); Tiers Lanterbur, J. Chem. Phys., 36, 1110 (1962)

<sup>5</sup> S. WINSTEIN, PRESSMAN and YOUNG, J. Amer. Chem. Soc., 61, 1645 (1939); YOUNG et al., ibid., 61, 1640 (1939); 65, 2099 (1943)

hydropentafluoropropylene, while the trans isomer of the olefin is derived from the *erythro* form IV.

By quantitative debromination of  $\text{CF}_3\text{-CFBr-CFBrH}$ , it is thus possible to obtain the two geometrical isomers of  $\text{CF}_3\text{-CF=CFH}$  in a ratio equivalent to that of the two diastereoisomers present in the dibromo derivative. Under the conditions described, the bromination of the olefin proceeds, however, via a radical route and quite probably the common intermediate obtained by addition of a Br atom to both the geometrical isomers is the radical  $\text{CF}_3\text{-CF-CFBrH}$ . On addition of another Br atom, this radical may react, for steric reasons, with a certain preference for the conformation V, rather than the conformation VI. Consequently, independently of the isomeric composition of the starting  $\text{CF}_3\text{CF=CFH}$ , bromination gives a major proportion of the *threo* form III, rather than the *erythro* form IV of 1-hydro-1,2-dibromo-pentafluoropropane.



The ratio observed experimentally for the two diastereoisomers (70:30) corresponds to a difference in free energy between the two conformations V and VI of  $\sim 0.5$  Kcal/mole, this difference being in agreement with what is expected for conformations of the type indicated.

*Cis-trans isomerization of 1-hydropentafluoropropylene.* - Having established with certainty that the two compounds obtained by dehydrofluorination with alkalis of dihydrohexafluoropropane are the two geometrical isomers of 1-hydropentafluoropropylene, and having identified their configuration, we performed a test relating to the relative thermodynamic stability of the two isomers.

To this end, we determined the compositions at equilibrium of their mixture, at various temperatures in the range  $300\text{-}550^\circ$ .

The process adopted consisted in heating in a closed container either a pure isomer or a mixture of the two isomers, for a time sufficient to reach a constant composition for each temperature.

In a few cases, especially at lower temperatures, to accelerate the production of an equilibrium composition, a small proportion (about 0.1%) of bromine was added as catalyst. The results of these experiments are reported in Table I. As may be seen, at a given temperature, the compositions reached at equilibrium starting from the pure cis isomer are equal to those obtained starting from mixtures of the two isomers: a real equilibrium is thus involved.

The equilibrium constant

$$K = \frac{[\text{cis}]_{\text{eq}}}{[\text{trans}]_{\text{eq}}}$$

relating to the  $\text{trans} \rightleftharpoons \text{cis}$  isomerization varies substantially with the temperature. It may be seen in Figure 1 that the variation of  $\log K$  with the inverse of the absolute temperature, in the range examined, is linear with a very good approximation; this may be expressed by the equation:

$$\log K = -0.34 + \frac{870}{T}.$$

We were able to establish that by irradiating with UV light, in the absence of possible catalysts, the isomerization may be obtained even at room temperature between the cis and trans forms. A 40:60 mixture of trans and cis 1-hydropentafluoropropylene, irradiated at room temperature in the gaseous phase, was in fact transformed remarkably quickly, giving rise to a mixture containing more than 99% of cis isomer. This composition is in entire agreement with the equilibrium composition that may be extrapolated from Figure 1 at room temperature.

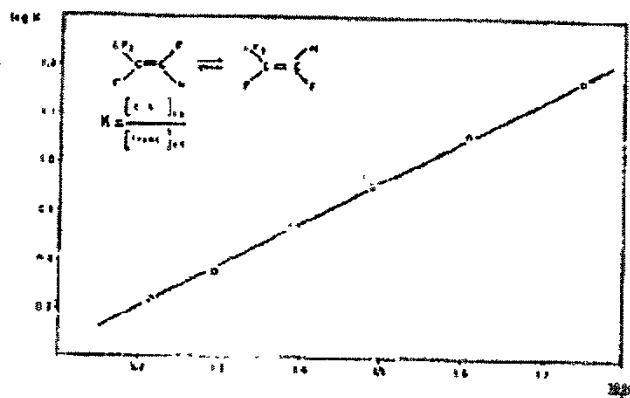


Figure 1 - Equilibrium composition at various temperatures of cis and trans 1-hydropentafluoropropylene

The results obtained make it possible to determine with appreciable accuracy the thermodynamic data relating to the trans-cis isomerization of the olefin. Result:  $\Delta H = +3.9 \pm 0.1$  Kcal/mole;  $\Delta S_{400\text{C}} = -1.45 \pm 0.05$  cal/mole  $^{\circ}\text{K}$ .

It may be observed that while the variation in entropy is practically of the same order of magnitude as that usually observed for these isomerizations, a difference in stability of virtually 4 Kcal in favour of the cis form of 1-hydropentafluoropropylene is appreciably high. This may probably be due in part to the possible formation of hydrogen bonds between the proton in position 1 and the fluorine atoms of the  $\text{CF}_3$  group; this is also confirmed by the very low value of the coupling constant  $JF_{(A)}$ ,  $F_{(B)}$  which indicates a probable deformation of the bond angles.

TABLE I

TRANS-CIS ISOMERIZATION OF 1-HYDROPENTAFLUOROPROPYLENE

Temperature °C	Time Hours	% cis in the initial mixture	% cis in the final mixture	$K = \frac{[\text{trans}] \text{ eq}}{[\text{cis}] \text{ eq}}$
300 (*)	3	100	97.5	-
300 (*)	10	100	93.7	14.9
300 (*)	24	100	93.9	15.4
350 (*)	10	100	92.0	11.5
400	1	95	94.2	-
400 (*)	3	95	90.0	9.0
450	1	95	93.0	-
450 (*)	3	95	88.1	7.4
450 (*)	3	77	88.5	7.7
450 (*)	3	60	88.3	7.5
500	0.2	95	91.4	-
500	1	95	86.0	6.1
500	3	95	85.5	5.9
500	5	95	86.0	6.1
500	5	60	85.5	5.9
550	1	95	84.0	5.25
550	3	95	84.0	5.25

(\*) In the presence of about 0.1 vol% of bromine.

It should also be noted in this respect that, whereas in the 1,2-disubstituted ethylenic derivatives, the *trans* configuration is normally the lower energy configuration, in numerous cases of derivatives substituted with halogen atoms, it is, on the other hand, the *cis* configuration that is the more stable configuration<sup>6</sup>.

<sup>6</sup> R. E. WOOD and D. P. STEVENSON, J. Amer. Chem. Soc., 63, 1650 (1941); K. S. PITSEN and J. L. HELLENBERG, J. Amer. Chem. Soc., 76, 1493 (1954); N. C. CRAIG and E. A. ENTEMANN, J. Amer. Chem. Soc., 83, 3047 (1961).

## EXPERIMENTAL SECTION

*1,2-Dihydrohexafluoropropane.* - The hydrogenation of hexafluoropropylene was performed by sending a stream of 18 NI/hour of  $C_3F_6$  (produced by Montecatini, titre greater than 99.5%) and 20 NI/hour of hydrogen, in a  $5 \times 25$  cm glass tubular reactor containing 120 g of palladium on  $Al_2O_3$  (1.5% Pd) powder, arranged on layers of glass wool. The reactor was immersed in a bath of oil thermally regulated to  $130^\circ C$  and a thermoelectric couple gave an indication of the temperature in the internal reaction zone ( $170-180^\circ C$ ). The exiting gases, washed first with 10% KOH solution and then with concentrated sulphuric acid, were collected by condensation at  $-78^\circ C$ . From 605 g of  $C_3F_6$ , 600 g of crude product were obtained, which, by gas chromatographic analysis (column of silica gel,  $80^\circ$ ), was found to be constituted of 5% of unconverted  $C_3F_6$  and 95% of  $C_3F_6H_2$ . 98% yield. Dihydrohexafluoropropane was obtained in pure form by rectification: b.p.  $-6-6.5^\circ C$ . Molecular weight, by gas density at  $25^\circ C$ , found 153, calc. 152.

*Dehydrofluorination of  $CF_3-CFH-CF_2H$  by pyrolysis.* - A steel tubular reactor, of inside diameter 22 mm, maintained horizontal and filled with fused KCl granules, was used. The tube was heated, with an external oven, over a working length of 70 cm, to a temperature of  $700 \pm 10^\circ C$ , and 300 g of  $C_3F_6H_2$  were fed in, at a constant rate, over a period of 4 hours. The gases exiting the reactor were washed with 10% KOH solution, dried by passing over  $CaCl_2$  granules and collected by condensation at  $-78^\circ C$ . 220 g of crude pyrolysis product were thus obtained. Gas chromatography (column of silica gel) revealed the presence of about 3% of head products, not identified, 20% of unconverted  $C_3F_6H_2$  and 77% of an apparently single product, having an intermediate retention time. This product was separated out by distillation, b.p.  $-18, -22^\circ C$ , and was found to have a molecular weight of 133 (by vapour density at  $25^\circ C$ ) (theoretical for  $C_3F_5H = 132$ ). When subjected to gas chromatographic analysis on a 1 m column of sodium zeolite and 1 m of alumina + 2% squalane ( $t = 40^\circ$ ) it was resolved into three compounds. The compound having the smallest retention time, and present in a proportion of about 30%, was separated out in pure form by gas chromatography and also by accurate fractional distillation: b.p.  $-21^\circ C$ . On IR spectrophotometry, it was found to be identical to a sample of  $CF_3-CH=CF_2$  prepared via another route<sup>7</sup>. The other two isomers, I (53%) and II (17%) at a higher retention time, were separated in pure form only by gas chromatography (2 m column of alumina + 10% squalane,  $80^\circ C$ ) and the IR absorption spectrum in the gaseous phase was recorded therefrom.

<sup>7</sup> R. N. HASZELDINE and B. R. STEELE, J. Chem. Soc., 923 (1954).



- I (cis  $\text{CF}_3\text{-CF=CFH}$ )      C-H  $3135\text{ cm}^{-1}$ ; C=C  $1740\text{ cm}^{-1}$ ; other bands at:  $1395, 1320, 1212, 1180, 1075, 865, 830, 730\text{ cm}^{-1}$ .
- II (trans  $\text{CF}_3\text{-CF=CFH}$ )      C-H  $3092\text{ cm}^{-1}$ ; C=C  $1720\text{ cm}^{-1}$ ; other bands at:  $1410, 1265, 1225, 1177, 1130, 845, 638, 575, 525\text{ cm}^{-1}$ .

*Oxidation of the mixture of I and II.* - 3.8 grams of a mixture constituted of 76% of I and 24% of II were quantitatively oxidized in a solution of  $75\text{ cm}^3$  of acetone with 25 g of  $\text{KMnO}_4$ , by maintaining under reflux with a condenser at  $-78^\circ\text{C}$  for two hours. At the end, the acetone was filtered and evaporated off to dryness; the residual salts were treated in a distillation flask with  $5\text{ cm}^3$  of concentrated  $\text{H}_2\text{SO}_4$ . On heating, 2.8 g (85%) of  $\text{CF}_3\text{-COOH}$  were distilled, b.p.  $73\text{-}6^\circ\text{C}$ .

*Dehydrofluorination of  $\text{C}_3\text{F}_6\text{H}_2$  with KOH.* - 1000 g of 80% KOH were heated to  $140\text{-}150^\circ\text{C}$  in a metal container. By means of a 5 cm weighing tube, 600 g of  $\text{C}_3\text{F}_6\text{H}_2$  were bubbled into this liquid phase, over a period of one hour, the exiting product being collected by condensation at  $-78^\circ\text{C}$ . By distillation, 34 g of untransformed dihydrohexafluoropropane and 480 g of olefin  $\text{C}_3\text{F}_5\text{H}$  (conversion: 92%; 98% yield) were separated out. This olefin, on gas chromatographic analysis, was found to be constituted solely of the isomers I and II, in a ratio of 95:5. Via an accurate fractional distillation, performed at atmospheric pressure with a heat-insulated column, of inside diameter 20 mm, filled to a height of 130 cm with Heli-pack 2917 Podbielniak, it was possible to separate from this mixture 420 g of pure compound I, b.p.  $-18.5^\circ\text{C}$ , and 54 g of a mixture of 60% I and 40% II, b.p.  $-18^\circ\text{C}$ .

*Hydrogenation of cis and trans 1-hydropentafluoropropylene.* - Under the conditions first described for the hydrogenation of  $\text{C}_3\text{F}_6$ , 30 g of  $\text{C}_3\text{F}_5\text{H}$  constituted of 60% of isomer I and 40% of II gave 27 g of crude product which was analyzed by gas chromatography and subjected to fractional distillation. This product was found to be constituted of: 0.9% I; 0.8% II; 5.0% of  $\text{CF}_3\text{-CFH-CH}_3^{(2)}$ , b.p.  $-1\text{-}0^\circ\text{C}$ , molecular weight found 117, calc. 116; 93.3% of  $\text{CF}_3\text{-CFH-CFH}_2^{(2)}$ , b.p.  $20\text{-}2^\circ\text{C}$ , molecular weight (by vapour density at  $100^\circ\text{C}$ ) found 134.5, calc. 134. When analyzed with various gas chromatography columns, this compound was shown to be definitely a single product.

*Bromination of cis and trans 1-hydropentafluoropropylene* - 13 g of bromine and 10 g of cis- $\text{C}_3\text{F}_5\text{H}$  were placed in a  $20\text{ cm}^3$  glass flask, at  $-78^\circ\text{C}$ . The flask, sealed, was maintained at room temperature for about ten hours, exposed to light and stirred gently. The contents of the flask were then washed with a sodium metabisulfite solution, dried and distilled. 21.5 g of the dibromo derivative were thus obtained, b.p.  $89\text{-}90^\circ\text{C}$ ;  $n_D^{20} = 1.3812$ ;  $d_4^{24} = 2.157$ . Analysis:

found %: F 31.90; Br 54.30;  
for  $C_3F_5Br_2H$  calc.: 32.55; 54.77.

This dibromo derivative was chromatographed on a 1 m. carbowax and 2 m diethyl sebacate column ( $t = 70^\circ C$ ) and was found to be composed of two substances, present in proportions of 70% and 30%. A sample of 14.6 g (0.05 g mol) of  $CF_3-CFBr-CFBrH$  was debrominated by the action of 13 g of powdered Zn in 35 cm<sup>3</sup> of boiling ethanol. The gaseous product produced was first collected in a trap cooled with liquid air and then gasified in a gas burette over Hg. 1130 cm<sup>3</sup> (about 95%) of  $CF_3-CF=CFH$  were thus obtained, which is found to be constituted of 70% of cis isomer and 30% of trans isomer.

Under similar conditions, the bromination of 7 g of a 60:40 mixture of cis and trans  $C_3F_5H$  was performed. 15 g of  $C_3F_5Br_2H$  were obtained, and resolved by gas chromatography into the two diastereoisomers again in a ratio of about 70:30.

*Cis trans isomerization of  $CF_3-CF=CFH$ . - Thermal.* - An elongated quartz flask (2 × 20 cm) closed at one end and connected at the other end, via a capillary tube, to a mercury manometer and to a three-way tap, was used as container. The flask was placed inside a heat-regulatable tubular oven; the temperature measurement was given by a thin thermoelectric couple placed in contact with the wall of the flask, in the central area. The flask, already at the desired temperature, was placed under a high vacuum and the olefin  $C_3F_5H$  was introduced therein until atmospheric pressure was reached. In the tests that were performed in the presence of bromine, this was introduced before the olefin and dosed on the basis of a vapour pressure measurement.

After the time desired for the isomerization, the gas contained in the flask was rapidly and quantitatively collected in a container placed under high vacuum and cooled with liquid air. The product was thus gasified and analyzed by gas chromatography.

*Photochemistry.* - The isomerization in this case is performed in a glass flask of capacity 41, equipped with a thermometer, a mercury manometer and an internal quartz sheath in which was housed the UV radiation generator (Hanau, type Q 81, power consumption 70 watts) cooled by circulation of water. The container was placed under a high vacuum and a 60:40 mixture of cis and trans 1-hydropentafluoropropylene was then introduced therein, up to a pressure of 600 mmHg. Irradiation was performed for five hours, during which the temperature of the gas in the flask was maintained at about 25°C and no pressure variation was observed. A sample of gas was then analyzed: this was found to be constituted virtually of pure cis- $CF_3-CF=CFH$ , containing less than 1% of the trans isomer. After continuing the UV irradiation for a further five hours, the composition of the gas did not change further.

We gratefully acknowledge the assistance of Doctor A. L. Segre of the Istituto di Chimica Industriale del Politecnico di Milano, for the section relating to the nuclear magnetic resonance.