*Journal of Fluorine Chemistry*, *36* (1987) 385–394

Received: November 13, 1986; accepted June 10, 1987

# ALKYLATION OF PERFLUORO-2-METHYL-2-PENTYLCARBANION WITH ALKYL AND ALLYL HALIDES

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## SUMMARY

Perfluoro-2-methyl-2-pentylcarbanion, generated from perfluoro-4-methyl-2-pentene in an aprotic solvent, reacted with halides RX, where R = alkyl or allyl and X = I, Br, or Cl, to give fluorohydrocarbons of the general formula $CF_3CF_2CF_2C(CF_3)_2R$. No reaction with iso-propyl iodide and with 1-iodo-2,2,2-trifluoroethane occurred. The reaction with 1-iodo-3,3,3-trifluoropropane resulted in the formation of 3,3,3-trifluoropropene and 2-H-perfluoro-2-methylpentane.

## INTRODUCTION

Compounds having large perfluorinated groups in the molecule because of their numerous applications are of great importance to fluoroorganic chemistry. Looking for methods of the synthesis of such compounds we turn our attention to perfluoro-2-methyl-2-pentylcarbanion. This carbanion, generated from the "thermodynamic" dimer of hexafluoropropene, **viz.** perfluoro-2-methyl-2-pentene, has been reported by Knunyants **et al** [1] to be stable enough to react with benzyl bromide to give an excellent yield of 1-phenyl-2,2-bis (trifluoromethyl)-3,3,4,4,5,5,5-heptafluoropentane, and with allyl bromide to give 4,4-bis(trifluoromethyl)-5,5,6,6,7,7,7-heptafluoro-1-heptene [2]. Reactions of perfluoro-2-methyl-2-pentylcarbanion with oxiranes have also been reported [3].

0022-1139/87/$3.50

We undertook studies on the alkylation of perfluoro-2-methyl-2-pentylcarbanion with alkyl and allyl halides and the results are described in the present paper.

## RESULTS AND DISCUSSION

Perfluoro-4-methyl-2-pentene 1, the "kinetic" dimer of hexafluoropropene, was used as the precursor of perfluoro-2-methyl-2-pentylcarbanion. This alkene in a highly polar solvent undergoes the fluoride ion promoted isomerisation to perfluoro-2-methyl-2-pentene 2 [4-6], which in a reversible addition of fluoride ion forms perfluorocarbanion 3.

$$\underset{\underline{1}}{(CF_3)_2CFCF{=}CF_3} \xrightarrow{F^-} \underset{\underline{2}}{(CF_3)_2C{=}CFCF_2CF_3} \xrightleftharpoons{F^-} \underset{\underline{3}}{CF_3CF_2CF_2\bar{C}(CF_3)_2}$$

Dimer 1 was prepared in nearly quantitative yield and with more than a 95% selectivity by the potassium fluoride induced dimerisation of hexafluoropropene in acetonitrile at ambient temperature.*

Perfluorocarbanion 3 easily substituted halogen atoms, particularly iodine, in alkyl halides 4 to give coupled fluorohydrocarbons 5. Usually, due to the protonation of the carbanion, small amount of 2-H-perfluoro-2-methylpentane, $(CF_3)_2CHCF_2CF_2CF_3$, was formed and when dimethylformamide was used as a solvent, especially at 60°C, certain amount of alkene 1 was consumed by reaction with the solvent to form a complex mixture of unidentified products.

$$\underset{\underline{3}}{CF_3CF_2CF_2\bar{C}(CF_3)_2} \quad + \quad \underset{\underline{4}}{RX} \longrightarrow \underset{\underline{5}}{CF_3CF_2CF_2C(CF_3)_2R} \quad + \quad X^-$$

X = I, Br, (Cl)

4a,5a ; R = $CH_3$- 4b,5b ; R = $CH_3CH_2$- 4c,5c ; R = $CH_3CH_2CH_2$-

4d,5d ; R = $CH_3CH_2CH_2CH_2$- 4e,5e ; R = $CH_2{=}CHCH_2$-

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* *Ishikawa and Mizumo [7] using this same reaction system at 90°C obtained a 89% yield of the mixture of oligomers with a 83% selectivity for dimer 1.*

Yields of fluorohydrocarbons 5 were strongly dependent on the reactivities of alkyl halides 4, on the source of fluoride ion, on the properties of the solvent, and on the reaction conditions. Results are summarised in Table 1.

The highest reactivity towards carbanion 3 was shown by methyl iodide 4a; very high yields of the corresponding alkane 5a were also obtained in the CsF-DMF or CsF-diglyme systems at 20°C as in the KF-DMF system at 60°C. Ethyl iodide 4b, as evidenced by moderate yield of 5b obtained in the KF-DMF system and by no reaction in the KF-diglyme system (Table 1, runs 11 and 12) is less reactive than methyl iodide. Still less reactive are n-propyl iodide 4c and n-butyl iodide 4d; good yields of alkanes 5c and 5d were obtained only in the most active CsF-DMF system at 60°C (Table 1, runs 15 and 19).

Nearly quantitative yield of 5a was obtained from methyl bromide but the comparison of the results obtained under identical conditions from ethyl iodide and ethyl bromide (runs 7 and 13) suggests that, in general, alkyl bromides are less reactive towards carbanion 3 than are the corresponding alkyl iodides.

The influence of a halogen on the rate of its substitution by perfluoro-2-methyl-2-pentylcarbanion has also been shown in the reactions with allyl halides 4e. In the KF-DMF system under the same reaction conditions the bromide gave considerably lower yield of the allylated product 5e than the iodide but the yield obtained from the corresponding chloride was negligible (runs 20, 21, and 22). However, after sufficiently long reaction time both allyl iodide and bromide gave comparable yields of 5e.

The reactions of the highly branched carbanion 3, as could be expected, were found to be strongly sensitive to steric factors; no reaction took place with **iso**-propyl iodide and with primary **iso**-butyl iodide only small amounts of the expected product, **viz.** $CF_3CF_2CF_2$-$C(CF_3)_2CH_2CH(CH_3)_2$ was formed (GLC identification only).

The order of reactivities of the halides investigated so far towards perfluoro-2-methyl-2-pentylcarbanion 3 is as follows:

$$\mathrm{MeI,MeBr} > \mathrm{EtI,AllI} > \mathrm{n\text{-}PrI,n\text{-}BuI,} \gg \mathrm{EtBr} > \mathbf{iso}\text{-}\mathrm{BuI,AllCl} \gg$$
$$> \mathbf{iso}\text{-}\mathrm{PrI}$$

TABLE 1

Reactions of perfluoro-2-methyl-2-pentylcarbanion 3 with alkyl and allyl halides 4.

| Run | Alkyl halide | Reaction conditions | | | | Products ratio[a] | | | Yield of 5 |
|---|---|---|---|---|---|---|---|---|---|
| | | MF | Solvent | Temp. ($^{o}$C) | Time (h) | 5 | 2 + 8 | 4 | (mole %)[b] |
| 1 | $CH_3I$ | CsF | DMF | 20 | 20 | 90.5 | 9.5 | | 77.5 |
| 2 | | CsF | diglyme | 20 | 18 | 91.6 | 8.5 | | 78.8 |
| 3 | | KF | DMF | 20 | 66 | 25.2 | 73.1 | 1.7 | 18.8 |
| 4 | | KF | DMF | 60 | 18 | 98.2 | 0.8 | | 77.1 |
| 5 | | KF | diglyme | 60 | 18 | 30.3 | 65.3 | 4.4 | 26.1 |
| 6 | $CH_3Br$ | CsF | DMF | 18 | 48 | 99.0 | 1.0 | | 99.0 |
| 7 | $CH_3CH_2I$ | CsF | DMF | 20 | 18 | 78.6 | 17.5 | 3.9 | 67.8 |
| 8 | | CsF | DMF | 60 | 18 | 90.9 | 3.6 | 5.5 | 87.5 |
| 9 | | CsF | diglyme | 20 | 18 | 86.0 | 9.7 | 4.3 | 80.3 |
| 10 | | CsF | diglyme | 60 | 18 | 93.6 | 3.1 | 3.3 | 87.6 |
| 11 | | KF | DMF | 60 | 18 | 39.3 | 37.2 | 12.2[c] | 35.6 |
| 12 | | KF | diglyme | 150 | 18 | | 100.0 | | |
| 13 | $CH_3CH_2Br$ | CsF | DMF | 18 | 48 | 19.1 | 77.4 | 3.5 | 17.0 |
| 14 | $CH_3(CH_2)_2I$ | CsF | DMF | 20 | 18 | 52.4 | 30.1 | 17.5 | 42.0 |
| 15 | | CsF | DMF | 60 | 18 | 81.2 | 10.2 | 9.6 | 75.7 |

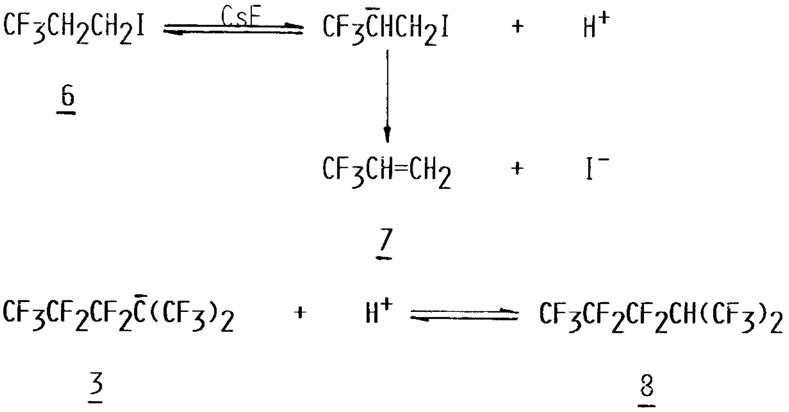
| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 16 | | CsF | diglyme | 20 | 18 | 50.0 | 37.7 | 11.3 | 43.2 |
| 17 | | KF | DMF | 60 | 18 | 8.6 | 23.2 | 36.6[c] | 7.6 |
| 18 | $CH_3(CH_2)_3I$ | CsF | DMF | 20 | 18 | 47.9 | 41.1 | 11.0 | 43.0 |
| 19 | | CsF | DMF | 60 | 18 | 72.6 | 16.5 | 10.9 | 74.8 |
| 20 | $CH_2$=$CHCH_2I$ | KF | DMF | 60 | 18 | 68.4 | 18.3 | 5.6[c] | 63.7 |
| 21 | | KF | DMF | 60 | 36 | 75.3 | 14.5 | 5.5[c] | 70.8 |
| 22 | $CH_2$=$CHCH_2Br$ | KF | DMF | 60 | 18 | 48.7 | 27.5 | 13.0[c] | 44.0 |
| 23 | | KF | DMF | 60 | 42 | 74.9 | 4.0 | 2.1[c] | 70.2 |
| 24 | $CH_2$=$CHCH_2Cl$ | KF | DMF | 60 | 18 | 11.2 | 31.3 | 21.9[c] | 7.5 |
| 25 | $(CH_3)_2CHI$ | CsF | DMF | 60 | 18 | | 60.6 | 20.9[c] | |
| 26 | $(CH_3)_2CHCH_2I$ | CsF | DMF | 60 | 18 | 11.7 | 52.7 | 35.6 | 6.2 |

[a] GLC estimate in the crude reaction mixture after removal of the solvent.

[b] GLC yields based on the amount of the crude mixture of products.

[c] A number of unidentified products of high retention time was. also present.

Attempted alkylations of carbanion 3 with short-chain iodo-trifluoroalkane failed. No reaction occurred with 1-iodo-2,2,2-trifluoroethane. The reaction mixture consisted of the substrate, dimer 2, and 2-H-perfluoro-2-methylpentane 8*. The reaction with 1-iodo-3,3,3-trifluoropropane 6 in the CsF-DMF system resulted in total dehydroiodination of 6 to give 3,3,3-trifluoropropene 7 and in protonation of the carbanion to give compound 8. This was because of the acidity of the central carbon atom in iodo-trifluoropropane 6 and because of the basicity of caesium fluoride. No reaction occurred when potassium fluoride was used instead of caesium fluoride.



New fluorohydrocarbons 5a-d are colourless liquids; boiling points, mass spectra, and elemental analyses are given in Table 2 and the $^{19}F$ and $^1H$ NMR data in Table 3. The $^{19}F$ NMR spectra showed a characteristic pattern consisting of four signals. These compounds are stable liquids immiscible with water and with methanol. They distill without decomposition and the methyl derivative 5a showed extreme thermal stability; when passed in a stream of nitrogen through a quartz tube at 400°C no visible decomposition occurred [8]. These compounds are able to dissolve large amounts of oxygen and carbon dioxide.

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* *It has been checked in separate experiments that heating of a mixture of dimer 1, DMF, and CsF or KF in the absence of an alkyl halide always leads to the formation of certain amounts of 8.*

TABLE 2

Properties and analyses of fluorohydrocarbons 5.

| Compound | M.W. | B.p. (°C) | Mass spectrum m/z (rel.intensity) | Found/calculated C | H | F |
|---|---|---|---|---|---|---|
| $CF_3CF_2CF_2C(CF_3)_2CH_3$ 5a | 334.09 | 89.0 | 315(3)(M-F)$^+$, 227(11), 215(14), 195(5) 177(14), 169(12), 145(7), 127(39), 119 (7), 77(16), 69(100) | 25.26/25.16 | 0.83/0.91 | 73.93/73.93 |
| $CF_3CF_2CF_2C(CF_3)_2CH_2CH_3$ 5b | 348.12 | 110.5 | 229(4)(M-$C_2F_5$)$^+$, 169(4), 145(4), 100(4) 69(28), 47(14), 29(100), 28(12), 27(10) | 27.65/27.60 | 1.30/1.45 | 70.95/70.95 |
| $CF_3CF_2CF_2C(CF_3)_2CH_2CH_2CH_3$ 5c | 362.15 | 123.5 |  | 29.65/29.85 | 1.80/1.95 | 68.22/68.20 |
| $CF_3CF_2CF_2C(CF_3)_2CH_2(CH_2)_2CH_3$ 5d | 376.18 | 138.0 |  | 32.02/31.93 | 2.37/2.41 | 65.67/65.66 |
| $CF_3CF_2CF_2C(CF_3)_2CH_2CH{=}CH_2$ 5e | 360.00 | 119.5* | 360(11)M$^+$, 191(24), 171(27), 151(12) 145(36), 119(4), 69(37), 41(100), 39(22) | 29.83/30.01 | 1.30/1.40 | 68.60/68.59 |

* Reported b.p. 116 - 118°C [2].

TABLE 3

$^{19}F$ and $^{1}H$ NMR data for compounds 5.*

$\overset{a}{C}F_3\overset{b}{C}F_2\overset{c}{C}F_2C(\overset{d}{C}F_3)_2R$

| Nucleus | Chemical shift (p.p.m.)** | | | | |
|---|---|---|---|---|---|
| | 5a | 5b | 5c | 5d | 5e |
| F(a) | 80.5(t) | 80.7(t) | 80.6(t) | 80.7(t) | 80.8(t) |
| F(b) | 109.7(sp) | 107.7(sp) | 107.6(sp) | 107.6(sp) | 107.6(sp) |
| F(c) | 122.2 | 123.7 | 123.5 | 123.2 | 123.4 |
| F(d) | 66.8(qn) | 63.9(qn) | 63.9(qn) | 63.8(qn) | 61.1(qn) |
| H($CH_3$) | 1.78 | 1.30 | 1.00 | 0.97 | |
| H($CH_2$) | | 2.35 | 1.75<br>2.20 | 1.40<br>1.70<br>2.22 | 3.02(d)*** |

t - triplet, qn - quintet, sp - septet

* Observed F-F coupling constants: J(FaFc) = 13.7 - 14.3 Hz, and J(FbFd) = J(FcFd) = 11.2 - 11.6 Hz.

** From internal $CCl_3F$ for $^{19}F$ (positive upfield) and from internal TMS for $^{1}H$ spectra

*** Vinylic protons: $\delta$ = 5.33(d), 5.38(d), and 5.92 p.p.m., J(**trans** H-H) = 16 Hz, and J(**cis** H-H) = 4 Hz.

## EXPERIMENTAL

Boiling points were determined by distillation or in capillary (Sivoloboff) and are uncorrected. The $^{1}H$ and $^{19}F$ NMR spectra were recorded with a JEOL-4H-100 spectrometer and the mass spectra with an Analytical GCMS System LKB-2091. The GLC analyses were performed with a Chromatron GCHF.18.3.4. instrument (G.D.R.) using a 3.5 m x 4 mm column packed with Chromosorb G coated with 3% Silicon Oil SE-52.

Alkyl halides 4 were pure grade commercial reagents. 1-Iodo-2,2,2-trifluoroethane and 1-iodo-3,3,3-trifluoropropane were prepared from iodoacetic acid and 3-iodopropionic acid, respectively, by fluorination with sulphur tetrafluoride [9].

Dimethylformamide was purified by the azeotropic (benzene-water) removal of impurities, distillation under reduced pressure, and drying over molecular sieves 4A until the content of water dropped below 0.02%.Diglyme was purified by refluxing with sodium metal until blue with benzophenon, distillation, and then redistillation from lithium aluminium hydride.

## Alkylation of perfluoro-2-methyl-2-pentylcarbanion 3 with alkyl halides 4.

The reactions were carried out in a glass pressure tube fitted with the Rotaflo valve. Freshly heated caesium fluoride (7.0 g, 46 mmole) or potassium fluoride ( 4.0 g, 68 mmole) was placed in the reaction tube and a mixture of dimer 1 (12 g, 40 mmole), alkyl halide (40 mmole), and dimethylformamide (30 ml) was quickly added. The tube was vigorously shaken and, if required, heated (with a flexible heating band) for the required time. The reaction mixture was diluted with water, the bottom organic layer was separated, washed with water, dried over anhydrous magnesium sulphate, and subjected to the GLC analysis (Table 1). Combined products of a few runs were distilled through a Büchi Fisher-type column to give fluorohydrocarbons 5 of 99.5 - 99.9% purity (GLC estimate). Lower boiling fractions (47 - 60°C) were identified by the $^{19}$F NMR spectroscopy as mixtures of the dimer 2 [6] and 2-H-perfluoro-2-methylpentane 8 [10].

## Reaction of dimer 1, caesium fluoride, and 1-iodo-3,3,3-trifluoropropane 6.

Caesium fluoride (3 g, 20 mmole), dimer 1 (6 g, 20 mmole), 1-iodo-3,3,3-trifluoropropane 6 (4.9 g, 20 mmole), and dimethylformamide (25 ml) were placed in the reaction tube and shaken at 60°C for 18 hours. After the reaction the tube was found to contain large amount of a gas under high pressure. The tube was immersed in liquid nitrogen, evacuated, and the volatile products were distilled under vacuum into two traps, the first immersed in a dry ice - acetone bath, the second in liquid nitrogen. A product collected in the first trap remained liquid when warmed up to ambient temperature (vapour pressure ca. 60 Torr). It was shown by the GLC to consist of two compounds in the ratio of 22 : 78; these compounds were separated by distillation and identified by the NMR spectroscopy as dimer 2 and 2-H-perfluoro-2-methylpentane 8, respectively. A product collected in the second trap was evaporated into calibrated volume to give 17.3 mmole of a gas which was identified by the IR spectroscopy (100 mm cuvette, pressure = 5 Torr) as 3,3,3-trifluoropropene 7 (the spectrum was identical with that of an authentic sample).

## ACKNOWLEDGMENT

This work has been supported by the Polish Academy of Sciences within the project C.P.B.P.-01.13.1.21.

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