

Skeletal Rearrangements during the Fluorination of C₆-Hydrocarbons over Cobalt(III) Trifluoride

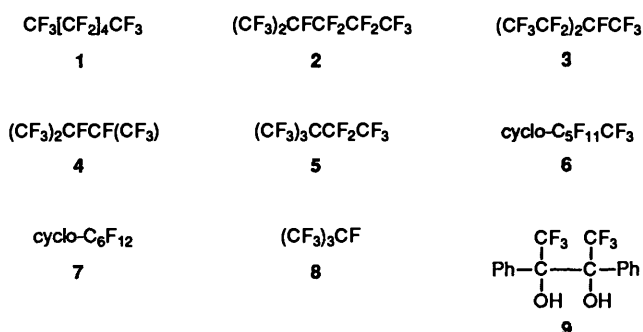
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Perfluorination of hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, methylcyclopentane and cyclohexane over cobalt(III) trifluoride gave, in each case except perhaps cyclohexane, a mixture of linear, branched and cyclic C₆-fluorocarbons: the degree of skeletal rearrangement (excluding cyclohexane) varied from *ca.* 7% (methylcyclopentane) to 96% (2,2-dimethylbutane). A carbocation mechanism, which does not proceed to equilibrium, is suggested.

It is becoming clear^{1,2} that both major methods of perfluorination—the electrochemical method and the use of transition metal fluorides—can lead to extensive skeletal rearrangements of hydrocarbon chains and rings. For example, a linear C_n-chain can give a mixture of linear, branched and cyclic C_n-products. Early workers^{3a} detected cyclic products from the cobalt trifluoride fluorination of linear hydrocarbons but, hardly surprisingly given their lack of NMR techniques, missed³ the isomerization to branched ones. There has, in fact, been no systematic study of this phenomenon and we now report an example: the perfluorination, over cobalt trifluoride, of several C₆-hydrocarbons (hexane, 2-methylpentane, 3-methylpentane, 2,2-dimethylbutane, 2,3-dimethylbutane, methylcyclopentane and cyclohexane).

Results and Discussion

The fluorinations were carried out in the usual way^{4–6} on the C₆-compounds listed above, with the perfluoro products being separated from the hydrofluoro products by azeotropic distillation with propanone.⁷ The mixtures of perfluoro compounds were analysed by ¹⁹F NMR spectroscopy (the spectral analyses were quite straightforward, see Table 2), mainly by integration of the CF₃ signals. The products were 1–7 (Scheme 1), with 8 being formed in one case.



Scheme 1

The results are summarized in Table 1. The figures for the cyclohexane fluorination should be treated with caution (see Experimental section).

The skeletal rearrangements during the fluorinations are clearly not reaching equilibrium—if they were then the open-chain substrates, at least, would give the same product mixture. It may be of interest to note that with the C₆-hydrocarbons the equilibrium composition lies in favour⁸ of 2,2-dimethylbutane: this skeleton is most definitely not favoured in our fluorinations.

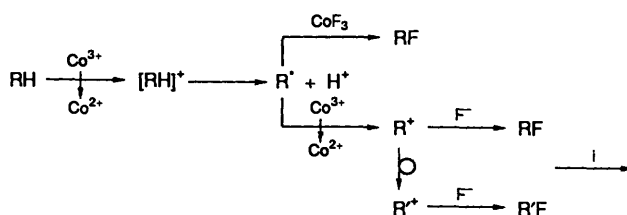
Table 1 Product Composition from the Fluorination of C₆-Hydrocarbons

| Substrate | Product (mole %) ^a | | | | | | |
|---------------------------------|-------------------------------|----------|----------|----|----|----------|-----|
| | 1 | 2 | 3 | 4 | 5 | 6 | 7 |
| Hexane | 76 | 11 | 5 | 0 | 1 | 7 | 0 |
| 2-Methylpentane | 9 | 55 | 9 | 0 | 2 | 25 | 0 |
| 3-Methylpentane | 7 | 9 | 57 | tr | 1 | 21 | 0 |
| 2,2-Dimethylbutane ^b | tr | 18 | 16 | 4 | 43 | 12 | tr |
| 2,3-Dimethylbutane | tr | 21 | 7 | 5 | 50 | 17 | 0 |
| Methylcyclopentane | 4 | 1 | 1 | 0 | 0 | 93 | tr |
| Cyclohexane | <i>c</i> | <i>c</i> | <i>c</i> | 0 | 0 | <i>d</i> | 100 |
| 3-Methylpent-2-ene | 7 | 7 | 61 | tr | 1 | 24 | 0 |

^a This Table gives the composition of the perfluoro C₆-product of Table 3. ^b *ca.* 7% of (CF₃)₃CF (8) also detected. ^c Trace quantities probably present—analysis difficulties (see NMR analysis section). ^d *ca.* 2% almost certainly present.

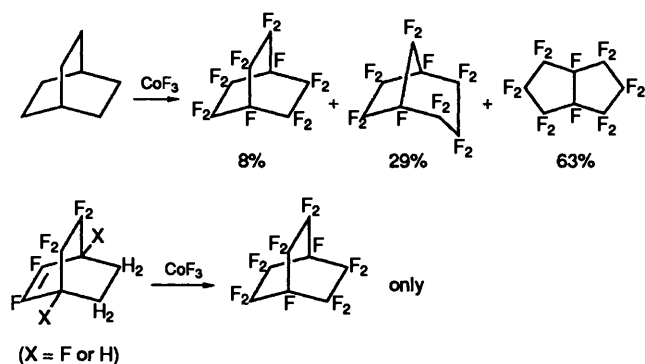
With the C₆-carbocations, only tertiary species would be found⁹ at equilibrium; again this is not favoured in the present work—consider hexane itself. Nevertheless, we suggest that our results are best explained by the formation of carbocation intermediates in the fluorinations, with these cations only rearranging early in a fluorination because heavily fluorinated cations would not be expected to rearrange as there would be no suitable migrating group. Alternatively, carbocations might only form early in a fluorination, with the radical intermediates being quenched by the equivalent of fluorine atoms rather than being oxidized to the cations. Consistent with this, the pinacol 9 (Scheme 1) is known not to rearrange, even under forcing conditions,¹⁰ either because the usual initiating cation does not form, or, more likely, because it does not rearrange [the cation PhCH⁺(CH₃)CF₃ is known¹¹ to form from the corresponding alcohol, albeit under very forcing conditions].

We propose, as an outline, the mechanism shown in Scheme 2.

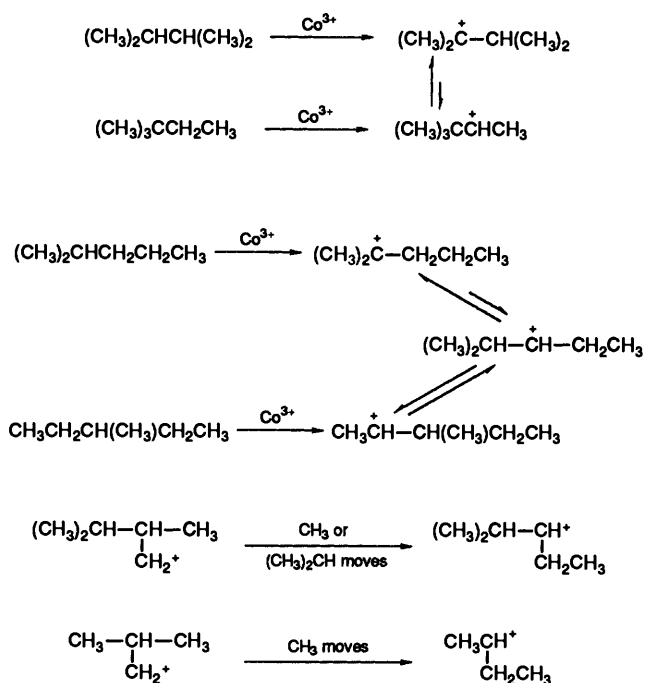


Scheme 2 *i*, Followed by further similar steps on RF and R'F

An initial oxidation of a substrate to a radical cation by Co³⁺ is established¹² in the case of aromatics; the later steps



Scheme 3



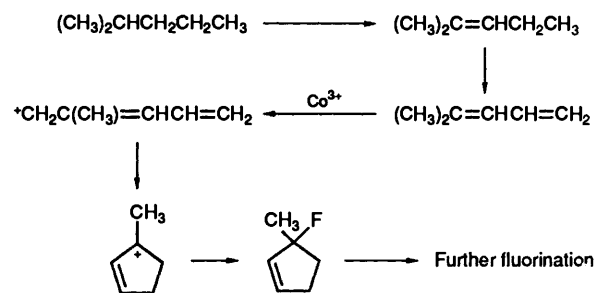
Scheme 4

(oxidation of radical to cation, quenching of cation by F^-) also bear considerable resemblance to steps in the aromatic fluorination mechanism.

Carbocation rearrangements during cobalt trifluoride fluorinations have been noted before¹³ (Scheme 3). Of further interest here is the absence of rearrangement when partially fluorinated bicyclo[2.2.2]octenes are fluorinated: as mentioned above, this suggests that either carbocations do not form late in a fluorination,¹³ or, if they do, they do not rearrange.

It is easy to see how the 2- and 3-methylpentane and the 2,2- and 2,3-dimethylbutane skeletons can interconvert *via* their relatively stable secondary and tertiary cations (Scheme 4), but there are problems with other interconversions. At first sight, it would seem that the 2,3-dimethylbutane skeleton could convert into the 2-methylpentane as shown in Scheme 4. However, if this can occur, then why does the conversion of 2-methylpropane to butane not occur⁵ during fluorination? A further problem is the interconversion of linear and branched structures: for these to proceed *via* carbocations, rearrangements into very unstable primary cations must occur, in which case why is butane not converted⁶ to 2-methylpropane during fluorination? There may be a route *via* protonated cyclopropanes, but we leave discussion of this and other points until we have obtained further data.

A final apparent anomaly is the formation of perfluoromethyl-



Scheme 5 Note: this sequence could occur later in the fluorination as well

cyclopentane as overwhelmingly the major cyclization product, even though the six-membered ring is stable to fluorination [this same point had been noted by early workers^{3a} in the cobalt(III) trifluoride fluorination of octane]. This may occur through dehydrogenation (exemplified in Scheme 5) which is known to take place during fluorinations—tetrahydrothiophene formed some thiophene (over $KCoF_4$)¹⁴ and cyclohexane some benzene (over CeF_4)¹⁵ under rather special conditions, and in both cases the fluorination products from the aromatics and their saturated counterparts were the same (the conversion of cyclohexane into benzene may go some way towards explaining why the six-membered ring remains largely intact during fluorination). We have tested the possibility of dehydrogenation in the aliphatic field by fluorinating 3-methylpent-2-ene (Table 1): the product composition was much the same as that from 3-methylpentane. Although this does not prove that desaturation occurs during the fluorination of aliphatics, it does show that it cannot be ruled out.

An alternative possibility for all our rearrangements and cyclizations is that they are due not to cobalt(III) trifluoride, but to the hydrogen fluoride produced during the fluorinations. At the high temperatures involved, HF induced reactions certainly cannot be dismissed lightly. We have, however, largely excluded this possibility by fluorinating 2-methylpentane under conditions where not all of it reacted. The *ca.* 10% of hydrocarbon recovered was still 2-methylpentane and contained <1% of any other hydrocarbon. Since the perfluorocarbon products from the fluorination of this substrate were rearranged or cyclized to the extent of 45% (Table 1), this result shows clearly that an HF-catalysed process does not occur at the hydrocarbon stage. In any case, even if it had, it should have favoured⁸ 2,2-dimethylbutane, the skeleton least favoured in our fluorinations.

As mentioned earlier, rearrangements at partially fluorinated stages seem not to occur,¹³ although the particular example (a bicyclo[2.2.2]octene) was different from any of those in the present work.

All this strongly suggests that HF-catalysed rearrangements and cyclizations do not occur during cobalt(III) trifluoride fluorinations, although it must be admitted that they cannot be excluded with certainty at very lightly fluorinated stages, or for alkene intermediates. Such possibilities would be very difficult to test experimentally.

There is a possibility of C-C bond cleavage at the high temperatures of fluorination. Low boiling materials ($\leq C_4$) would have been lost because of our isolation procedure, and this may be the explanation for the low yields obtained in the fluorinations of the two dimethylbutanes. Indeed, with 2,2-dimethylbutane a very small amount of perfluoro-2-methylpropane (**8**) was detected. Homolytic cleavage of the $(CH_3)_3C-CH_2CH_3$ bond is the obvious possibility [and similarly with $(CH_3)_2CH-CH(CH_3)_2$], but carbocation routes cannot be ruled out.

Table 2 ^{19}F Spectral Assignments^a

| Compound | Shifts ^{b,c} | Carbon atom | Couplings/Hz to CF_3^c |
|--|-----------------------|-------------|---|
| $^1\text{CF}_3^2\text{CF}_2^3\text{CF}_2\text{CF}_2\text{CF}_2\text{CF}_3$ | 81.3 (81.2) | 1 | The signal is an apparent triplet (12.8) but extra lines show that it is second-order |
| | 122.5 (122.4) | 3 | |
| | 126.1 (125.9) | 2 | |
| $(^1\text{CF}_3)_2^2\text{CF}^3\text{CF}_2^4\text{CF}_2^5\text{CF}_3$ | 72.5 (72.0) | 1 | $J_{1,2}$ 5.8; $J_{1,3}$ |
| | 185.6 (185.8) | 2 | 11.6; $J_{1,4}$ 8.7; |
| | 114.9 (115.0) | 3 | $J_{2,5}$ 1.4; $J_{3,5}$ |
| | 124.7 (124.8) | 4 | 12.4 (12.2) |
| $(^1\text{CF}_3^2\text{CF}_2)_2^3\text{CF}^4\text{CF}_3$ | 81.0 (80.8) | 5 | $J_{1,4}$ and $J_{3,4}$ 7.2; $J_{2,4}$ 10.9; $J_{2,4}$ 14.5. The CF_3 -1 signal is very complex and clearly second-order |
| | 80.4 (80.3) | 1 | |
| | 117.3 (116.7) | 2 | |
| | 184.7 (184.4) | 3 | |
| | 71.3 (71.0) | 4 | |

^a Only those compounds (1–3) for which hitherto unrecorded parameters have been measured are tabulated. The spectral details for compounds 4–8 were very similar to those cited in the literature.^{2,5} ^b In ppm upfield from CFCl_3 . ^c Literature values^{2,5} in parentheses.

Table 3 Fluorination of C_6 -hydrocarbons over cobalt(III) trifluoride

| Substrate | Starting quantity/g | Crude product/g | Perfluoro- C_6 -product/g ^a |
|--------------------|---------------------|------------------|---|
| Hexane | 67 | 164 | 64 |
| 2-Methylpentane | 50 | 123 | 74 |
| 3-Methylpentane | 50 | 101 | 60 |
| 2,2-Dimethylbutane | 50 | 26 | 13 |
| 2,3-Dimethylbutane | 50 | 61 | 33 |
| Methylcyclopentane | 200 | 202 | 138 |
| Cyclohexane | 80 | 360 ^b | 230 ^b |
| 3-Methylpent-2-ene | 21 | 33 | 8 |

^a See Table 1 for the composition of these products. The weight differences between this column and the previous one are attributable mainly to partially fluorinated materials-fluorohydrocarbons. ^b The crude product is semi-solid. It was purified by washing with water, skimming the semi-solid mass from the surface of the water and drying this by pressing it between filter papers. It is difficult to handle and considerable losses can result due to its volatility.

Experimental

Fluorinations.—*2-Methylpentane.* The pentane (50 g) was fluorinated in a stirred tubular reactor⁴ by adding it dropwise to a heated (360 °C) bed of cobalt(III) trifluoride (10 kg) over 3 h. The product was collected in a cooled (−78 °C) trap and residual products were swept from the reactor with nitrogen (25 dm³ h^{−1}) for 2 h. The total product (123 g), after being washed with water, was mixed with an equal volume of propanone, distilled through a vacuum-jacketed column packed with Dixon gauze spirals, and condensed into a Dean–Stark trap. The mixed perfluoro- C_6 products (74 g) collected as a lower layer and were separated, washed with water and dried (CaCl_2), and a sample was subjected to ^{19}F NMR analysis (Table 2). GC and NMR analysis of the distillation residue showed it to be very complex, and to contain hydrogen.

The fluorinations of the other substrates were carried out in a similar manner, and the results are summarized in Table 3.

When a similar fluorination was carried out on 2-methylpentane (30 g) but introducing it to the reactor over a shorter period (1 h), the crude product (38 g), analysed by GLC, contained ca. 10% (by volume) of unreacted starting material, together with a larger number of partially fluorinated products, some of which had the same GLC retention times as the other C_6 -hydrocarbons used in the present study. Extraction of 21 g of this product with benzyl alcohol (2 × 12 g), followed by vacuum stripping (ca. 0.4 mmHg at room temperature) of the extracted hydrocarbon from the alcohol, gave 2-methylpentane (0.74 g), which was identified by ^{13}C NMR spectroscopy, and which contained <1% of any of the other C_6 -hydrocarbons used in this study. GLC analyses were carried out with dinonyl phthalate as the stationary phase. Benzyl alcohol also extracted very small quantities of fluoro- and fluorohydro-carbons which were insufficient to interfere with the GLC analysis. The benzyl alcohol left after vacuum stripping still contained some 2-methylpentane, but again <1% of any of the other hydrocarbons.

NMR Analysis.— ^{19}F NMR spectra were run on a Perkin-Elmer R12B (56.4 MHz) or a JEOL FX90 (84.26 MHz) on neat crude samples, except for the cyclohexane product (largely solid perfluorocyclohexane) which was measured in dilute solution in CHCl_3 . The considerable dilution necessary to achieve solution of the perfluorocyclohexane made the minor products much more difficult to detect and, hence, to analyse accurately. Spectral assignments are given in Table 2.

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