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REARRANGEMENTS DURING THE EXHAUSTIVE FLUORINATION OF ALIPHATIC HYDROCARBONS

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Fluorination of aromatic compounds with transition metal fluorides (CoF_3, MnF_3, etc) takes place via radical cations and is relatively well understood; for aliphatic substrates this is not so.

Fluorination of n-butane and iso-butane over CoF_3 shows that the ease of replacement of aliphatic H by F falls in the order: tert-C-H >sec.-C-H >prim. -C-H, although this can be affected by the amount of fluorine already in the molecule.

Skeletal rearrangements occur during the CoF_3 fluorination of hydrocarbons and increase as the length of the chain increases, being $\sim$ 1% for butane and $\sim$50% for octane Skeletal modifications are also observed with cyclic compounds (e.g. cyclodecane $\xrightarrow{CoF_3}$ perfluorodecalin). Chain-branching and ring formation both occur. These rearrangements and modifications are markedly suppressed if a small amount of fluorine is present in the substrate.

It is suggested that both radical and carbocationic species (not primary) are involved in the fluorination, with the latter becoming less prevalent as the amount of fluorine in a molecule increases. The rearrangements are postulated to occur in the carbocations via protonated cyclopropanes.

Skeletal rearrangements also occur in the aliphatic portions of molecules subjected to electro-chemical fluorination; carbocations are again probably involved.

Exhaustive fluorination with elemental fluorine, although difficult to carry out on a large scale, does not lead to rearrangement; radical intermediates are probable here.

If pure linear fluorocarbons are required, then at present only elementa fluorine or procedures originating with telomerization may be employed.