

An intermolecular migration of trifluoromethyl anion

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Abstract

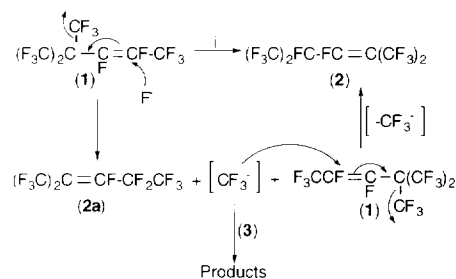
A fluoride-ion-induced rearrangement of a perfluorinated alkene perfluoro-4,4-dimethylpent-2-ene proceeds by migration of trifluoromethyl, giving perfluoro-2,4-dimethylpent-2-ene. It has been demonstrated that this rearrangement involves intermolecular transfer of trifluoromethyl as an anion

Keywords: Perfluorinated alkenes; Trifluoromethyl anion; Intermolecular migration.

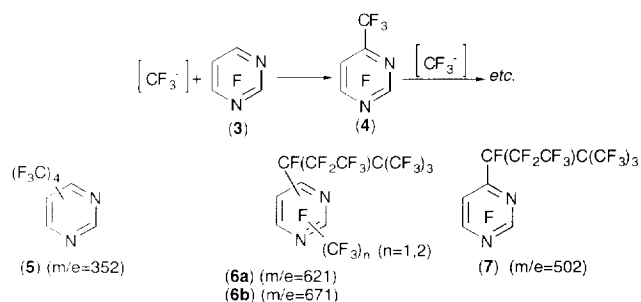
Fluoride-ion-induced reactions of perfluoroisobutene and perfluoropropene gave perfluoro-4,4-dimethylpent-2-ene **1**, using a cooled system [1a], but perfluoro-2,4-dimethylpent-2-ene **2** was obtained when the fluorinated alkenes were reacted over caesium fluoride at 200 °C [1b]. We now find that **1** undergoes a remarkable rearrangement to **2** on heating with caesium fluoride. Reaction of **1** with dry caesium fluoride in sulpholan, in a stirred system at 150–160 °C, for 5 h, gave **2** in almost quantitative yield, although potassium fluoride was ineffective for the process. The structure of **2** followed simply from the ¹⁹F NMR spectrum, which showed δ_f : –54.2 and –58.2, each int. 3, [=C(CF₃)₂]; –73.2, int. 6, [(CF₃)₂CF–]; –94.3, int. 1, (–CF=); and –182.3 ppm, int. 1, [(CF₃)₂CF–].

This unusual migration of trifluoromethyl attracted our interest, and we have attempted to establish the nature of the migrating species. It seemed most likely that trifluoromethyl anions would be involved, but we were surprised at the high efficiency for such a process, since we might have anticipated significant loss of fluoride from this relatively unstable species. However, a mechanism involving migration of trifluoromethyl as a radical could also be described.

We have conducted trapping experiments using perfluorinated heterocyclic compounds that are well-known to be highly susceptible to nucleophilic attack (see, for example, Ref. [2]), in the hope of intercepting trifluoromethyl anions, but not radicals. When pentafluoropyridine was added to the reaction mixture, **1** was converted to **2** without any significant reduction in the yield of **2**. However, in an analogous exper-



Reagents and conditions: i, CsF, sulpholan, 150–160 °C, 5h.



Scheme 1.

iment in which tetrafluoropyrimidine **3** was added, then the reaction product did not contain any of **2**. It has previously been established that tetrafluoropyrimidine **3** is about 2000 times more reactive to nucleophiles than pentafluoropyridine [3], and this difference has allowed the trapping agent **3** to compete efficiently with **1** for the displaced anions.

The products of the trapping experiments were complex mixtures, from which we could only obtain meaningful infor-

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mation by mass spectrometry/GLC. Nevertheless, analysis of the mixtures using this technique showed clear evidence for various trifluoromethylpyrimidine derivatives, e.g. **4** and **5**, but these were accompanied by a variety of mixed systems in which anions derived from **1**, by addition of fluoride ion, could be discerned, e.g. **6a**, **6b** and **7**. However, we did not see strong evidence for significant concentrations of the intermediate alkene **2a**, and we concluded that **2a** is probably present in the mixture as the stable tertiary carbanion, formed by addition of fluoride ion to **2a**, which, of course, would not be observed by MS–GC. It was not feasible, however, to separate this complex system.

These results enable us to write a simple mechanism for the conversion of **1** to **2**, as shown in Scheme 1, and the efficiency of the process indicates that the trifluoromethyl anion has a relatively short lifetime before interception by **1** or **3** in the trapping experiments.

References

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