Journal of Fluorine Chemistry, 10 (1977) 157 – 158
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Received: March 1, 1977

SHORT COMMUNICATION

Perfluoro-[bis(methyl)propyl]methylcarbanion - a new stable perfluorocarbanion

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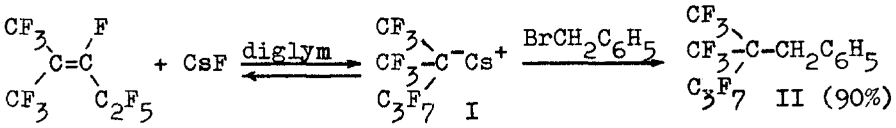
It is known that perfluoroolefins are capable of a reversible fluoride ion addition in polar aprotic solvents to give the respective perfluorocarbanions [1,2]. Such perfluorocarbanions are extensively applied as perfluoroalkylating agents [3]. Synthetical usefulness of this method is limited by the ability of most perfluoroolefins (both in aliphatic [4,5] and alicyclic [6] series) to oligomerise under the action of fluoride ion. This explains why perfluorotert.-butylanion is the most convenient perfluoroalkylating agent formed readily upon addition of fluoride ion to perfluoroisobutene: the reactions involving this perfluorocarbanion usually are not accompanied by formation of oligomeric products [7].

The present work is concerned with the synthesis of a new stable tertiary perfluoro-[bis(methyl)propyl]methylcarbanion (1), produced in the course of a reversible fluoride ion addition to perfluoro-2-methyl-2-pentene, the readily available hexafluoropropene dimer [8]. This perfluorocarbanion easily reacted with electrophilic agents. Benzyl bromide, for example, smoothly reacts with this carbanion to give 1-phenyl-2,2-bis(trifluoromethyl)-3,3,4,4,5,5,5-heptafluoropentane (II), and no oligomeric products are formed.



$$(CF_3)_2C{=}CF(C_2F_5) + CsF \xrightleftharpoons{diglym} (CF_3)_2(C_3F_7)C^-Cs^+ \ \text{I} \xrightarrow{BrCH_2C_6H_5} (CF_3)_2(C_3F_7)C{-}CH_2C_6H_5 \ \text{II (90\%)}$$

EXPERIMENTAL

The ^{1}H and ^{19}F NMR spectra were taken on Perkin-Elmer (60 MHz) and Hitachi-H-60 (54.6 MHz) spectrometers, respectively.

1-Phenyl-2,2-bis(trifluoromethyl)-3,3,4,4,5,5,5-heptafluoropentane (II).

50 ml of diglym and 18 g (0.12 mole) of freshly calcinated CsF were placed into a three-necked round-bottomed flask with a stirrer, dropping funnel and reflux condenser. Then 30 g (0.1 mole) of perfluoro-2-methyl-2-pentene was added. The reaction mixture was stirred for one hour at 50-60°C. Then 21 g (0.12 mole) of benzyl bromide was added slowly dropwise, after which the reaction mixture was stirred for 2 hours at 50-60°C and allowed to stay overnight. The mixture was treated consecutively with 5% HCl, water, $NaHCO_3$, water, pyridine, again with 5% HCl and water and dried over $MgSO_4$. 37 g of II (90%), b.p. 66-68°/6 mm Hg, was obtained. Found: C 38.1, H 1.85, F 60.1%. $C_{12}H_7F_{13}$. Calculated: C 38.0, H 1.70, F 60.3%. ^{19}F NMR:(from CF_3COOH as an outer standard) δ=-14.9 ppm [$(CF_3)_2$-group] , δ=3.2 ppm (CF_3-group), δ=27.9 ppm and δ=45.9 ppm (CF_2-groups). ^{1}H NMR: δ=3.07 ppm (CH_2) and δ=6.94 ppm (C_6H_5).

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