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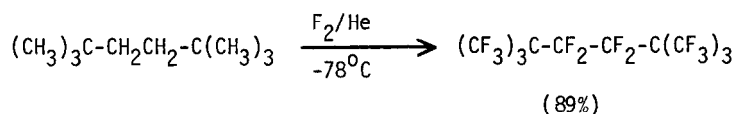
SYNTHESIS OF HIGHLY BRANCHED FLUORINE COMPOUNDS; THE SYNTHESIS AND CHARACTERIZATION OF F-2,2,5,5-TETRAMETHYLHEXANE

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RESULTS AND DISCUSSION

Direct fluorination of 2,2,5,5-tetramethylhexane has resulted in a convenient synthesis of the white, crystalline compound, F-2,2,5,5-tetramethylhexane in 89.2% yield:



Perfluorinated hydrocarbons often exhibit very unusual properties compared to their hydrocarbon analogs [1]. We have previously investigated the synthesis of highly fluorinated branched alkanes [2-4]. Recent interest has been stimulated in our laboratory by the potential of highly branched fluorocarbons as blood substitutes, etc. [5]. This has led to the fluorination of 2,2,5,5-tetramethylhexane.

Comparison of the physical properties of a series of perfluoro branched alkanes is now possible. Given in Table 1 are the physical properties of perfluoro-neopentane [2], tetramethylethane [3], 2,2,4,4-tetramethylpentane [4] and 2,2,5,5-tetramethylhexane. These four compounds provide an interesting comparison of unusual fluorocarbon compound structural similarities.

Comparison of the perfluorinated compounds shows a dramatic deviation from expected physical properties. Perfluorotetramethylpentane is a liquid at room temperature, while perfluoroanalogs of neopentane, tetramethylethane and tetramethylhexane are all volatile, white solids. This

TABLE 1

Spectral Properties

	IR (cm^{-1})	MS (m/e)	NMR (F^{19})	M.P. ($^{\circ}\text{C}$)*
$\text{C}(\text{CF}_3)_4$ ref. [2]	1300, 1190, 980, 720	269 (P-F)	-13.92	72.5 - 73
$(\text{CF}_3)_3\text{CC}(\text{CF}_3)_3$ [3]	1285, 1260, 1245, 1205, 1135, 880, 850, 735, 715, 535, 500	(P-38)	-22.0	108**
$(\text{CF}_3)_3\text{CCF}_2\text{C}(\text{CF}_3)_3$ [4]	1300, 1285, 1270, 1235, 1195, 1175, 1150, 1095, 1025, 990, 815, 750, 780, 715	469 (P-F)	-17.1 (J=14.9) +20.2	-24 - -25
$(\text{CF}_3)_3\text{CCF}_2\text{CF}_2\text{C}(\text{CF}_3)_3$	1295, 1280, 1229, 1170, 1125, 995, 790, 750, 739, 710	519 (P-F)	-15.07 ^a _b (J=14.0) +21.67 ^b	59-60

* Sealed capillary.

** Sublimes, melting point not reported.

a 5 lines: 10:29:44:31:10.

b 11 lines.

Physical Properties

difference is believed to result from the inability of perfluorotetramethylpentane to pack in a crystalline lattice as the other three compounds are able to.

Previously [4], we reported possible steric difficulties in replacing the last hydrogen in the synthesis of perfluorotetramethylpentane. In this compound, the methylene protons are the most difficult ones to replace with fluorine. In the fluorination of tetramethylhexane, two methylene groups are present. This results in the presence of partially fluorinated tetramethylhexanes which can be converted to perfluoro materials by continued fluorination at room temperature. At -78°C , an activation energy problem makes it difficult to remove the central methylene protons. This is the same phenomenon observed for the methylene protons in tetramethylpentane [4], dimethyladamantane and tetramethyladamantane [6]. However, by continuing the reaction at room temperature or higher, it is possible to fluorinate smoothly the methylene protons. A careful balance of fluorine concentration and temperature must still be used to prevent fragmentation of the carbon-carbon backbone at temperatures above subambient.

Analysis of the partially fluorinated tetramethylhexanes has proven difficult due to the complexity of both F^{19} and H^1 NMR spectra. However, two major products are $(\text{CF}_3)_3\text{CCF}_2\text{CFHC}(\text{CF}_3)_3$ and $(\text{CF}_3)_3\text{CCFHCH}_2\text{C}(\text{CF}_3)_3$ with melting points of 49-50.5 and 51-52.5, respectively. These compounds were characterized by P-F^+ ions in their mass spectrum and by F^{19} and H^1 NMR spectra after glc separation. Other partially fluorinated materials can be obtained by having the reaction proceed at -78°C only, with no fluorination at room temperature. When no fluorination is allowed to occur at room temperature, the yield of $(\text{CF}_3)_3\text{CCF}_2\text{CF}_2\text{C}(\text{CF}_3)_3$ is extremely low, on the order of a few percent.

Continued synthesis of highly fluorinated organic compounds can result in compounds of interesting structures and properties. It appears that direct fluorination is the method of choice for synthesis of such compounds.

EXPERIMENTAL

Mass spectra were obtained on a Bell and Howell CEC-491 mass spectrometer at 70 eV. NMR spectra were obtained on a Varian HA-100 spectrometer at 94.1 MHz, locked on trifluoroacetic acid. Infrared spectra were recorded on a Beckman IR-20A spectrometer using a Pyrex gas cell with KBr windows.

Reaction

Hydrogenation of 2,2,5,5-tetramethylhexene (from Chemical Samples Company) in pentane leads to 2,2,5,5-tetramethylhexane [7]. The pentane was not removed from the tetramethylhexane. Under the conditions of the experiment, pentane should not interfere with the reaction.

A 1.0 ml (0.76 g $C_{10}H_{22}$) sample of tetramethylhexane in pentane was injected into the 4-zone low temperature reactor [3] with zone 2 at $-78^{\circ}C$. (Pentane comprised approximately 20% by weight of the material injected.) The following reaction conditions were then used:

F_2 (cc/min)	He (cc/min)	Temperature	Time (hr)
1.5	20	1,2,3,4 (-78) [*]	24
1.5	8	1,2,3,4 (-78)	24
1.5	8	2,3,4 (-78)	24
1.5	0	2,3,4 (-78)	24
1.5	0	3,4 (-78)	24
1.5	0	4 (-78)	24
1.5	0	1,2,3,4 (RT)	48
1.5	4	1,2,3,4 (RT)	10
1.5	20	1,2,3,4 (RT)	16
0	30	1,2,3,4 (RT)	48

*Indicates particular zone at temperature.

During the reaction, the volatile materials were collected in a $-78^{\circ}C$ dry ice trap. Upon removal of the dry ice trap, 2.1 g of mixed products were recovered, of which, after gas chromatographic purification, 2.0 g of F-2,2,5,5-tetramethylhexane (n.c.) was isolated, constituting an 89.2% yield. [Infrared. 1295(vs), 1280(vs), 1229(m), 1170(w), 1125(vw), 995(s), 790(w), 750(m), 739(m), 710(m) cm^{-1} . F^{19} NMR. -15.07 (CF_3)^a, $+21.67$ (CF_2)^b; a: 5 lines, 10:29:44:31:10, b: 11 lines. (Spectrum recorded at $50^{\circ}C$ in CCl_4 .) Mass Spectrum. 519 (P-F)⁺, 497, 481, 431, 319, 301, 269, 231, 181, 131, 119, 69; with 69 the largest m/e peak.] Separation was accomplished on a 3/8" x 25' column with 10% Fluorosilicon QF-1-0065 on Chromosorb P. Minimal separation occurred with a SE-30 column. A comparison of the spectra of several highly branched perfluorocarbons may be seen in Table 1.

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