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Preliminary communication

Perfluoro-2-propenyl mercurials

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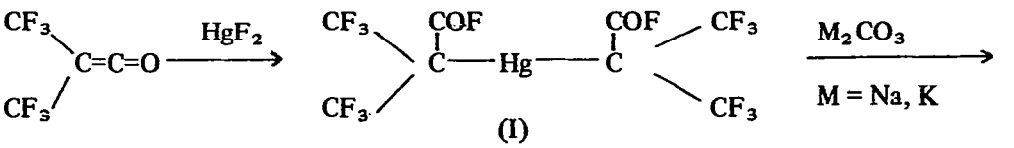
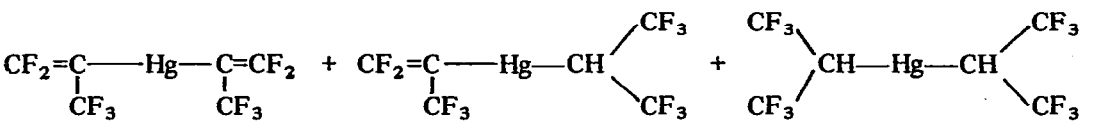
Up to now, trifluorovinyl mercury derivatives were the only representatives of perfluoroalkenyl mercurials[1]. Now we wish to report the synthesis of mercury compounds containing the perfluoro-2-propenyl group.

Bistrifluoromethylketene, like perfluoroisobutene[2], adds mercuric fluoride giving α,α'-mercuric bis(perfluoroisobutyryl) fluoride (I) in high yield. Treatment of I with sodium or potassium carbonate gives a mixture of bis(perfluoro-2-propenyl)mercury (II), perfluoro-2-propenylperfluoro-2-H-2-propylmercury (III) and bis(perfluoro-2-H-2-propyl)mercury (IV).



(I)



(II) (III) (IV)

Bis(trifluoromethyl)ketene (22.5 g, 0.126 mole) was added to a stirred slurry of mercuric fluoride (17.0 g, 0.072 mole) in 50 ml of dry dimethoxyethane; the absorption was exothermal. 10 g of freshly calcinated and powdered potassium fluoride were then added and the solvent was evaporated in vacuo. When the residue was distilled at 2 mm pressure 25.2 g of (I) (70%) were obtained (b.p. 72–74°; crystallizes at room temperature) (Anal.: found: C, 16.20; F, 44.62. $C_8F_{14}O_2Hg$ calcd.: C, 16.15; F, 44.73%). ^{19}F NMR spectrum (chemical shifts from external CF_3COOH): CF_3, doublet at −22.3 ppm $J(CF_3-F)$ 14.8 Hz, with mercury satellites, $J(^{199}Hg-^{19}F)$ 163 Hz; CFO, heptet at −120.4 ppm.

7.5 g of bis(trifluoromethyl)ketene were allowed to react with 5.5 g of HgF_2 in 30 ml

of dry dimethoxyethane. 5 g of sodium carbonate were then added, and the stirring was continued at room temperature until the evolution of gas ceased. The solvent was evaporated in vacuo and the residue was distilled at 5 mm pressure. The fraction with b.p. 42–45° was collected (1.81 g) and analysed by GLC and mass-spectrometric methods by means of a Varian CH-8 instrument (GLC: 5% of QF-1 on Chromosorb-W, 70°). The mixture contained 55, 34.7 and 7.6% of the compounds II, III and IV, respectively. Mass-spectrum of II (*m/e*★, fragment): 464, M; 445, M–F; 333, C_3F_5Hg. Mass-spectrum of III: 484, M; 465, M–F; 353, C_3HF_6Hg; 333, C_3F_5Hg; C_3HF_6Hg/C_3F_5Hg = 1/7.5. Mass-spectrum of IV: 504, M; 484, M–HF; 353, C_3HF_6Hg; 333, C_3F_5Hg; C_3HF_6Hg/C_3F_5Hg = 9/1. The IR spectrum of the mixture shows an absorption band at 1710 cm^{-1} (C=C). The ^{19}F NMR spectrum contains the signals of perfluoro-2-propenyl and of perfluoro-2-H-2-propyl groups, moreover the corresponding signals of all three compounds practically coincide. Perfluoro-2-propenyl group: CF_3, -26.3 ppm; F(1), -9.5 ppm; F(2), -16.6 ppm; $J(^{199}Hg–F(CF_3))$ 131.6 Hz; $J(^{199}Hg–F(1))$ 236.7 Hz; $J(^{199}Hg–F(2))$ 323.7 Hz; $J(F(CF_3)–F(1))$ 12.4 Hz; $J(F(CF_3)–F(2))$ 16.6 Hz; $J(F(1)–F(2))$ 15.6 Hz. Perfluoro-2-H-2-propyl group: CF_3, -22.6 ppm, $J(H–F)$ 11.3 Hz; $J(^{199}Hg–F)$ 188.4 Hz.

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★The data for ^{202}Hg are given.