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PENTAFLUOROPHENYLCHLORINE(III) DIFLUORIDE

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SUMMARY

Pentafluorophenylchlorine(III) difluoride has been prepared by the oxidation of pentafluorophenyl chloride at 117°C with elemental fluorine.

INTRODUCTION

The perfluoroalkliodine(III) difluorides have been prepared by the use of a perfluoroalkyl iodide and either ClF_3 or elemental fluorine [1]. Pentafluorophenyliodine (III) difluoride was prepared by Schmeisser, Dahmen, and Sartori [2] by the use of elemental fluorine. Chambers, Oates, and Winfield [3] found that $C_6F_5IF_2$ was less stable than the analogous $C_6F_5IF_4$. Since derivatives of IF_3 had been prepared, the authors were interested in preparing similiar derivatives of ClF_3.

We now report that pentafluorophenylchlorine(III) difluoride was synthesized by a reaction between pentafluorochlorobenzene and elemental fluorine.

RESULTS AND DISCUSSION

Pentafluorophenylchlorine(III) difluoride was synthesized by allowing 10 mmoles of pentafluorochlorobenzene and 10 mmoles of elemental fluorine to react in a Monel cylinder at 117°C for 18 hours. The liquid product was purified by gas chromatography.

$C_6F_5ClF_2$ was isolated by trapping the appropriate peak from the gas chromatograph. Air was rigorously excluded during the entire process.

Pentafluorophenylchlorine(III) difluoride was a colorless liquid (Boiling Point 96-98^oC) which fumed when exposed to air. It was found to oxidize 2.0 equivalents of iodide per mole of compound. Analysis: required for $C_6F_5ClF_2$: C, 29.96; F, 55.29; Cl, 14.74. Found: C, 29.79; F, 55.07; Cl, 14.90. The ^{19}F nuclear magnetic resonance spectrum at 25^oC consist of complex multiplets, (2:2:1:2) at + 153.9, -141.63, -157.05 and -162.25 ppm ($CFCl_3$). This spectrum is consistent with that of the pentafluorophenyl group and there was no spectrum observed in the hexadiene region. The ^{19}F-^{19}F spin-spin coupling between ^{19}F nuclei bound to the Cl and the ortho aromatic-^{19}F nuclei was found to be 19 Hz. The liquid phase infrared spectrum contains absorptions at 741 (m), 703 (s), 640 (vs), 621 (vs), 553 (vs), 530 (s), 502 (w), 459 (s), 425 (s), 395 (m), 370 (m), 334 (m), 315 (vs), 301 (m), 278 (m), 242 (vw), and 220 (vw) cm^{-1}. The observed absorptions at 741, 703 and 530 cm^{-1} are similiar to the absorptions reported for chlorine trifluoride [4] at 742, 702 and 538 cm^{-1} respectively.

Molecular ions at m/e 240 and 242 accompanied by supporting fragmentation patterns, were present in the mass spectrum along with the isotopic ratio of approximately 3:1 as expected for the ^{35}Cl and ^{37}Cl. The mass spectrum of $C_6F_5ClF_2$ consists of peaks assigned to $C_6F_5ClF_2^+$ (13), $C_6F_5ClF^+$ (0.71), $C_6F_5Cl^+$ (26), $C_6F_4Cl^+$ (0.92), $C_6F_6^+$ (6.7), $C_6F_5^+$ (29), $C_6F_4^+$ (0.72), $C_5F_3^+$ (100), ClF_2^+ (1.1), ClF^+ (0.7), and Cl^+ (0.2). In the cleavage scheme (Fig. 1), the masses given refer to the ^{35}Cl isotope, and the peak +2 for ^{37}Cl was noted in every case. A prominent peak observed at m/e 167 is due to possible loss of chlorine difluoride radical from the molecular ion. The extremely intense base peak, observed at m/e 117, was a result of $C_5F_3^+$ [5,6]. According to Beynon, Saunders and Williams, $C_5F_3^+$ had been found to be an abundant ion in the spectra of many aromatic compounds. The peak at m/e 240 showed a very weak metastable peak at $m^* = 144.0$ from the process: $240^+ \longrightarrow 186^+ + ClF^o$. There are metastable ions corresponding to formation of m/e 202,

$240^{+} \longrightarrow 202^{+} + 2F^{o}$ (m^{*}, obs; 170.0, calc., 170.0)

and

$221^{+} \longrightarrow 202^{+} + F^{o}$ (m^{*}, obs; 184.5, calc., 184.6)

followed by further breakdown of the 202^{+} ion:

$202^{+} \longrightarrow 183^{+} + F^{o}$ (m^{*}, obs; 165.6, calc., 165.8)

EXPERIMENTAL

Chloropentafluorobenzene was purchased from PCR, Inc. After the boiling point was checked, the compound was used as received. Elemental fluorine, purchased from Air Products, Inc., was passed through a -78°C trap before use.

Elemental analyses were performed by the Galbraith Laboratories, Inc., Knoxville, Tennessee. Infrared spectra were recorded with a Perkin-Elmer model 225 spectrophometer using a 0.1 mm liquid cell fitted with polyethylene windows. ^{19}F nuclear magnetic resonance spectra were obtained with a Varian EM 390 spectrometer using $CFCl_3$ as an internal reference. The mass spectrum was determined with a Consolidated Electrodynamics Corporation model 21-104 mass spectrometer.

Early in the investigation, a series of experiments were carried out to determine the optimum fluorinating conditions based on percent yield. Maintaining the fluorine to pentafluorochlorobenzene ratio at 1.0, reactions were carried out at 0, 10, 117, 128, and 220°C following techniques similiar to those described below. 117°C was considered to be the optimum reaction temperature.

During the course of this investigation the following procedures were carried out on a routine basis: A manifold was used to condense 2.02 g (10 mmoles) of pentafluorochlorobenzene into a previously evacuated and cooled (-78°C) Monel pressure reactor (volume = 0.392 l). Liquid nitrogen was used to reduce the temperature of the reactor to -196°C and 10 mmoles of elemental fluorine were allowed to flow into the reactor from a fluorine metering tank. Very dry helium gas was added to bring the reactor pressure to 4 atm. The reactor was closed and placed in an oven maintained at 117°C for 18 hours. Then the reactor was reconnected to the manifold, cooled to -196°C, and evacuated. At all times moisture

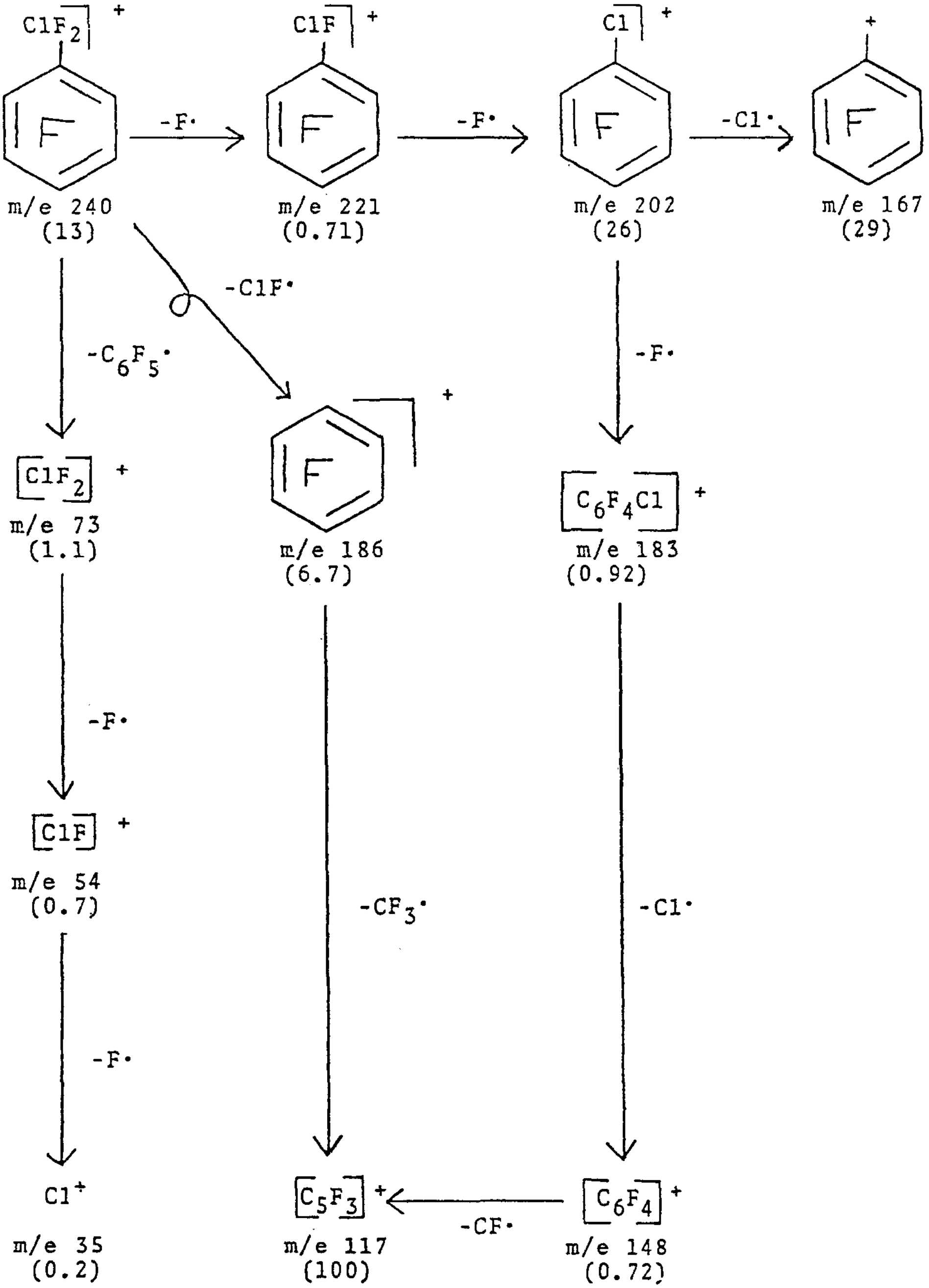

Fig. 1. Cleavage scheme as observed from mass spectrum

was rigorously excluded. The products, liquid at 25°C, were analyzed using a Varian 90P-3 gas chromatograph and a 3/8 inch x 20 foot column packed with 30% SE-30 on Chromosorb P. Analysis showed the product to be 44% $C_6F_5ClF_2$, 46% C_6F_5Cl, and 10% polymer. The hydrolysis of $C_6F_5ClF_2$ was carefully studied in Teflon. Although hydrogen fluoride gas was produced, the expected oxide was unstable and could not be isolated.

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