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SYNTHESIS OF 1,2 DIFLUORO-1,2-BIS(PENTAFLUOROPHENYL)DICHLORANE

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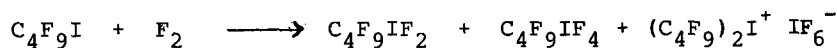
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SUMMARY

1,2-Difluoro-1,2-bis(pentafluorophenyl)dichlorane is a new class of organic polyvalent chlorine compound. The closeness of the retention time of this compound and that of chloropentafluorobenzene made its purification difficult. All attempts to obtain this compound in high yield have failed. 1,2-Difluoro-1,2-bis-(pentafluorophenyl)dichlorane is prepared by fluorination of chloropentafluorobenzene at 128°C with elemental fluorine. It has been characterized by ¹⁹F n.m.r., i.r., mass spectroscopy and elemental analysis.

INTRODUCTION

Earlier, Obaleye and Sams reported the successful syntheses of tri and pentacoordinated halogen compounds. C₆F₅ClF₂ [1] was obtained by the oxidation of C₆F₅Cl with the elemental fluorine. C₆F₅BrF₄ [2] was prepared by direct fluorination of C₆F₅Br. Recently, C₃F₇BrF₄ [3] has been synthesized by the elemental fluorination of C₃F₇Br. Rondestvedt [4] discovered that the reaction product from diluted perfluorobutyl iodide and fluorine was the new perfluorobutyliodine(III) difluoride contaminated with varying amounts of perfluorobutyliodine(V) tetrafluoride and a solid believed to be bis(perfluorobutyl)iodonium hexafluoriodate.



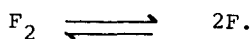
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This paper describes the preparation and characterization of 1,2-difluoro-1,2-bis(pentafluorophenyl)dichlorane which was accidentally prepared during the synthesis of $C_6F_5ClF_2$. To our knowledge this constitutes the first example of a chlorane class of compounds.

RESULTS AND DISCUSSION

The products from preparation were purified by distillation and gas chromatography. The fraction that boiled above 118°C was collected. It was necessary to exercise extreme precautions in the distillation of the sample in order not to allow moisture to condense to the collected fraction. 1,2-difluoro-1,2-bis-(pentafluorophenyl)dichlorane was isolated from the distilled fraction by trapping the appropriate peak from the gas chromatograph.

1,2-Difluoro-1,2-bis(pentafluorophenyl)dichlorane was a colorless liquid (boiling point 121-123°C). It changed to pale yellow when exposed to air for several hours. It appears likely that $C_6F_5Cl(F)Cl(F)C_6F_5$ decomposes on heating by a process involving the formation of C_6F_5ClF radicals. The following free radical mechanism is postulated for the formation of 1,2-difluoro-1,2-bis(pentafluorophenyl)dichlorane with chloropentafluorobenzene and fluorine:



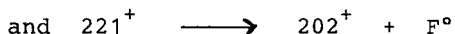
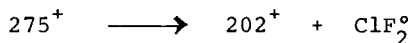
Specific evidence for this statement is not available but decomposition mechanism for R_fIF_2 has been suggested to involve radical intermediate ($R_fIF.$) [4]. The intermediate ($C_6F_5\dot{C}lF$) in our own case dimerizes rather than disproportionates. Also, the dissociation energy of fluorine is very low (approx. 37 kcal/mole); and so it is likely that the fluorination process proceeds by a radical mechanism [5].

Dichlorane is more stable thermally and less reactive chemically than chlorine trifluoride. The unusual stability of this compound could be attributed to the presence of two pentafluorophenyl groups which appear symmetrically arranged, especially as these are unique substituents that impart improved stability to many compounds [6]. "Many of the unusual properties of perfluoroaromatic compounds, cannot be simply ascribed to a strong electron-withdrawing effect of the pentafluorophenyl ring but rather to the unusual π system that results from p- π interactions" [7]. However, it was interesting to find that chloropentafluorobenzene, which does react with ClF_3 at -78°C , did not seem to react with $\text{C}_6\text{F}_5\text{Cl}(\text{F})\text{Cl}(\text{F})\text{C}_6\text{F}_5$ at that temperature.

The ^{19}F nuclear magnetic resonance spectrum [first order $(\text{AD}_2\text{H}_2\text{X})_2$] contains complex multiplets at $\delta(\text{F}_\text{A}) - 156.58$, $\delta(\text{F}_\text{D}) - 161.88$, $\delta(\text{F}_\text{H}) - 140.39$, $\delta(\text{F}_\text{X}) + 138.35$. This spectrum is consistent with that of a compound with a pentafluorophenyl group. The resonance at 138.35 assigned to the $-\text{ClF}$ group is far upfield in the region where one would expect to find the resonance of fluorine bonded to electronegative elements. Chlorine trifluoride showed a similar signal at 116 [8]. The $^{19}\text{F} - ^{19}\text{F}$ spin-spin coupling between ^{19}F nuclei bound to the Cl and the ortho aromatic ^{19}F nuclei was found to be 15 Hz. The $\text{C}_6\text{F}_5\text{ClF}_2$ resonates at -157.05 , -162.25 , -141.63 and $+153.9$ [1].

Some infrared band assignments can be made by comparison with the spectra of $\text{C}_6\text{F}_5\text{ClF}_2$ [1] and ClF_3 [9] as follows: bands at 730, 694 and 531 are due to Cl-F stretching vibrations; since these bands are similar to those of chlorine trifluoride 742, 702 and 538 cm^{-1} respectively [9]. The frequencies at about 459 and 316 cm^{-1} are the C-Cl stretching vibrations. The assignments are made in complete analogy with $\text{C}_6\text{F}_5\text{ClF}_2$. The bands of moderate intensity centering at 466 and 660 cm^{-1} which cannot be compared are suggested to result from $\text{Cl} - \text{Cl}$ stretching mode.

A stable mass-cracking pattern for $C_6F_5Cl(F)Cl(F)C_6F_5$ was obtained from mass spectrometer. Parent ion (m/e 442) was present. Extensive fragmentation of the substance was noticed as shown in the experimental. Other peaks containing more than one chlorine atoms were also identified: $C_6F_5Cl(F)Cl^+$ (0.31), $C_6F_5Cl_2^+$ (0.19), and CCl_2^+ (0.24). The base peak at m/e 202 was from the processes:



The latter process was supported by the metastable peak at $m^* =$ obs., 184.3; calc., 184.6. An intense peak at m/e 221 may be due to elimination of the same m/e 221 from the molecular ion. There was a metastable peak at $m^* =$ obs., 177.2, calc., 177.6 corresponding to formation of m/e 221 from further breakdown of the 275^+ ion,



The direct loss of a chlorine radical from the base peak was confirmed by the presence of a weak metastable ion at $m^* =$ obs., 138.1; calc., 138.1. Loss of a chlorine monofluoride radical from the base peak was also supported by the metastable peak at $m^* =$ obs., 144.3; calc., 144.8. Common to many aromatic fluorinated compounds and found in 1,2-difluoro-1,2-bis(pentafluorophenyl)-dichlorane was a large peak at 117 mass units corresponding to the ion ($C_5F_3^+$), a species also very common in the spectra of pentafluorophenyl halides [10].

The isolation of the dichlorane is dependent on the reaction temperature and stoichiometry; further reaction is indicated by the appearance of a viscous liquid.

EXPERIMENTAL

Chloropentafluorobenzene, which is available from PCR, Inc., was used without further purification. Elemental fluorine was purchased from Air Products, Inc., and passed through a $-78^\circ C$ trap or through a tower filled with sodium fluoride pellets for removal of traces of hydrogen fluoride before use. All manipulations and reactions were carried out in vacuo.

Elemental analyses were performed by the Midwest Microlab, Ltd., Indianapolis, Indiana. Infrared spectra were obtained by using a Perkin-Elmer 225 spectrophotometer with a 0.1mm cell fitted with polyethylene windows. Polyethylene windows proved to be satisfactory, apparently because they formed a protective surface layer when treated gingerly with $(C_6F_5ClF)_2$ or ClF_3 . ^{19}F nuclear magnetic resonance spectra were recorded using a Varian EM 390 spectrometer with CCl_3F as an internal standard. Chemical shifts are given as values, in p.p.m. positive to low field of CCl_3F . Mass spectra were determined with a consolidated ElectroDynamics corporation 21-104 mass spectrometer with an electron multiplier detector. Samples were introduced directly into the liquid inlet system.

1,2-difluoro-1,2-bis(pentafluorophenyl)dichlorane was formed as a by-product during the synthesis of pentafluorophenylchlorine(III) difluoride [1] by reaction of chloropentafluorobenzene with fluorine.

A series of experiments were performed analogous to those of the preparation of pentafluorophenylchlorine(III) difluoride[1] in order to determine the optimum fluorinating conditions based on percent yield of 1,2-difluoro-1,2-bis(pentafluorophenyl)dichlorane. The best molar ratio and optimum temperature were found to be 1.0 and 128°C, respectively. The reactor was charged to a pressure of 4 atm. prior to reaction. After each reaction, the mixture was allowed to come to room temperature and the bulk of the liquid was transferred from the Monel reactor into a dried brown glass bottle or polytetrafluoroethylene (PTFE) container for low temperature storage (10°C). There was no decomposition observed in the storage bottle (10°C) for at least 1 month of storage. The products, liquid at 25°C, were analyzed by a Varian 90P-3 gas chromatograph equipped with a 3/8 inch x 20 foot column packed with 30% SE-30 on Chromosorb P. Samples for analysis were obtained by trapping the dichlorane into an ampoule, which was then sealed off. Analysis: Found: C, 32.3; F, 51.6; Cl, 15.9. $C_6F_5Cl(F)Cl(F)C_6F_5$ requires C, 32.5; F, 51.5; Cl, 16.0.

The liquid phase infrared spectrum contains absorption bands at 764(w), 730(m), 694 (s), 660 (m), 621 (vs), 555 (s), 531 (s), 466 (m), 459 (s), 427 (w), 395 (m), 370 (m), 334 (m), 316 (vs), 301 (w) and 274 (m) cm^{-1} .

Assignments (for the most abundant isotope) of the fragments in the mass spectrum of 1,2-difluoro-1,2-bis(pentafluorophenyl)-dichlorane are [m/e, ion, abundance (%): 442, $\text{C}_6\text{F}_5\text{Cl}(\text{F})\text{Cl}(\text{F})$, 0.59; 275, $\text{C}_6\text{F}_5\text{Cl}(\text{F})\text{Cl}(\text{F})^+$, 5.15; 259, $\text{C}_6\text{F}_5\text{ClF}_3^+$, 5.54; 240, $\text{C}_6\text{F}_5\text{ClF}_2^+$, 1.98; 221, $\text{C}_6\text{F}_5\text{ClF}^+$, 90.18; 202, $\text{C}_6\text{F}_5\text{Cl}^+$, 100; 186, C_6F_6^+ , 50.92; 183, $\text{C}_6\text{F}_4\text{Cl}^+$, 8.51; 178, $\text{C}_4\text{F}_5\text{Cl}^+$, 6.93; 171, $\text{C}_5\text{F}_4\text{Cl}^+$, 24.14; 167, C_6F_5^+ , 45.40; 155, C_5F_5^+ , 8.51; 148, C_6F_4^+ , 6.93; 147, $\text{C}_3\text{F}_4\text{Cl}^+$, 7.52; 133, $\text{C}_5\text{F}_2\text{Cl}^+$, 39.26; 117, C_5F_3^+ , 93.25; 109, $\text{C}_3\text{F}_2\text{Cl}^+$, 12.27; 101, CFCl_2^+ , 28.89; 98, C_5F_2^+ , 25.93; 93, C_3F_3^+ , 31.66; 85, CF_2Cl^+ , 22.76; 79, C_5F^+ , 19.20; 74, C_3F_2^+ , 8.51; 69, CF_3^+ , 31.27; 55, C_3F^+ , 5.74; 43, C_2F^+ , 31.66 and 35, Cl^+ , 0.99.

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