AN UNUSUAL TRANSFORMATION OF PERFLUORINATED 1- AND 3-

PHENYLPROPENES TO POLYFLUOROCHLOROINDANES

BY THE ACTION OF A1C13

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The reaction of perfluorinated 1- and 3-phenylpropenes with $AlCl_3$ gives poly-fluorochloroindanes as the result of an intramolecular cyclization, apparently, by an electrophilic pathway.

Polyfluoroaromatic compounds, which have high reactivity relative to nucleophilic reagents, may undergo intramolecular nucleophilic substitution with the loss of a fluoride anion from the ortho position and the formation of polyfluorinated carbo- and heterocyclic compounds [1, 2]. Intramolecular radical ring closure with the loss of ortho fluorine atoms has also been described for polyfluoroarenes with the formation of polyfluoroarenecyclo-alkenes [3].

On the other hand, there have been no reports of electrophilic reactions of polyfluoroaromatic compounds involving intramolecular ring closure affecting a $C_{\rm ar}$ -F bond although examples corresponding to the formal elimination of a fluorine cation in polyfluoroarenonium ions have been examined by Shteingarts [4].

In this regard, the search for electrophilic intramolecular ring closure reactions for polyfluoroaromatic compounds holds interest both for elucidating their feasibility and expanding our understanding of electrophilic transformations of polyfluoroarenes.

We have shown that the reaction of perfluoro-3-phenylpropene (I) with $AlCl_3$ at $90-100^{\circ}C$ gives 1,1,3,3-tetrachlorohexafluoroindane (II) along with 1,1,3,3,5-pentachloropentafluoro-indane (III) and a small amount of pentafluorophenyl-2-fluorotetrachloropropene (IV).

The reaction of perfluoro-1-phenylpropene (V) with $AlCl_3$ under these conditions proceeds analogously



The action of hexafluoropropene on pentafluorobenzene in the presence of $AlCl_3$ also gives the formation of (II)-(IV) along with 2-fluoropentachloropropene (VI)

The reaction of (I) with $AlCl_3$ at 95-100°C in CCl_4 and at 70-80°C in CCl_4 and without solvent gives phenylpropenes (IV) and (V) as the major products along with indane (II). The finding of phenylpropene (V) may indicate its formation through isomerization of allyl deri-

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Ex- peri- ment No.	Starting com- pound, g	A1C1 ₃ , g	Reaction conditions			Mix- ture	Major mixture components by GLC, %*			
			т.°С	time, h	reactor	yield, g	(II)	(III)	(IV)	(V)
1	(1), 10	9	95-100	10	Flask	9.6	69	20	1	
$\frac{1}{2}$	(1), 10	9	70	10	Ampul	8.7	4.5	_	ī	66
3	(I). 0.4	0.36	95-100	10	.,	0,3	37	8	1.4	20
4	(1). 0.4	0.36	95-100	10	'n		13	5 ·	40	18
5	(I), 10	10 🕈	80	4	Flask	9.6	5	-	76	10
6	(1). 0.5	AlF ₃ 0.5	145	3	Ampul		Starting compound			
7	(V), 1.5	1.3	95-100	10	Flask	0,6	62	12	_ 1	1 7
8	(V), 0.4	0.36	95 - 100	1 10	Amoul	0.3	30	6	14	30

TABLE 1. Reaction of Pentafluorophenylperhalopropenes with $AlCl_3$

*Corresponds to the ¹⁹F NMR spectral data. †With added 2 g CCl₄. ‡With added 14 g CCl₄.

vative (I) by the action of the aluminum halide with the exception of AlF_3 . Propene (I) is recovered unchanged upon heating with AlF_3 at 145°C. The isomerization of (I) has been studied in the presence of SbF_5 [5-7]. The formation of indane (II) in the reaction of (I) and (V) with $AlCl_3$ proceeds as result of intramolecular cyclization, apparently by an electrophilic pathway. This reaction is accompanied by exchange of fluorine atoms by chlorine atoms. The scheme may be as follows:



The reaction of pentafluorobenzene with hexafluoropropene in the presence of $AlCl_3$ initially probably features electrophilic haloalkenylation with replacement of the hydrogen atom by the perhalopropenyl group with subsequent cyclization and formation of indane (II) according to a scheme analogous to that for the transformations of (I) and (V) with $AlCl_3$. Brovko et al. [6] have studied the reaction of pentafluorobenzene with hexafluoropropene in the presence of SbF_5 and showed the possibility of perfluoroalkenylation using the perfluoroallyl cation.

One of the pathways for the appearance of indane (III) among the reaction products may lie in the replacement of a fluorine atom by a chlorine atom in indane (II) by the action of $AlCl_3$ [8]. The formation of chloropropene (IV) apparently proceeds by the replacement of the fluorine atoms of the perfluoropropenyl group by chlorine in (I) and (V) by the action of $AlCl_3$ and, in the case of the reaction of pentafluorobenzene with hexafluoropropene, also with the participation of fluorochloropropenes. Thus, the reaction of pentafluorobenzene with 2-fluoropentachloropropene features the formation of (IV). 2-Fluoropentachloropropene may be formed from hexafluoropropene with $AlCl_3$ [9].

EXPERIMENTAL

The ¹⁹F NMR spectra were taken on a Varian A 56/60A spectrometer at 56.4 MHz in C_6F_6 , while the ¹³C NMR spectra were taken on a Bruker AC-200 spectrometer at 50.32 MHz relative to TNS. The IR spectra were taken on a UR-20 spectrometer for solutions in CCl₄. The Raman spectra were taken on a Coderg PH-1 spectrometer with a helium-neon laser (λ_{exc} 6328 Å). The molecular mass was determined on a Finnigan MAT 8200 mass spectrometer. The gas-liquid chromatographic analysis was carried out on an LKhM-72 chromatograph with a thermal conduction detector and linear temperature programming at 10°C/min on a 4000 × 4-mm column packed with SKTFT-50 silicone. Reaction of Pentafluorophenylperhalopropenes with $AlCl_3$. Phenylpropenes (I) and (V) and $AlCl_3$ were stirred in a flask or maintained in a sealed ampul with heating. The mixture was cooled and poured into ice water. The organic layer was separated, washed with water, and dried over MgSO₄. When CCl₄ was used, it was distilled off. The reaction mixtures were analyzed by ¹⁹F NMR spectroscopy and gas-liquid chromatography. The reaction conditions and results are given in Table 1.

In experiment 1, gas-liquid chromatography gave indane (II) as a pure compound and a fraction containing ~50% indanes (II) and (III). Indanes (II) and (III) were characterized by comparison of their IR and ¹⁹F NMR spectra with the spectra of known samples and their artificial mixture ((II):(III) = 1:1). The spectra of the samples obtained and authentic samples of (II) and (III) were identical [8].

Phenylpropene (IV) was isolated by distillation of the mixture obtained in experiment 5 in vacuum (bp 110-112°C (8 mm)), mp 32°C (from ethanol). Found: C, 29.86; F, 31.18; Cl, 38.73%. Molecular mass 361.8683 (by mass spectrometry). Calculated for $C_9F_6Cl_4$: C, 29.67; F, 31.32; Cl, 39.01%. Molecular mass 361.8658. IR spectrum (ν , cm⁻¹): 1515, 1650 (fluorinated aromatic ring). Analysis of the ¹⁹F and ¹³C NMR spectra of (IV) and (VI) permitted us to identify (IV) as Z-1-pentafluorophenyl-2-fluorotetrachloropropene. ¹⁹F NMR spectrum of (IV) (δ , ppm): 1.6 (2F_m), 12.7 (1F_p), 25.5 (2F_o), 76.4 (1F) (compare with the δ_F values for propene (VI) 72.0 ppm), $J_{F_m-F_p} = 20.3$, $J_{F_p-F_o} = 3.5$, $J_{F_o-F_\beta} = 2$ Hz. ¹³C NMR spectra of (IV) (δ , ppm): 87.7 (CCl₃), 106.7 (=CCl), 110.08 (C₁), 139 (C_m), 144.6 (C_p), 145.2 (C_o), 154.4 (=CF), $J_{C-F} = 37.5$ (CCl₃), 31.5 (=CCl), 264.2 Hz (=CF), and (VI): 88.4 (CCl₃), 115.7 (CCl₂=),

151.1 (CF=), $J_{C-F} = 34.5$ (CCl₃), 47.2 (=CCl₂), 265.7 Hz (=CF). The chemical shifts and $J_{C-F_{a}}$

values of the $-CCl_3$ and -CF groups in (IV) and (VI) are in accord. The value found for $\delta(=CCl-)$ is in agreement with the estimated value (108.8 ppm) obtained using $\delta(=CCl)$ in Z- $\alpha\beta$ -dichlorohexafluorostyrene (98.9 ppm) and the increment for replacing β -Cl by CCl₃ obtained by comparing CCl₂=CCl₂ and CCl₂-CClCCl₃ [10] and is equal to 9.9 ppm. The J_{C-F β} value of the =CCl-group (31.5 Hz) permits us to ascribe the Z structure to (IV) (in the case of C₆F₅CCl=CFCl, J_{C α -F β} is 28.8 Hz for the Z isomer and 42.23 Hz for the E isomer).* This assignment is also supported by comparison of J_{F α}-F β in the ¹⁹F NMR spectra of (IV) and the Z and E isomers of 1,3-dichloroperfluoro-1-phenylpropene [12].

Reaction of Pentafluorobenzene with Hexahalopropenes and $AlCl_3$. a. A mixture of 5.4 g pentafluorobenzene, 4 ml hexafluoropropene, and 8.5 g $AlCl_3$ was heated in a sealed ampul for 24 h at 90-100°C. Usual work-up gave 9 g of a mixture consisting of 14% pentafluorobenzene, 13% (II), 8% (III), 16% (IV), and 10% (VI).

b. By analogy to experiment 3, 0.2 g pentafluorobenzene, 0.3 g propene (VI), and 0.23 g $AlCl_3$ gave 0.3 g of a mixture containing ~5% phenylpropene (IV). The remainder consisted largely of the starting reagents.

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*For fluoroolefins, $J^{Z}_{C_{\alpha}-F_{\beta}} < J^{E}_{C_{\alpha}-F_{\beta}}$ [11].