Thermolytic transformations of polyfluoroorganic compounds
31.* Copyrolysis of 4-chlorotetrafluorobenzo trichloride with chlorodifluoromethane

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Copyrolysis of 4-chlorotetrafluorobenzotrichloride with chlorodifluoromethane (as the source of difluorocarbene) gave 4-chlorodifluoromethyl-α-chlorohexafluorostyrene, 1,4-dichlorotetrafluorobenzene, and 4-(chlorodifluoromethyl)chlorotetrafluorobenzene along with 4-chloro-α-chlorohexafluorostyrene. Possible routes for the formation of these products have been offered.

Key words: copyrolysis; 4-chloro-α-chlorohexafluorostyrene; 4-chlorodifluoromethyl-α-chlorohexafluorostyrene; difluorocarbene; polychlorofluorocyclohexadienes.

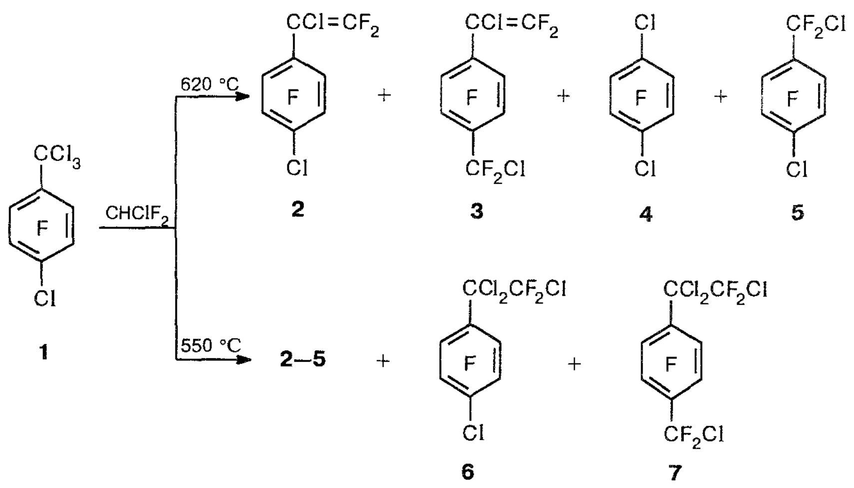
We have shown previously[2,3] that copyrolysis of pentafluorobenzotrichloride and a number of its derivatives with sources of dihalocarbenes affords α-chloroheptafluorostyrene and the corresponding polyfluorostyrenes. For example, the reaction of 4-chlorotetrafluorobenzotrichloride (**1**) with $CHClF_2$ and tetrafluoroethylene at 620 °C yields 4-chloro-α-chlorohexafluorostyrene (**2**).

We studied the reaction between compound **1** and $CHClF_2$ in more detail. Formally, styrene **2** could result from transformations involving the C—Cl bond in the benzyl position.[3] The participation of the C_{arom}—Cl bond remained unknown.

We showed that copyrolysis of compound **1** with $CHClF_2$ (620 °C) affords, in addition to the main product **2**, 4-chlorodifluoromethyl-α-chlorohexafluorostyrene (**3**). Small amounts of 1,4-dichlorotetrafluorobenzene (**4**) and 4-(chlorodifluoromethyl)chlorotetrafluorobenzene (**5**) were also detected in the reaction mixture. When the temperature of the reaction was decreased to 550 °C, along with products **2**—**5**, 4-(α,α,β-trichlorodifluoroethyl)chlorotetrafluorobenzene (**6**) and 4-(α,α,β-trichlorodifluoroethyl)chlorodifluoromethyltetrafluorobenzene (**7**) were also formed (Scheme 1).

The formation of styrene **2** may have a mechanism analogous to the mechanism given in the literature[3] involving insertion of difluorocarbene into a C—Cl bond of the CCl_3 group of compound **1** and subsequent

Scheme 1



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* For Part 30, see Ref. 1.

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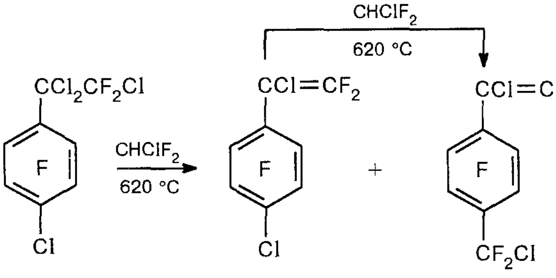
dechlorination of the intermediate compound **6**. This is confirmed by the facts that the latter compound is isolated when the temperature of copyrolysis of **1** with $CHClF_2$ is decreased to 550 °C and that copyrolysis of compound **6** with $CHClF_2$ at 620 °C gives styrene **2**. In this case, styrene **3** is also obtained (Scheme 2).

Scheme 2



6 **2** **3**

One of the routes for the formation of styrene **3** in the reaction of compound **1** with $CHClF_2$ is the insertion of difluorocarbene into the C_{arom}—Cl bond of styrene **2**. Styrene **3** is actually formed in the copyrolysis of styrene **2** with $CHClF_2$ at 620 °C, though in a smaller amount than in the reaction of compound **1** with $CHClF_2$ under similar conditions.

This fact, as well as the presence of ethylbenzene **6** in the products of the reaction of compound **1** with $CHClF_2$ at 550 °C and the formation of styrene **3** in the copyrolysis of ethylbenzene **6** with $CHClF_2$ (620 °C), allow one to suggest that alternative pathways for the formation of styrene **3** may exist. These are the insertion of difluorocarbene into the C—Cl bond of the intermediate cyclohexadienes (**A** or **B**) that may result, for example, from isomerization of compounds **1** and **6** (Scheme 3).

Polyfluorinated methylenecyclohexadienes have been prepared only recently.[4] Copyrolysis of α,α-dichlorooctafluoroethylbenzene with tetrafluoroethylene affords their analog, *viz.*, perfluoro-7-methylbicyclo[4.3.0]nona-1,4,6-triene.[1] Preparation of *N*-chloriminochloropolyfluorocyclohexadienes[5] and their pyridine analogs,[6] in particular, by thermal isomerization of *N,N*-dichloroperfluoroarylamines, has also been reported.

Dichlorobenzene **4** may probably arise similarly to chloropentafluorobenzene[2,3] due to replacement of the trichloromethyl and polychlorofluoroethyl groups in compounds **1** and **6** by chlorine atoms. Dichlorobenzene **4** was found to be the major product of thermolysis of compounds **1** and **6** in the absence of $CHClF_2$.

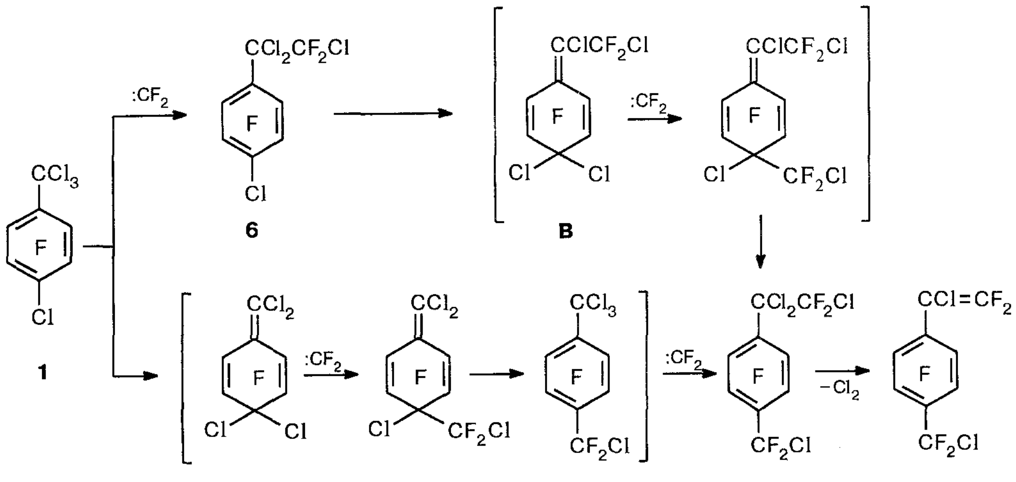
In a like manner, compound **5** may be formed from ethylbenzene **7**. Another pathway for this compound, *i.e.*, the insertion of difluorocarbene into the C_{arom}—Cl bond of dichlorobenzene **4**, is unlikely under these conditions, since among the products of copyrolysis of the latter with $CHClF_2$, only trace amounts of compound **5** are detected.

Ethylbenzenes **6** and **7** were also prepared by reactions of styrenes **2** and **3** with PCl_5 at 250 °C. The process involves partial replacement of the side chain by chlorine and gives compounds **4** and **5**, and tetrachloro-1,1-difluoroethane (Scheme 4).

Experimental

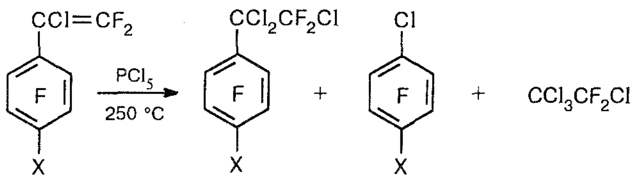
^{19}F NMR spectra were recorded on a Bruker WP-200 spectrometer in CCl_4 and $CDCl_3$. C_6F_6 was used as the internal standard. IR spectra were obtained on a UR-20

Scheme 3



6 **B** **1** **A** **7** **3**

Scheme 4



2, 3 **6, 7** **4, 5**

X = Cl (**2**, **4**, **6**)
X = CF_2Cl (**3**, **5**, **7**)

spectrometer in CCl_4, and UV spectra were run on a Specord UV-VIS spectrophotometer in EtOH. Mol. weights were determined on a Finnigan-MAT 8200 mass spectrometer. GLC analysis was carried out on an LKhM-7A chromatograph with a heat-conductivity detector and linear temperature programming (10 °C min^{-1}); a 4000×4 mm column with SKTFT-50 and SKTFV-803 (15 % each on Chromosorb) was used; N_2 (200 mL min^{-1}) and He (60 mL min^{-1}) were used as carrier gases. The components were identified by adding authentic samples. Preparative GLC was carried out under the conditions of the analytical GLC using SKTFT-50 on zeolite (125 °C, N_2).

Pyrolysis of compounds 1, 2, 4, and 6. Polyfluoroaromatic compounds were passed through a heated quartz tube (400×20 mm) placed in an electric furnace, at a rate of 25—30 g h^{-1} in a flow of $CHClF_2$ (15—20 L h^{-1}) or argon (5—10 L h^{-1}). The reaction mixture was distilled with steam, and the products were analyzed by GLC and IR and ^{19}F NMR spectroscopy. Individual compounds **2**, **3**, and **4** from run *3* (Table 1) were isolated by rectification. Compound **5** was isolated from the enriched fraction using preparative GLC. The experimental conditions and the compositions of the reaction mixtures are presented in Table 1. The presence of compounds **2**—**7** in the reaction mixtures was confirmed by IR and ^{19}F NMR spectroscopy and GLC.

Compound **3**, b.p. 102 °C (40 Torr). Found (%): C, 32.20; Cl, 21.30; F, 46.67. Mol. weight 329.9252 (MS). $C_9Cl_2F_8$. Calculated (%): C, 32.63; Cl, 21.45; F, 45.92. Mol. weight 329.9249 (^{35}Cl). IR, ν/cm^{-1}: 1745 (C=C); 1490, 1655 (fluor. arom. ring). UV, λ_{max}/nm (ε): 208 (12400), 256 (5300), 290 sh (2900). ^{19}F NMR, δ: 23.3 (2 F(3,5)); 26.7 (2 F(2,6)); 81.1 (1 F(*y*)*, $J_{F(y),F(x)} = 17.5$, $J_{F(y),F(2,6)} = 7.5$ Hz); 82.2 (1 F(*x*), $J_{F(x),F(y)} = 17.5$, $J_{F(x),F(2,6)} = 1.5$ Hz, *cf.* Ref. 3); 115.4 (2 F, CF_2Cl, $J_{CF_2, F(3,5)} = 30$, *cf.* Ref. 7: $J_{CF_2,o\text{-}F} = 31.5$ Hz for $C_6F_5CF_2Cl$).

Compound **5**, b.p. 81—82 °C (40 Torr). Found (%): C, 30.93; Cl, 26.23; F, 42.24. Mol. weight 267.9283 (MS). $C_7Cl_2F_6$. Calculated (%): C, 31.23; Cl, 26.39; F, 42.38. Mol. weight 267.9281. IR, ν/cm^{-1}: 1497, 1633 (fluor. arom. ring). UV, λ_{max}/nm (ε): 214 (10406), 227 (10520), 281 (1960). ^{19}F NMR, δ: 22.9 (2 F(3,5)); 23.5 (2 F(2,6)); 115.6 (2 F, CF_2Cl, $J_{CF_2,F(3,5)} = 30$ Hz).

Preparation of 4-(α,α,β-trichlorodifluoroethyl)chlorotetrafluorobenzene (6) and 4-chlorodifluoromethyl-α,α,β-trichlorodifluoroethyltetrafluorobenzene (7). *A*. A mixture of 10 g of styrene **2** and 22 g of PCl_5 was heated for 6 h in a sealed tube at 250 °C. The tube was cooled and opened, and the reaction mixture was poured on ice. The organic layer was washed with water and dried with $MgSO_4$ to give 11.7 g of a mixture that contained, according to GLC, three major products: compounds **6** and **4**, and CCl_3CF_2Cl (64, 20, and 14 %, respectively). Dichlorobenzene **4** and ethylbenzene **6** were isolated by vacuum distillation. According to GLC, the mixture from the trap contained compound **4** (39 %) and CCl_3CF_2Cl (58 %). The presence of the latter was confirmed by spectroscopic data. The IR spectrum of the mixture is in agreement with the spectra of individual compound **4** and CCl_3CF_2Cl (see Ref. 8). The ^{19}F NMR spectrum exhibited

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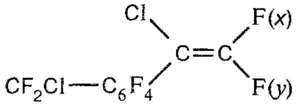

Table 1. Thermal transformations of compounds **1**, **2**, **4**, and **6**

Run	Starting compound*	Gas	Temperature /°C	Yield of the mixture /g	Content in the mixture (%) (GLC)			
					2	**3**	**4**	**5**
1	**1**	$CHClF_2$	550	0.88	34	7	9	3**
2	**1**	$CHClF_2$	620	0.68	52	14	6	4
3	**1**	$CHClF_2$	620	1490.0	58	19	7	5
4	**1**	$CHClF_2$	690	0.87	46	9	13	6
5	**1**	Ar	620	1.43			50	
6	**2**	$CHClF_2$	620	0.75	75	7	1—2	<1
7	**2**	Ar	620	0.81	87		1—2	
8	**4**	$CHClF_2$	620	0.75			95	2—3
9	**6**	$CHClF_2$	620	0.64	78	10		
10	**6**	Ar	620	0.54	44		46	

* The following amounts of the starting compound were used: run *3* — 1500 g, run *5* — 1.8 g, each of the other runs — 1 g.
** The mixture also contained compounds **6** (34 %), **7** (5 %), and **1** (8 %).

two signals, δ 22.4 and 97.4. The latter was assigned to CCl_3CF_2Cl (see Ref. 9: δ 97.4). The analysis of the mass spectrum of the mixture confirms the presence of both components: a peak at *m/z* 167 corresponds to CCl_3CF_2Cl $[M-Cl]^+$, and dichlorobenzene **4** is responsible for the peaks at *m/z* 218 $[M]^+$ and 183 $[M-Cl]^+$.

Compound **6**, b.p. 100 °C (25 Torr). Found (%): C, 27.13; Cl, 39.81; F, 32.24. Mol. weight 349.8667 (MS). $C_8Cl_4F_6$. Calculated (%): C, 27.27; Cl, 40.34; F, 32.39. Mol. weight 349.8658. IR, ν/cm^{-1}: 1480, 1630 (fluor. arom. ring). UV, λ_{max}/nm (ε): 217 (13000), 230 (14300), 283 (2100). ^{19}F NMR, δ: 22.8 (2 F(2,6); 33.5 (2 F(3,5)); 99.1 (2 F, CF_2Cl, $J_{CF_2,F(3,5)} = 16.2$ Hz, *cf.* Refs. 1, 10: $J_{CF_2,o\text{-}F} = 16.5$ Hz for $C_6F_5CCl_2CF_2Cl$).

B. The interaction of 5 g of styrene **3** with 9.5 g of PCl_5 as described in procedure *A* gave 5.5 g of a mixture. Vacuum distillation afforded compound **7** and a fraction containing benzyl chloride **5** (85 %). In addition, a mixture containing compound **5** (57 %) and CCl_3CF_2Cl (28 %) was obtained. The presence of these products was confirmed in a way similar to that in procedure *A*. Compound **7**, b.p. 106 °C (17 Torr). Mol. weight determined by high-resolution mass spectrometry: 399.8622. $C_9Cl_4F_8$. Calculated: mol. weight 399.8626 (^{35}Cl). IR, ν/cm^{-1}: 1476, 1640 (fluor. arom. ring). UV, λ_{max}/nm (ε): 209 (14600), 221 (14000), 290 (3300). ^{19}F NMR, δ: 23.9 (2 F(3,5)); 35.4 (2 F(2,6)); 99.6 (2 F, β-CF_2Cl, $J_{CF_2,F(2,6)} = 16.75$ Hz); 114.6 (2 F, 4-CF_2Cl, $J_{CF_2,F(3,5)} = 29.5$ Hz).

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