Organic Chemistry

Thermolytic transformations of polyfluoroorganic compounds 30.* Copyrolysis of α,α -dichlorooctafluoroethylbenzene with tetrafluoroethylene

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The reaction of α, α -dichlorooctafluoroethylbenzene with tetrafluoroethylene as a source of difluorocarbene has been studied. The copyrolysis of these compounds gave not only the expected products, decafluoro- α -methylstyrene and α -chloroheptafluorostyrene, but also noticeable amounts of perfluoro-1-methylindan and perfluoro-7-methylbicyclo[4.3.0]nona-1,4,6-triene along with perfluoro-3-methylindene and octafluorostyrene. It has been suggested that indan and the triene are formed with the participation of the C₆F₅CCICF₃ radical through sigmatropic shifts of fluorine atoms in the intermediate bicyclic compounds. The reaction of α, α -dichlorodecafluoropropylbenzene with tetrafluoroethylene afforded α chloroheptafluorostyrene as the main product.

Key words: copyrolysis; decafluoro- α -methylstyrene, perfluoro-7-methylbicyclo[4,3,0]nona-1,4,6-triene; perfluoro-1-methylindan; polyfluoroalkylbenzyl radicals; sigmatropic shifts of fluorine atoms.

Previously¹ we have described copyrolysis of α,α -dichlorooctafluoroethylbenzene (1) with chlorodifluoromethane, which gave predominantly decafluoro- α methylstyrene (2), along with α -chloroheptafluorostyrene (3), α -chloro- α -hydrooctafluoroethylbenzene, and chloropentafluorobenzene (4). It has been considered that the formation of compound 2 occurs with the participation of difluorocarbene. In order to elucidate the more general pattern of the behavior of α -chloroperfluoroalkyl aromatic derivatives, we have studied the transformation of compound 1 in the presence of another source of difluorocarbene, *viz*, tetrafluoroethylene (TFE).

Copyrolysis of these compounds at 620 °C afforded equal amounts of compound 2 and perfluoro-1methylindan (5) as the main products. Unexpectedly, perfluoro-7-methylbicyclo[4.3.0]nona-1,4,6-triene (6) was obtained in this reaction. The reaction mixture contained compounds 3, 4, perfluoro-3-methylindene (7), and octafluorostyrene (8) as well (Scheme 1).

A decrease in the reaction temperature to 520-540 °C resulted in the reversal of the ratio between products 5 and 6, which had been ~2:1 in the

^{*} For part 29, see Ref. 1.

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former run, and the yield of compound **6** was as high as 16 %. At 650 °C, the reaction mixture contained practically no compound **6**.

The formation of decafluoro- α -methylstyrene 2 may result from the insertion of difluorocarbene (formed upon the thermolysis of TFE) into the C—Cl bond of compound 1 followed by dechlorination of the resulting compound, α,β -dichlorooctafluoroisopropylbenzene (9) (cf. Ref. 1). Actually, the thermolysis of compound 9 in a flow of argon or TFE at 620 °C gives decafluoro- α methylstyrene 2 as the main product along with α chloroheptafluorostyrene 3. In the reaction with TFE small amounts of bicyclic compounds 5 and 6 were also detected.

We cannot rule out completely the possibility of the formation of decafluoro- α -methylstyrene 2 in the reac-

tion of compound 1 with TFE through coupling of difluorocarbene with perfluorophenylmethylcarbene (A) which could be generated from compound 1. The thermolysis of compound 1 in the absence of TFE gave octafluorostyrene 8 as one of the main products,¹ which attests to this way of generating carbene A. The formation of styrene 8 in this reaction or in the copyrolysis of 1 with TFE may occur by isomerization of carbene A.



The appearance of chlorostryrene **3** upon the pyrolysis of compound **9** may be explained by the participation of intermediate benzyl-type radicals, $C_6F_5CCICF_2X$ (X = F, Cl), with the subsequent elimination of X[•]. The generation of benzyl radicals could occur by cleavage of the C-CF₂X (X = F, Cl) bonds in the starting compound **9**. Bicyclic products **5** and **6** are formed upon the reaction of $C_6F_5CCICF_3$ with TFE.

The formation of smaller amounts of compounds 5 and 6 from derivative 9 and TFE at 620 °C than from the similar reaction of dichlorooctafluoroethylbenzene 1 with TFE may indicate that in the latter case most part of the reactions do not involve compound 9.

The formation of compounds 5 and 6 in the reaction of dichlorooctafluoroethylbenzene 1 with TFE may be due to the interaction of TFE with the $C_6F_5\dot{C}ClCF_3$ radical which is generated by the homolysis of the C–Cl bond in 1 (Scheme 2). Perfluoro-1-methylindan 5 is formed by a route similar to that suggested for the formation of perfluoroindan² from hexafluorobenzylidene dichloride and TFE.

The appearance of triene $\mathbf{6}$ could be due to transformations of the intermediate compounds \mathbf{B} , \mathbf{C} , and \mathbf{D} . The possibility of the isomerization of compound $\mathbf{6}$ to



′g Gas <i>T</i> /°C	Amount/g	Yield of the	Content of the main products (yield with respect to theoretical) (%), according to GLC								
			starting compound	2	3	4	5	6	7	8	
TFE 620	12	15.7		17(23)	5(8)	Traces	18(22)	10(12)	5(7)	2(3)	
TFE 530	16	15.4	14	11(11)	3(3)		9(8)	18(16)	. /	3(4)	
TFE 650	2	1.5		22(18)	7(6)		23(16)	• • •		3(3)	
TFE 620	0	0.2	5	30(19)	10(7)	3(3)	6(3)	8(4)		2(5)	
Ar 620	0	0.3	15	20(13)	7(5)	13(20)	• /	• /		. ,	
TFE 620	0	0.25					35	6	40		
TFE 620	0	1.10					92				
TFE 470	1	0.7	5		56						
TFE 620	1	2.0			58	Traces					
Ar 620	1	0.5			60	15					

Table 1. Pyrolitic transformations of compounds 1, 5, 6, 9, and 10

* Run 1.

form 5 during thermolysis of 6 in the presence of TFE was shown in a separate run. This also occurs on prolonged storage of triene 6 in a sealed ampule at room temperature (according to the ¹⁹F NMR data, compound 6 was $\sim 3/4$ converted to perfluoro-1-methylindan 5 over a period of 10 years).



Transformations of **B** to **D**, **C** to **5** and **6**, and **6** to **5** may occur through sigmatropic shifts of fluorine atoms.

The defluorination of triene 6 is apparently one of the routes for the formation of indene 7. The defluorination of perfluoro-1-methylindan 5 into indene 7 does not occur under similar conditions.

Compound **6** affords, under the action of CsF at 250 °C, practically individual perfluoro-1-methylindan **5**.

In order to synthesize an analog of triene 6 we studied the copyrolysis of α,α -dichlorodecafluoropropylbenzene (10) with TFE. However, the direction of the transformation of compound 10 turned out to be different, and α -chloroheptafluorostyrene 3 was obtained as the main reaction product (Scheme 3).

The formation of this compound probably involves radical E and subsequent cleavage of its C--C bond



 $(-CF_2-CF_3)$, which is weaker than the C-F bond $(-CF-CF_3)$ (the energy of the C-C bond in F

 CF_3-CF_3 is 83 kcal mol⁻¹,³ while that of the C-F bond is 107-121 kcal mol⁻¹ cf. Ref. 4).

Chloroperfluorobenzene 4 may be formed by the replacement of a heptafluoropropyl group by chlorine.¹ This process occurs to a larger extent in the pyrolysis of compounds 1, 9, and 10 in the absence of TFE.

Experimental

¹⁹F NMR spectra were obtained on a WP-200 spectrometer in CDCl₃. C₆F₆ was used as the internal standard. IR spectra were recorded on a UR-20 spectrophotometer in CCl₄. The UV spectrum was measured on a Specord UV-VIS spectrometer in heptane. Molecular masses were determined on a Finnigan MAT 8200 mass spectrometer. GLC analyses were performed on an LKhM-7A chromatograph equipped with a katharometer, on 4000×4 mm columns, with SKTFT-50, SKTFB-803, and QF-1 polysiloxanes (15 % each on Chromosorb) with temperature programing (10 deg min⁻¹), and N₂ (200 mL min⁻¹) and He (60 mL min⁻¹) were used as the carrier gases. The components of the mixture were identified by adding authentic samples. For preparative GLC, SKTF-50 on zeolite was used (125 °C, N₂).

Pyrolytic transformations of compounds 1, 9, and 10. A polyfluoroaromatic compound was passed through a heated quartz tube (400×20 mm) placed into an electric furnace in a flow of TFE (~15 L h⁻¹) or argon (~5 L h⁻¹) at a rate of ~25 g h⁻¹. The reaction mixture was steam-distilled, dried with MgSO₄, and analyzed by GLC and IR and ¹⁹F NMR spectroscopy. Individual compounds were isolated by preparative GLC. The presence of the known compounds **2**—**5** and **7,8** in the reaction mixture was confirmed by comparing the IR and ¹⁹F NMR spectra of the reaction mixtures, the fractions enriched in the compound under examination, and pure products with those of the individual compounds and by GLC.

The experimental conditions and the compositions of the reaction mixtures are presented in Table 1. From the mixture obtained in run 1 (see Table 1), fractions enriched in compounds 2–8 were obtained. From these fractions, pure compounds 2, 5, and 6 were isolated by preparative GLC. Com-

pound 6: Found (%): C, 34.50; F, 65.34. Molecular mass 347.9806 (mass spectrum). C₁₀F₁₂. Calculated (%): C, 34.48; F, 65.52. Molecular mass 347.9808. IR, v / cm⁻¹: 1642, 1699, 1746 (C=C). UV, λ_{max} / nm: 244 (log ε 4.33), 253 (log ε 4.25). ¹⁹F NMR, δ: 21.1 (q.t.m, 1 F, F(5)); 22.0 (br.t, 1 F, F(4)); 40.3 (t.m, 1 F, F(2)); 49.5 and 54.1 (m, 4 F, F(8,9)); 57.6 (d.d.d.m, $J_{F(3)-F(2)} = J_{F(3)-F(4)} = 22$ Hz, $J_{F(3)-F(5)} = 12$ Hz, J = 2.5 Hz, 2 F, F(3), (cf. Refs. 5, 6: δ CF₂ values for polyfluoro-1,4-cyclohexadienes and polyfluorocyclohexadienones are 47–62 ppm, $J_{F(3)-F(2)} = J_{F(3)-F(4)} = 20-25$ Hz, $J_{F(3)-F(5)} = 10-15$ Hz); 104.3 (d.d.t, $J_{F(7)-F(5)} = 26$ and J = 5 и 2.5 Hz, 3 F, F(7)).

Preparation of α,β-dichlorodecafluoroisopropylbenzene (9). A mixture of decafluoro-α-methylstyrene 2 (1.5 g) and PCl₅ (2.8 g) was heated in a sealed tube for 8 h at 230–250 °C. The tube was cooled, and its contents were poured on ice. The organic layer was washed with water and dried with MgSO₄ to give 1.4 g of a mixture which contained, according to GLC, 93 % of compound 9 and 5 % of the starting 2. Distillation *in vacuo* (59 °C, 5 Torr) afforded product 9. Its molecular mass (367.9217) was determined by high-resolution mass spectrometry. C₉Cl₂F₁₀. Calculated: molecular mass 367.9217 (³⁵Cl). IR, v/cm⁻¹: 1490, 1560, 1650 (fluorinated arom. ring). ¹⁹F NMR, δ: 3.1 (2 *m*-F); 15.4 (*J*_{p-F-m-F} = 21.0 Hz, *J*_{p-F-o-F} = 7.5 Hz, 1 *p*-F); 34.8 (2 *o*-F); 97.2 (*J*_{CF3-O-F} = 24 Hz, *J*_{CF3-F(β)} = 12.5 Hz, *J*_{CF3-F(β')} = 11 Hz, 3 F, CF₃); 105.2 and 108.8 (*J*_{gem} = 170 Hz, *J*_{F(β)-o-F} = 25 Hz, *J*_{F(β)-o-F} = 14.5 Hz, 2 F(β,β'), AB-system, *cf.* Refs. 7, 8).

Preparation of α, α -dichlorodecafluoropropylbenzene (10). AlCl₃ (29 g) was added to a boiling solution of perfluoropropylbenzene (46 g) in 45 mL of CCl₄. The mixture was heated with stirring for 10 h, cooled, and poured on ice. The organic phase was separated, washed with water, dried with MgSO₄, and concentrated. Distillation *in vacuo* gave 49.2 g of compound 10, b.p. 110 °C (56 Torr).

Found (%): C, 29.14; Cl, 19.60; F, 51.51. Mol. mass 367.9199 (mass spectrum). C₉Cl₂F₁₀. Calculated (%): C, 29.27; Cl, 19.24; F, 51.49. Mol. mass 367.9217. IR, ν / cm^{-1} : 1490,

1530, 1650 (fluorinated arom. ring). ¹⁹F NMR, δ: 2.1 (2 *m*-F); 14.8 ($J_{p-F-m-F} = 21$ Hz, $J_{p-F-o-F} = 7.5$ Hz, 1 *p*-F); 33.6 (2 *o*-F); 48.0 ($J_{F(β)-o-F} = 15.5$ Hz, 2 F(β)); 86.2 ($J_{F(γ)-o-F} = 2.5$ Hz, 3 F(γ)).

The reaction of compound 6 with CsF. A mixture of compound 6 (0.4 g) and CsF (0.09 g) was heated in a sealed tube at 250 °C for 4 h. The contents of the tube were extracted with CCl₄, and the ¹⁹F NMR spectrum of the resulting solution was recorded. According to the spectrum, the mixture contained predominantly perfluoro-methylindan 5.

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