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THERMOLYTIC REACTIONS OF POLYFLUOROORGANIC
COMPOUNDS XVII*, SYNTHESIS AND PYROLYSIS OF
POLYFLUOROPHENYLCYCLOPROPANES

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SUMMARY

Synthesis of perfluorophenylcyclopropane (I) and 1-chloro-1-pentafluorophenyltetrafluorocyclopropane (II) is described and their pyrolysis at 620°C is studied. Pyrolysis of compounds (I) and (II) is shown to give perfluorostyrene (III) and α -chloroheptafluorostyrene (IV) as the main products, together with a small amount of perfluoroindan (V) and 1-chlorononafluoroindan (VI), respectively. Styrene (III) was obtained by bromofluorination of styrene (IV) and subsequent dehalogenation of the resultant α -chloro- β -bromooctafluoroethylbenzene (VII).

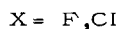
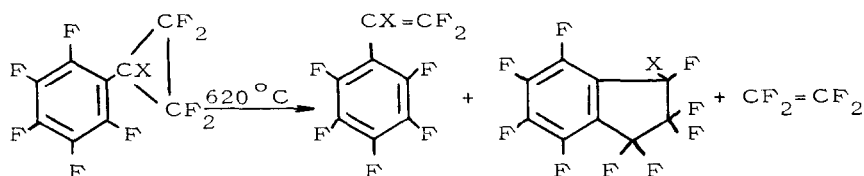
INTRODUCTION

Recently we found an essential difference in the course of copyrolysis reactions of tetrafluoroethylene with pentafluorobenzotrichloride and of tetrafluoroethylene with hexafluorobenzalchloride. In the case of pentafluorobenzotrichloride the main reaction product was styrene (IV), accompanied by indan (VI) and other compounds, whereas in the case of hexafluorobenzalchloride the reaction gave indan (V), and small amounts of styrene (III) and indan (VI) [2]. Participation of pentafluorophenylhalocarbenes and polyfluorophenylcyclopropanes was suggested as one of the possible means of

* For Part XVI, see ref. [1].

contained six signals at $\delta = 26.5$ (2 o-F), 17.8 (1 p-F), 15.0 (2 β -F), 6.4 (2 β -F), 3.3 (2 m-F) and -17.0 (1 α -F) ppm. The chemical shift of the fluorine α -atom of the propane ring corresponds to chemical shifts of the fluorine atoms at tertiary carbon atoms in other perfluorinated compounds [7-9]. The fine structure of the fluorine atom signals of the difluoromethylene groups contained the expected AB system with $J_{FF}^{gem} = 205$ Hz. The ^{19}F NMR spectrum of phenylcyclopropane (II) contained five signals at $\delta = 26.4$ (2 o-F), 20.3 (1 p-F), 17.9 (2 β -F), 15.7 (2 β -F) and 3.8 (2 m-F) ppm. The fine structure of the fluorine atoms of the difluoromethylene groups again contained the expected AB system with $J_{FF}^{gem} = 179$ Hz. The δ - and J-values of fluorine atoms of the difluoromethylene groups of the cyclopropane ring in compounds (I) and (II) are in good agreement with those for other polyfluorinated cyclopropanes [7,8].

Phenylcyclopropanes (I) and (II) were pyrolysed and copyrolysed with tetrafluoroethylene at 620°C . The reaction mixtures obtained both in the pyrolysis of phenylcyclopropanes (I) and (II) and in their copyrolysis reactions with tetrafluoroethylene contained predominantly styrenes (III) and (IV) and indanes (V) and (VI), respectively (Table 1). According to the IR and mass spectrometry data, the gas entrapped during the pyrolysis of compounds (I) and (II) contained tetrafluoroethylene.



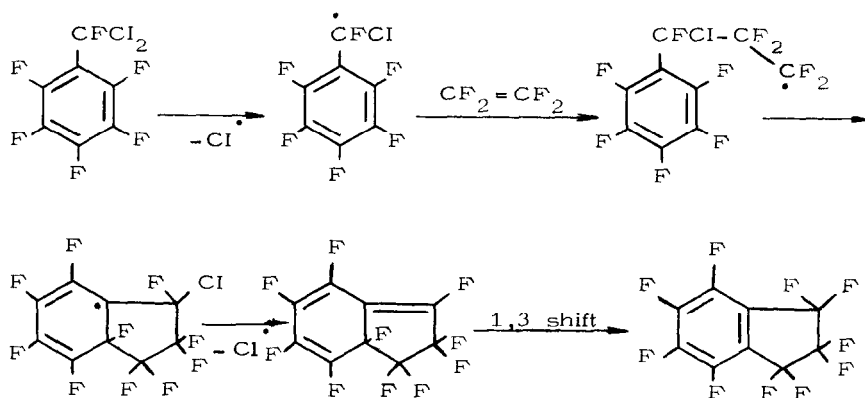
From these data it can be inferred that the main pathway of the transformation of phenylcyclopropanes (I) and (II) under the reaction conditions is their decomposition into the corresponding styrenes (III, IV) and, apparently, difluorocarbene.

The formation of indanes (V) and (VI) from the corresponding polyfluorophenylcyclopropanes is in agreement with the results of

the recently described thermal isomerization of 1-phenyl-2,2-difluorocyclopropane into 2,2-difluoroindan [10] and with the suggestion in ref. [6] concerning isomerization of 1-pentafluorophenyl-1,2-dichlorotrifluorocyclopropane into 1,3-dichlorooctafluoroindan. Part of the indan (V) in the copyrolysis reaction of hexafluorobenzalchloride with tetrafluoroethylene could possibly have been formed in a similar manner.

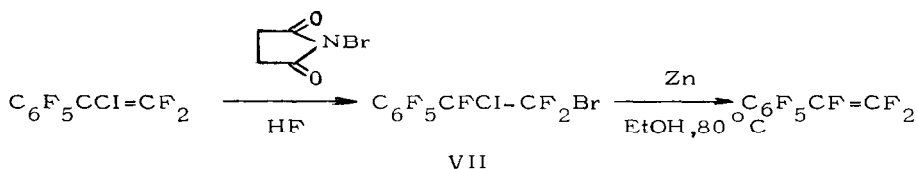
Tetrafluoroethylene has practically no effect on the course of the pyrolysis of phenylcyclopropanes (I) and (II). The predominance of styrenes (III) and (IV) in these reactions conforms with the earlier suggestion that these compounds appear in the copyrolysis reactions of pentafluorobenzotrifluoride and hexafluorobenzalchloride with tetrafluoroethylene through thermal decomposition of the corresponding phenylcyclopropanes (I, II). These data, however, furnish no answer to the question whether the formation of phenylcyclopropanes (I) and (II) takes place in the copyrolysis reactions of pentafluorobenzotrifluoride and hexafluorobenzalchloride with tetrafluoroethylene.

The results obtained also show that phenylcyclopropane (I) is evidently not responsible for the formation of indan (V) as the main product of the copyrolysis reaction of hexafluorobenzalchloride and tetrafluoroethylene [2]. The formation of indan (V) in the reaction can be supposed to proceed through the hexafluoro-*d*-chlorobenzyl radical according to the following scheme:



The formation of indan (V) with the participation of the perfluorobenzyl radical is described in [9].

Perfluorostyrene (III), which is necessary for the synthesis of phenylcyclopropane (I), was obtained by bromofluorination of styrene (IV) with subsequent dehalogenation of the resulting ethylbenzene (VII).



The structure of ethylbenzene (VII) is confirmed by the ^{19}F NMR spectrum which contained six signals at $\delta = 1.4$ (2 m-F), 13.7 (1 p-F), 28.0 (2 o-F), 47.6 (1 α -F), 100.0 (1 β -F), 101.1 (1 β -F) ppm. The fine structure of the signals at $\delta = 100.0$ and 101.1 ppm contained an AB system with $J_{\text{FF}}^{\text{gem}} = 178$ Hz (cf. ref. [6]).

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument for 5% solution in CCl_4 . ^{19}F NMR spectra were recorded on a Varian A-56/60A spectrometer operating at 56.4 MHz for compounds without a solvent (C_6F_6 as an external standard). UV spectra were recorded on a Specord UV VIS instrument for solutions in heptane. The molar concentration was 10^{-4} . Gas-Liquid Chromatography (GLC) analyses were performed on a LHM-7A instrument, equipped with a catharometer and linear temperature programming capability (10°C per min), using stainless steel columns (4 m \times 4 mm) packed with 15% SKTFT-50 or 15% SE-54 on Chromosorb W.

SYNTHESIS OF PERFLUOROSTYRENE (III)

(a) α -Chloro- β -bromooctafluoroethylbenzene (VII) (nc)

In a polyethylene vessel, cooled to -70°C , 20 g of styrene (IV), 100 ml of liquid hydrogen fluoride and 40 g of N-bromo-succinimide were charged.

The mixture was shaken for 12 hours at room temperature, then the contents were poured onto ice and extracted with methylene chloride; the extract was washed with water to obtain a neutral reaction and dried over MgSO_4 . The result was 20 g of a mixture containing, according to GLC, 92% of ethylbenzene (VII). Vacuum distillation of 160 g of the mixture gave fractions (104 g) containing 96-99% (b.p. $77^\circ\text{C}/10\text{mm Hg}$) of compound (VII). Other fractions (47 g) contained 50-57% of compound (VII).

(b) Dehalogenation of α -chloro- β -bromooctafluoroethylbenzene (VII)

A solution of 32 g of ethylbenzene (VII) in 5 ml of ethanol was added, under stirring, to 50 g of zinc dust and 60 ml of absolute ethanol, and the mixture was boiled for 5 hours. Zinc was then filtered off, the filtrate distilled, and the $75-80^\circ\text{C}$ b.p. fraction collected and washed with water (300 ml); the organic layer was separated and dried over MgSO_4 . Styrene (III) was thus obtained (14.9 g). Steam distillation of the solid residue gave an additional 2.9 g of styrene (III). According to GLC, the combined fraction contained 98% of styrene (III). IR spectra of the styrene obtained and the authentic styrene (III) were identical.

PERFLUOROPHENYLCYCLOPROPANE (I) (nc)

A mixture of 3 g of styrene (III) and 5 ml of hexafluoropropylene oxide was heated (190°C , 4 h) in a stainless steel bomb (15 ml). The reaction mixture was washed with water to obtain a neutral reaction and dried over MgSO_4 ; 1.5 g of a mixture were thus obtained. This mixture, according to GLC, contained 84% of phenylcyclopropane (I), 5% of indan (V), and 8% of the starting styrene (III). To separate out the mixture, 18 g were brominated with 2.5 ml of bromine at $40-50^\circ\text{C}$. The mixture was then washed with a sodium metabisulphite solution, dried over MgSO_4 and distilled in a vacuum. The result was one fraction (9 g, b.p. $50^\circ\text{C}/40\text{ mm Hg}$) containing, according to GLC, 95.5% of phenylcyclopropane (I), and another fraction (3.5 g) containing 87% of phenylcyclopropane (I). For the 9 g fraction, analysis gave: C, 35.76, 36.02; F, 63.29, 63.65%; M (mass spectrum) 289;

C_9F_{10} requires C, 36.24; F, 63.76%; M 298. UV spectrum, λ_{max} , nm ($\log \epsilon$): 220 (3.69), 271 (3.14). IR spectrum, cm^{-1} : 1530, 1660 (C_6F_5).

1-CHLORO-1-PENTAFLUOROPHENYLTETRAFLUORO-CYCLOPROPANE (II) (nc)

By following a procedure similar to that described above, from 3 g of styrene (IV) at 215-220°C 2.7 g of a mixture were obtained. This mixture, according to GLC, contained 51.5% of phenylcyclopropane (II), 11% of indan (VI) and 29.4% of the starting styrene (IV). 15 g of the mixture obtained by bromination (55-60°C, 6 h) and subsequent distillation in vacuum were purified from part of the styrene (IV), the result being fractions (8.4 g) which, according to GLC, contained 60-75% of phenylcyclopropane (II). The phenylcyclopropane (II) itself was isolated by preparative GLC (100°C, SKTFT-50 on zeolite, N_2). Analysis: C, 34.77, 34.69; Cl, 11.52, 11.45; F, 54.25, 53.98%. M (mass spectrum) 314, C_9ClF_9 requires C, 34.36; Cl, 11.28; F, 54.36%. M 314. UV spectrum, λ_{max} , nm ($\log \epsilon$): 220 (3.87), 270 (3.08). IR spectrum, cm^{-1} : 1520-1530, 1660 (C_6F_5).

PYROLYTIC TRANSFORMATIONS OF PHENYLCYCLOPROPANES (I) AND (II)

Phenylcyclopropanes (I) or (II) (0.2 g/min) were passed through a silica tube of 400 mm length and 20 mm diameter, heated at 620°C. The reaction products were collected in a receiver and subjected to GLC and ^{19}F NMR analysis. The gas formed during the pyrolysis was trapped at -110°C. The IR spectrum of the gas displayed absorption bands that are characteristic of tetrafluoroethylene (1190, 1340 cm^{-1}). Analysis: M (mass spectrum) 100. C_2F_4 requires M 100. The experimental conditions and composition of the mixtures obtained are given in Table 1.

TABLE 1

Pyrolysis of phenylcyclopropanes (I) and (II)

No. of starting compound	Charging (g)	Gas (flow rate, l/h)	Yield of mixture (g)	Composition of mixture (% according to GLC)*			
				III	IV	V	VI
I **	1.0	Ar (7)	0.55	77.4	-	19.4	-
I **	0.5	CF ₂ =CF ₂ (15)	0.50	71.2	-	22.6	-
II	0.8	Ar (7)	0.35	-	80.0	-	7.0
II	0.7	CF ₂ =CF ₂ (15)	0.78	-	74.0	-	6.0
I ***	0.24	-	0.18	66.0	-	29.0	-

* Corresponds to ¹⁹F NMR data.

** The data take into account the presence of 5% indan (V) in the starting phenylcyclopropane (I).

*** Thermolysis is carried out in an ampoule at 230°C.

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