THERMOLYTIC TRANSFORMATIONS OF POLYFLUOROORGANIC COMPOUNDS
XXIX.* FORMATION OF FLUORINE-CONTAINING STYRENES BY REACTIONS
OF BENZOTRICHLORIDE AND RELATED COMPOUNDS WITH DIHALOCARBENE
SOURCES

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SUMMARY

Reactions of polyfluorobenzotrichlorides, benzotrichloride
and $\alpha,\alpha$-dichloroperfluoroethylbenzene with sources of difluoro-
carbene and other dihalocarbenes lead to the formation of poly-
fluorostyrenes. Formation of polyfluorostyrenes is shown to pro-
ceed possibly by initial dihalocarbene insertion into the C-Cl
bond of the benzylic position with subsequent dechlorination of
the resulting product.

INTRODUCTION

Earlier, we have found various types of reactions of com-
pounds $C_6F_5CX_3$ (X=F,Cl,H) with the difluorocarbene source - tetra-
fluoroethylene. Thus, in octafluorotoluene the $CF_3$-group remains
unchanged in the course of the reaction [2]. At the same time,
in pentafluorobenzotrichloride and pentafluorotoluene the side
chain reacts with tetrafluoroethylene [3,4]. In pentafluorobenzo-
trichloride the $CCl_3$-group undergoes an unusual transformation
to form the halogeno-vinyl group $-CCl=CF_2$. Such a route to give
$\alpha$-chloroperfluorostyrene is of both theoretical and synthetic

* Ref. XXVIII, see [1].

interest. The process may formally be regarded as a reaction of
difluorocarbene with pentafluorobenzotrichloride involving the
benzyl position. Such transformations in the aromatic series are
practically uninvestigated and their regularities are unknown.

To study the general consistencies in the behaviour of
benzotrichlorides and related compounds in these reactions with
dihalocarbene sources, we investigated copyrolysis of the latter
with pentafluorobenzotrichloride, a number of its $\alpha$- and para-
substituted derivatives and benzotrichloride. As dihalocarbene
sources we took tetrafluoroethylene (TFE) and $CHClF_2$ ($:CF_2$),
$CHCl_2F$ ($:CFCl$), $CHCl_3$ ($:CCl_2$) [5].

RESULTS AND DISCUSSION

We have found that copyrolysis of pentafluorobenzotrichlo-
ride (I) with chlorodifluoromethane gives, as in the case of
tetrafluoroethylene [3], $\alpha$-chloroperfluorostyrene (II) as the
main product.
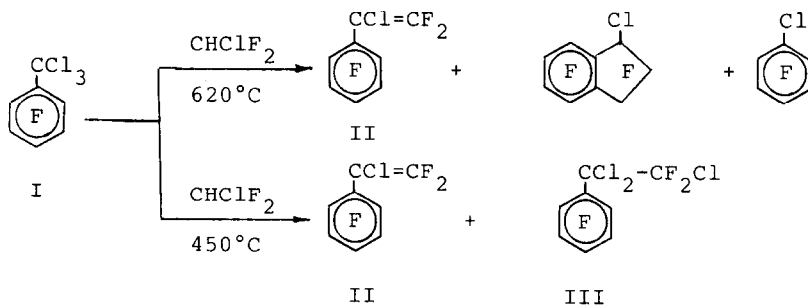


When the temperature of copyrolysis of compound (I) with
$CHClF_2$ was lowered to 450°C, the reaction was sluggish and gave
small amounts of styrene (II) and $\alpha,\alpha,\beta$-trichloroperfluoro-
ethylbenzene (III). Experimental conditions of the reactions of
polyfluoroaromatic compounds with difluorocarbene sources are
given in Table 1.

Formation of polyfluorostyrenes may proceed also in similar
reactions of benzotrichlorides, containing substituents in the
pentafluorophenyl ring. Thus copyrolysis of p-chlorotetrafluoro-
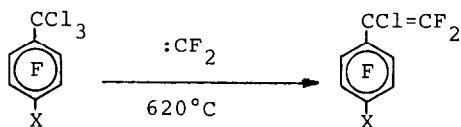benzotrichloride (IV) with TFE and $CHClF_2$ and of perfluoro-

TABLE 1

Copyrolysis of polyfluorinated benzotrihalogenides and ethylbenzenes with tetrafluoroethylene and difluorochloromethane

| Initial compound, g | | Gas* | Temperature, °C | Yield of mixture, g | Content of main products in mixture, %** | Yield of poly-fluorostyrenes, %*** |
|---|---|---|---|---|---|---|
| (I) | 570 | $CHClF_2$ | 620 | 554 | (II)-77, (XIV)-2, (XV)-3 | 80 |
| (I) | 7.2 | $CHClF_2$ | 450 | 4.9 | (I)-65, (II)-2.4, (III)-2 | 2 |
| (IV) | 85 | $CHClF_2$ | 620 | 75.6 | (VI)-65 | 60 |
| (IV) | 16 | $CF_2=CF_2$ | 620 | 18 | (VI)-39 | 47 |
| (V) | 13 | $CHClF_2$ | 620 | 9 | (VII)-65 | 47 |
| (VIII) | 124 | $CHClF_2$ | 620 | 98 | (IX)-44, (II)-11, (X)-24, (XI)-1 | 37-(IX), 10-(II) |
| (VIII) | 5.2 | $N_2$ | 620 | 3.1 | (VIII)-15, (XIII)-14, (XI)-21, (II)-5 | 10-(XIII), 3-(II) |
| (III) | 1.0 | $CHClF_2$ | 620 | 0.6 | (II)-87 | 66 |
| (III) | 0.9 | $CF_2=CF_2$ | 450 | 0.5 | (II)-58, (III)-10 | 47 |
| (XII) | 1.0 | $CHClF_2$ | 650 | 0.6 | (XIII)-10, (II)-20, (XII)-6, (XIV), (XV) and (X)- 2 each | 10-(XIII), 20-(II) |
| (XVI) | 0.7 | $CF_2=CF_2$ | 570 | 0.8 | (XIV)-46, (XV), (VI), (XI) and (XIII)- 1-2 each | - |
| (XVIII) | 1.0 | $CF_2=CF_2$ | 680 | 0.4 | (XIV)-30, (XVII)-29 | - |

*Flow rate, 1/h: $CHClF_2$-23, $CF_2=CF_2$-15, $N_2$-15. **According to GLC and $^{19}F$ NMR spectroscopy data.

p-isopropylbenzotrichloride (V) with $CHClF_2$ gave $\alpha$-chloro-p-chloroperfluorostyrene (VI) and $\alpha$-chloroperfluoro-p-isopropyl-styrene (VII) respectively.

$$
\underset{\substack{\text{CCl}_3 \\ \text{F} \\ \text{X}}}{\bigcirc} \xrightarrow[620°C]{:CF_2} \underset{\substack{\text{CCl}=CF_2 \\ \text{F} \\ \text{X}}}{\bigcirc}
$$

X=Cl    IV                          VI

X=C₃F₇   V                          VII

It is preferable to use difluorochloromethane rather than TFE to obtain polyfluorostyrenes (II) and (VI), since the reactions with difluorochloromethane give higer yields of the poly-fluorostyrenes. The reaction mixtures contain smaller amounts of by-products. For the preparation of other polyfluorostyrenes, difluorochloromethane may also appear to be more preferable than tetrafluoroethylene.

Substitution of one chlorine atom in the trichloromethyl group by a trifluoromethyl group did not change the main pathway found for benzotrichloride (I). The reaction of $\alpha,\alpha$-dichloroperfluoroethylbenzene (VIII) with difluorochloromethane led to the formation of perfluoro-$\alpha$-methylstyrene (IX). The reaction mixture contained also styrene (II), $\alpha$-hydro-$\alpha$-chloro-octafluoroethylbenzene (X) and traces of pentafluorochloro-benzene (XI).
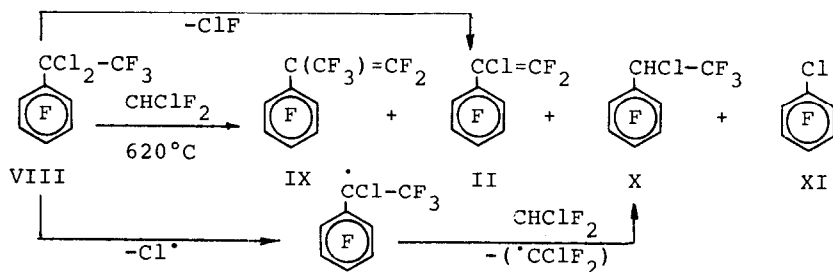


One of the routes to styrene (II) may involve dechloro-fluorination of the starting ethylbenzene (VIII), and compound (X) may be formed by substitution of the chlorine atom in the
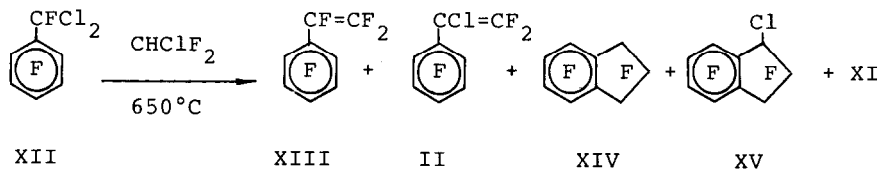
starting product by hydrogen, for example, by the radical mecha-
nism. Substitution of the chlorine atom in compound (I) by the
difluorochloromethyl group changed the course of the reaction.
Copyrolysis of compound (III) with TFE [3] and $CHClF_2$ gave
styrene (II).

CCl_2-CF_2Cl

⟨F⟩  CHClF_2  →  ⟨F⟩ CCl=CF_2  +  XI

620°C
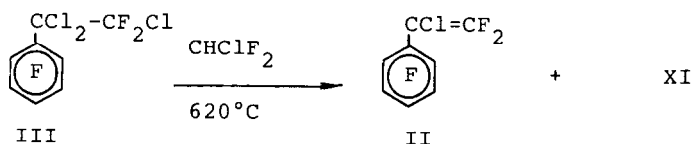
III                    II

The same route occurs in the thermolysis of ethylbenzene (III)
in the absence of a difluorocarbene source [3]. Dechlorination
proceeds smoothly even at 450°C. These data indicate that dechlor-
ination of compound (III) occurs before its interaction with
difluorocarbene.

Substitution of chlorine by fluorine in the trichloro-
methyl group of compound (I) led in the reactions with $CHClF_2$
and TFE [3] to a sharp decrease in the yield of perfluorostyrene
in comparison with the yield of styrene(II) in the reaction of
compound (I) with $CHClF_2$.

The reaction of hexafluorobenzalchloride (XII) with $CHClF_2$
gave, apart from perfluorostyrene (XIII), styrene (II) and small
amounts of perfluoroindan (XIV) and 1-chloroperfluoroindan (XV),
as well as compounds (XI).

CFCl_2

⟨F⟩  CHClF_2  →  ⟨F⟩ CF=CF_2  +  ⟨F⟩ CCl=CF_2  +  ⟨F⟩⟨F⟩  +  ⟨F⟩⟨F⟩ Cl  + XI

650°C

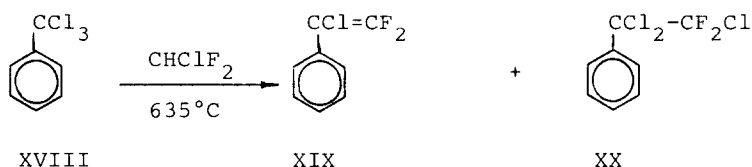XII            XIII      II       XIV        XV

Styrene (II) in this reaction is formed possibly via formation
of benzotrichloride (I), which may be represented in a similar
way as the transformation of pentafluorobenzylfluoride to penta-
fluorobenzylchloride [3].

At the same time, the reaction of benzalchloride (XII)
with TFE gives predominantly perfluoroindan (XIV) [3].
$\alpha,\alpha$-Chlorobromohexafluorotoluene (XVI) reacted with TFE to give
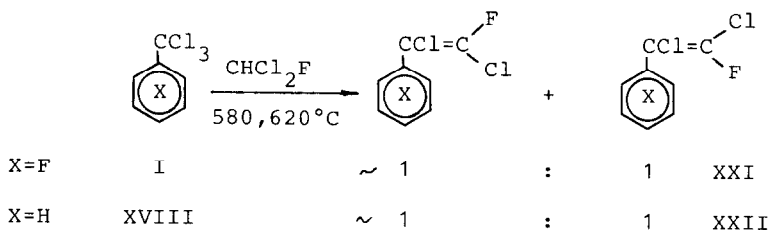also mainly perfluoroindan. Substitution of two chlorine atoms

by the two fluorine ones in benzotrichloride (I) did not allow
us to synthesize perfluorostyrene. Thus in the reaction of
heptafluorobenzylchloride (XVII) and TFE, perfluoroindan is
practically the only reaction product.

Transformations of benzotrichlorides to polyfluorostyrenes
are of quite a general character. These reactions take place
also in the non-fluorinated series. The reaction of benzotri-
chloride (XVIII) with difluorochloromethane afforded $\alpha$-chloro-
$\beta,\beta$-difluorostyrene (XIX) and a small amount of $\alpha,\alpha,\beta$-trichloro-
$\beta,\beta$-difluoroethylbenzene (XX).

$$CCl_3 \xrightarrow[635°C]{CHClF_2} CCl=CF_2 \quad + \quad CCl_2-CF_2Cl$$

XVIII               XIX                    XX

When the temperature was lowered to 575°C, compounds (XIX) and
(XX) were formed in comparable quantities, and at 535°C the
reaction  gave predominantly ethylbenzene (XX), see Table 2.

Apart from the reactions with difluorocarbene sources,
polyfluorostyrenes may also be formed by the reactions with
fluorochloro- and dichloro-carbene sources. Thus copyrolysis of
compounds (I) and (XVIII) with fluorodichloromethane gave <u>cis</u>-
and <u>trans</u>-$\alpha,\beta$-dichloroperfluorostyrene (XXI) and $\alpha,\beta$-dichloro-
$\beta$-fluorostyrene (XXII) respectively, in about equal amounts
(Table 2).

$$CCl_3 \xrightarrow[580,620°C]{CHCl_2F} CCl=C\begin{smallmatrix}F\\Cl\end{smallmatrix} \quad + \quad CCl=C\begin{smallmatrix}Cl\\F\end{smallmatrix}$$

| X=F | I | ~ 1 | : | 1 | XXI |
| X=H | XVIII | ~ 1 | : | 1 | XXII |

The reaction of pentafluorobenzotrichloride (I) with
chloroform yielded $\alpha,\beta,\beta$-trichloropentafluorostyrene (XXIII),
together with pentafluorobenzalchloride (XXIV) and compound
(XI), see Table 3.

TABLE 2

Thermolytic reactions of benzotrichloride (XVIII), styrene (XIX) and ethylbenzene (XX) with haloforms

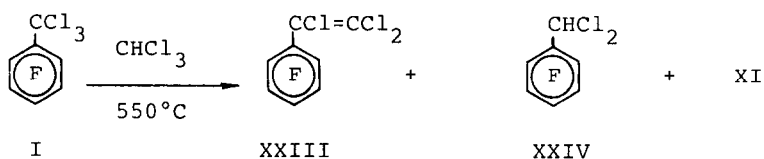| Initial compound, g | Gas* | Temperature, °C | Yield of mixture, g | Content of main products in mixture, %** | Yield of poly-fluorostyrenes, %** |
|---|---|---|---|---|---|
| (XVIII) 14 | $CHClF_2$ | 635 | 9.4 | (XIX)-23, (XX)-6 | 18 |
| (XVIII) 13 | $CHClF_2$ | 575 | 8.5 | (XIX)-33, (XX)-39, (XVIII)-3 | 24 |
| (XVIII) 2.6 | $CHClF_2$ | 535 | 1.4 | (XIX)-5, (XX)-33, (XVIII)-47 | 3 |
| (XVIII) 6.4 | $CHCl_2F$ | 620 | 6.4 | (XXII)-22, (XVIII)-5 | 24 |
| (XIX) 0.2 +<br>(XVIII) 0.4 | Ar | 535 | 0.2 | (XIX)-15, (XVIII)-52, (XX)<1 | - |
| (XX) o.46 | $CHClF_2$ | 620 | 0.4 | (XIX)-27, (XX)-absent | 30 |

*Flow rate, 1/h: $CHClF_2$-23, $CHCl_2F$-23, Ar-15. **According to GLC and $^{19}F$ NMR spectroscopy data.

TABLE 3

Copyrolysis of pentafluorobenzotrichloride (I) with $CHCl_2F$ and $CHCl_3$
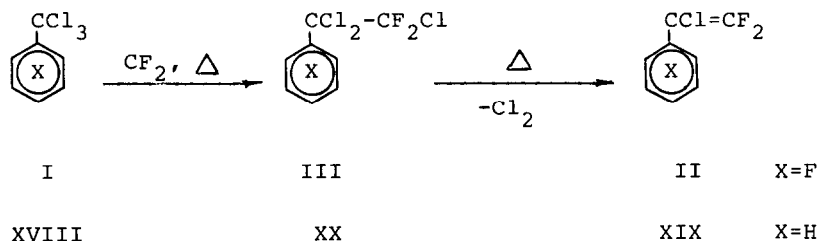
| Compound (I), g | Haloform, l/h (g) | Temperature, °C | Yield of mixture, g | Content of main products in mixture, %[**] | yield of poly-fluorostyrenes, %[*] |
|---|---|---|---|---|---|
| 112.0 | $CHCl_2F$ 15 | 580 | 260 | (XXI)-23 | 57 |
| 3.0 | $CHCl_2F$ 15 | 620 | 2.9 | (XXI)-47 | 46 |
| 2.9 | $CHCl_2F$ 50 | 580 | 2.8 | (XXI)-40 | 39 |
| 1.2 | $CHCl_3$ (4.7) | 550 | 1.9 | (XXIII)-11, (XXIV)-2.6, (XI)<1 | 17 |
| 1.0 | $CHCl_3$ (3.5) | 520 | 2.5 | (XXIII)-12, (XXIV)-15, (I)-7 | 29 |
| 1.0 | $CHCl_3$ (3.5) | 450 | 4.0 | (XXIII)-1, (XXIV)-6.4, (I)-16 | 4 |

[*] According to GLC and $^{19}F$ NMR spectroscopy data. [**] The rest are unidentified, mainly low boiling products.

CCl$_3$ / CHCl$_3$ (F-benzene ring) I $\xrightarrow{\text{CHCl}_3 \ 550°C}$ CCl=CCl$_2$ (F-benzene ring) XXIII $+$ CHCl$_2$ (F-benzene ring) XXIV $+$ XI

The yield of compound (XXIV) is increased by lowering the temperature. Raising the temperature of copyrolysis ($>550°C$) led to resinification of the product and, as a consequence, to a decreased yield of styrene (XXIII). Benzalchloride (XXIV) is possibly formed in a similar way as ethylbenzene (X). The sources of hydrogen may be chloroform [6] and hydrogen chloride formed by its thermolysis [7].

One of the possible mechanisms of formation of polyfluoro-styrenes is the initial insertion of dihalocarbenes into the C-Cl bonds of the benzyl position to give as intermediates ethyl derivatives of benzene, followed by their subsequent dehalogenation. This mechanism is supported by data on the reaction of benzotrichloride (I) and its non-fluorinated analogue with difluorochloromethane, which gave products which formally correspond to the products of difluorocarbene insertion into the C-Cl bond. Formation of ethylbenzenes (III) and (XX) in these reactions cannot occur by chlorination of the styrenes, since copyrolysis of styrene (XIX) with benzotrichloride (XVIII) as a potential chlorinating agent under conditions of interaction of the latter with CHClF$_2$ did not give ethylbenzene (XX). At the same time, thermolysis of ethylbenzenes (III) and (XX) under conditions of the reactions of benzotrichlorides (I) and (XVIII) with difluorocarbene sources proceeds smoothly with their dechlorination.

CCl$_3$ (X-benzene ring) I, XVIII $\xrightarrow{\text{CF}_2, \ \triangle}$ CCl$_2$-CF$_2$Cl (X-benzene ring) III, XX $\xrightarrow[-\text{Cl}_2]{\triangle}$ CCl=CF$_2$ (X-benzene ring) II, XIX

|  |  |  |
|---|---|---|
| I | III | II      X=F |
| XVIII | XX | XIX      X=H |

The possibility of difluorocarbene insertion into C-Cl bonds
at the benzylic position has been shown also for the reaction
of 1,1-dichloroperfluoroindan with $CHClF_2$ [8].

The observed decrease in the yield of perfluorostyrene
from compound (XII) and $CHClF_2$, as compared to the yield of
styrene (II) from benzotrichloride (I) and $CHClF_2$, was unexpec-
ted and it is difficult at present to offer an adequate explana-
tion for this phenomenon. Nevertheless, taking into account the
mechanism for the insertion of singlet methylene and similar
carbenes into the C-Cl bonds of chloroalkanes, which has been
assumed in ref. [9], it is possible to suggest the reason for
the difference in these processes. The side-chain fluorine atom,
due to its stronger $\sigma_I$ effect (0.52) as compared to $\sigma_I$ (0.47) of
chlorine [10], may be assumed to hinder the electrophilic attack
by difluorocarbene on the C-Cl bond in compound (XII) more than
in benzotrichloride (I). This may lead to the decreased yield
of perfluorostyrene. This suggestion is supported also by the
behaviour of compound (XVII) with the source of $:CF_2$.

In the case of the reaction of compound (IX) with difluoro-
chloromethane, apart from the inductive effect of the $CF_3$-group,
its steric effect on the process of $:CF_2$ insertion into the
C-Cl bond should also be taken into account

Other routes leading to the formation of polyfluorostyrenes
cannot be completely rejected. As in ref. [3], polyfluorosty-
renes may be assumed to be formed by recombination of carbenes.
Thus styrene (IX) could be formed by the recombination of
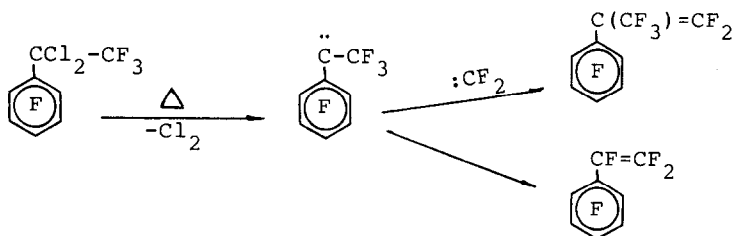difluorocarbene with perfluorophenylmethylcarbene.

TABLE 4

Elemental analysis data, IR and UV spectra of polyfluorinated styrenes and compound (x)*

| Compound | Found, % | | | Required, % | | | IR spectrum (cm$^{-1}$) | | UV spectrum |
|---|---|---|---|---|---|---|---|---|---|
| | C | Cl | F | C | Cl | F | C=C | fluorinated arom. ring | $\lambda_{max}$; nm (lg $\xi$) |
| $C_8ClF_7$ (II) | 36.3 | 13.7 | 49.7 | 36.3 | 13.4 | 50.3 | 1750 | 1665, 1531, 1515 | 242(3.53), 267(3.1) |
| $C_8Cl_2F_6$ (VI)** | | | | | | | 1745 | 1645, 1490, | 248(3.75), 278(3.09) |
| $C_{11}ClF_{13}$ (VII) | 32.0 | 9.0 | 59.0 | 31.8 | 8.6 | 59.6 | 1750 | 1665, 1495 | 258(3.57), 285(3.40) |
| $C_9F_{10}$ (IX) | 36.3 | – | 63.8 | 36.3 | – | 63.8 | 1750 | 1660, 1530, 1515 | 264(2.97) |
| $C_8Cl_2F_6$ (XXI) | 34.0 | 25.0 | 40.6 | 34.2 | 25.3 | 40.6 | 1650 | 1670, 1525, 1500 | 248(3.58), 273(3.14,sh.) |
| $C_8H_5ClF_5$ (XIX)** | | | | | | | 1720 | | |
| $C_8HClF_8$ (X)* | | | | | | | | 1655, 1525, 1510 | |

* Molecular weghts of compounds were determined by mass-spectrometry and are in agreement with the calculated ones. ** The element composition of compounds (VI), (XIX) and (X) was determined by high-resolution mass-spectrometry.

Generation of the latter may explain the formation of styrene (XIII) by the thermolysis of ethylbenzene (VIII).



VIII           XIII           II
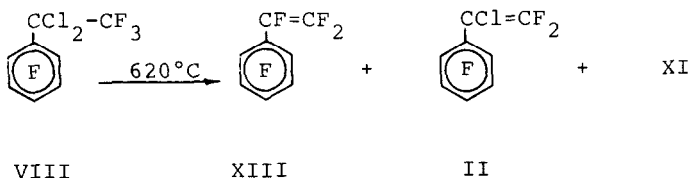
Yields of polyfluorostyrenes in the reactions of polyfluoro-benzotrichlorides with difluorochloromethane and tetrafluoro-ethylene are different. This may result from the different ratios of $:CF_2$ and TFE in these reactions.

Formation of polyfluoroindanes by copyrolysis of polyfluoro-benzotrihalogenides with difluorocarbene sources possibly proceeds with participation of radicals of the benzylic type [11].

Formation of compound (XI) in the reactions studied may proceed by substitution of the side chain by chlorine [3].

EXPERIMENTAL

$^{19}F$ and $^1H$ NMR spectra were recorded on a Varian A-56/60A at 56.4 and 60 MHz for compounds and reaction mixtures without a solvent. Chemical shifts are quoted in $\delta$ ppm down-field from $C_6F_6$ and TMS as external standards. IR spectra were obtained on a UR-20 spectrometer for solutions in $CCl_4$. UV spectra were recorded on a Specord UV-VIS instrument for solutions in heptane, $10^{-4}-10^{-3}$ mol/l. Mass-spectra were obtained on an AEI-MS 902. Elemental analysis data, IR and UV spectral data of polyfluoro-styrenes obtained in the work, and compounds (X) and (XX) are given in Table 4.

Copyrolysis of polyfluorobenzotrihalogenides and related compounds with haloform and tetrafluoroethylene

The aromatic compound was passed at the rate of 25 g/h, in a flow of TFE (15 l/h) or a haloform (23 l/h) through a quartz tube (400x20 mm) placed in an electric furnace. In the

TABLE 5

$^{19}F$ NMR spectra of styrenes (II), (VI), (VII), (IX), (XXI) and (XIX)

$$p\!-\!\underset{m}{\overset{x}{\left(F\right)}}\!\!-\!\underset{o}{C}\!=\!C\!\!\begin{smallmatrix}y\\z\end{smallmatrix}$$

| No. of compound | Chemical shift, ppm | | | | | | $J_{F-F}$, Hz | | |
|---|---|---|---|---|---|---|---|---|---|
| | m | p | o | x | y | z | y–z | y–o | z–o |
| (II)[a] | 1.3 | 12.4 | 25.4 | – | 81.4 | 80–0 | 23.5 | 2.0 | 6.3 |
| (VI) | 21.8 | – | 24.5 | – | 80.4 | 79.2 | 23.0 | 1.7 | 7.5 |
| (VII) | 30.3 | –13.6[b] / 89.4 | 28.6 | – | 83.4 | 82.6 | 20.0 | 1.0 | 7.0 |
| (IX)[c] | 2.1 | 13.5 | 26.5 | 104.5 | 95.0 | 93.2 | 1.5 | | 4.0 |
| (XXI)[d] | 2.8 | 13.5 | 26.7 | – | 95.0 | 92.0 | | 2.5 | 7.0 |
| (XIX)[e] | – | – | – | – | 80.9 | 75.4 | 35 | | |

[a] The spectrum of the styrene is in agreement with one reported in ref. [3]. [b] $\delta$ of the signals of the perfluoroisopropyl group ($-C\underline{F}(CF_3)_2$ and $-CF(C\underline{F}_3)_2$). [c] $J_{x-y}=19$, $J_{x-z}=10.5$ Hz. [d] A mixture of stereoisomers. [e] $^1H$ NMR, 7.3 ppm – aromatic ring.

case of chloroform, a solution of the aromatic compound in it
(mole ratio 1:10) was passed in a flow of argon (15 l/h). The
reaction mixture was steam-distilled, dried over $MgSO_4$ and anal-
ysed by GLC. The mixtures obtained by several similar proced-
ures were combined and fractionated. When the reactions were
conducted with small amounts of reagents, individual styrenes
were isolated by preparative GLC. The presence of the styrenes
(II), (XIII),(XX) and (XXIII), indanes (XIV) (XV), ethylbenzene
(III) and compound (X) in the mixtures was confirmed by compari-
son of the IR and ^{19}F NMR spectra of the reaction mixtures of
fractions enriched with the compounds, with those of individual
products and by GLC. The ^{19}F NMR spectral data are given in
Table 5.

The fluorine signals in the ^{19}F NMR spectra of the styr-
enes and ethylbenzenes were assigned on the basis of the chemical
shifts, spin-spin coupling constants (SSCC) and integral inten-
sities.

When the signals of the vinyl fluorine atoms in polyfluoro-
styrenes were assigned, their SSCC were additionally compared
with those for the vinyl fluorine atoms of other polyfluorosty-
renes [3,12,13]. For the difluoromethylene group of fluorine-
containing styrenes and olefins, the presence of the AB-system is
typical. Its value varies from 5.5 to 87 Hz [12,13,14].

Styrenes (II), (VI) and (VII) have close $J_{F-F}^{gem}$ values,
which may result from the presence of a $-CCl=CF_2$ group in them.
$J_{F-F}^{gem}$ of styrene (IX) proved to be small ($\sim 1.5$ Hz), which is
in agreement with the $J_{F-F}^{gem}$ value for perfluoro-p-$\alpha$-dimethyl-
styrene (5.5 Hz) [13].


Ethylbenzene (XI): ^{19}F NMR spectrum, 2.9 ($2F^m$, $J_{p-m}=19.5$
Hz), 11.7 ($1F^p$, $J_{p-o}=4.5$), 24.8 ($2F^o$), 91.5 ($CF_3$, $J_{o-CF_3}=11$ Hz);
^{1}H NMR- one signal at 5.5, $J_{H-F_{CF_3}}=7.5$ Hz (cf.13).


Ethylbenzene (XX): ^{19}F NMR spectrum, 103.8 ($CF_2$); ^{1}H NMR
spectrum - a multiplet at $\delta$ 7.8 (aromatic ring).

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