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THERMOLYTIC REACTIONS OF POLYFLUOROORGANIC COMPOUNDS. PART XXVII*. INTERACTION OF 1,1-DICHLOROPOLYFLUOROINDANES WITH HALOFORMS

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SUMMARY

A number of polyfluoro-1-methyleneindanes have been obtained by copyrolysis of 1,1-dichloropolyfluoroindanes with $CF_2=CF_2$, $CHClF_2$, $CHCl_2F$ and $CHCl_3$. A possibility is shown for the reaction of 1,1-dichloroctafluoroindan with $CHClF_2$ to proceed by way of difluorocarbene insertion into the C-Cl bond of the benzylic position of this indan, with subsequent dechlorination of the insertion product.

INTRODUCTION

Copyrolysis of pentafluorobenzotrichloride and its derivatives with haloforms and tetrahaloethylenes as sources of dihalocarbenes is known to give polyfluorinated styrenes and indanes [2]. In the case of haloforms the yield of styrenes increases and the yield of indanes decreases, compared with that for tetrahaloethylenes [2]. Continuing the investigation of high-temperature reactions of polyfluoroaromatic compounds containing chlorine atoms in the benzylic position, we now report the interaction of 1,1-dichloropolyfluoroindanes with sources of dihalocarbenes. This extends the range of compounds involved in such transformations, and explores the possibility of synthesizing in such a manner otherwise unavailable polyfluorinated methyleneindanes or their isomers - methylindenes. The above compounds are of interest, for instance, for studying the effect of fluorine atoms on the properties of aromatic and antiaromatic systems [3].

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[*] For communication XXVI cf. [1].

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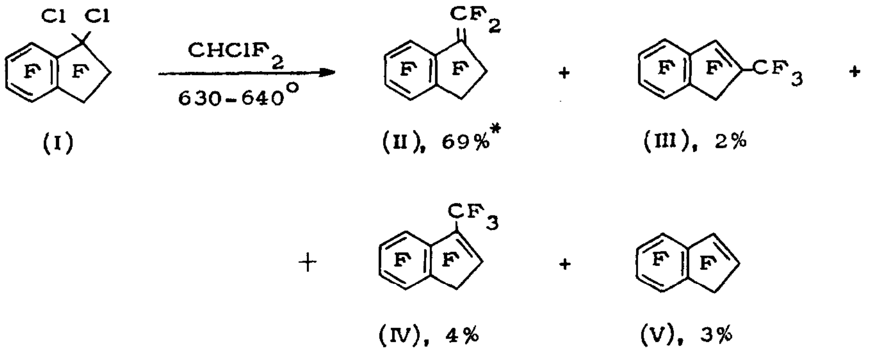
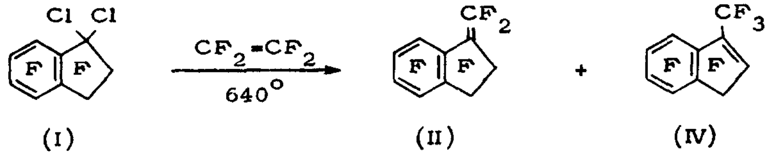
RESULTS AND DISCUSSION

We have shown, that in copyrolysis of 1,1-dichlorooctafluoroindan (I) with difluorochloromethane as a source of difluorocarbene [4] the main reaction product is perfluoro-1-methyleneindan (II). Other reaction products were perfluoro-2- (III) and -3-methylindenes (IV), as well as octafluoroindene (V).



Methyleneindan (II) was also the main product of the reaction of indan (I) with another source of difluorocarbene, namely, tetrafluoroethylene. In this case methylindene (IV) was also formed.



The IR and ^{19}F NMR spectra of indenes (III) and (V) were identical with the spectra of authentic samples [5]. The structures of compounds (II) and (IV) were confirmed by the elemental analysis data, spectral characteristics and chemical transformations. Thus, compound (II) under the action of caesium fluoride has been converted to

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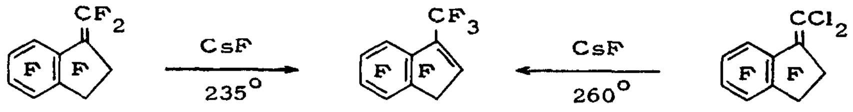
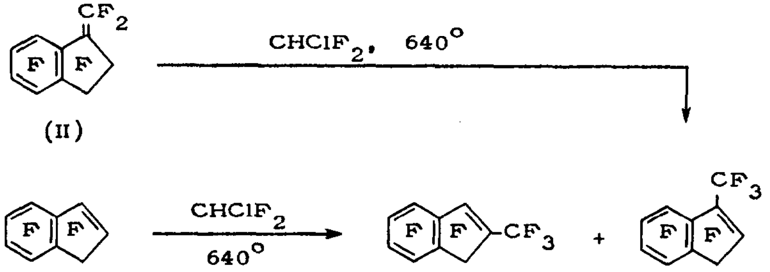
[*] The yield of compounds (according to GLC analysis and ^{19}F NMR spectra of fractions obtained by distillation of the reaction mixture) as calculated for compound (I) taken for the reaction.

methylindene (IV). In the absence of CsF this reaction does not take place. Methylindene (IV), in its turn, was obtained in a reverse reaction from the known 1-dichloromethyleneoctafluoroindan (VI) [6] and caesium fluoride.



(II) (IV) (VI)

Under the conditions of the reaction between compound (I) and $CHClF_2$, methyleneindan (II) is partially isomerized to methylindene (IV). It has been shown, that the latter, together with methylindene (III) isomeric to it, in addition, appears to be the product of interaction of indene (V) with $CHClF_2$.

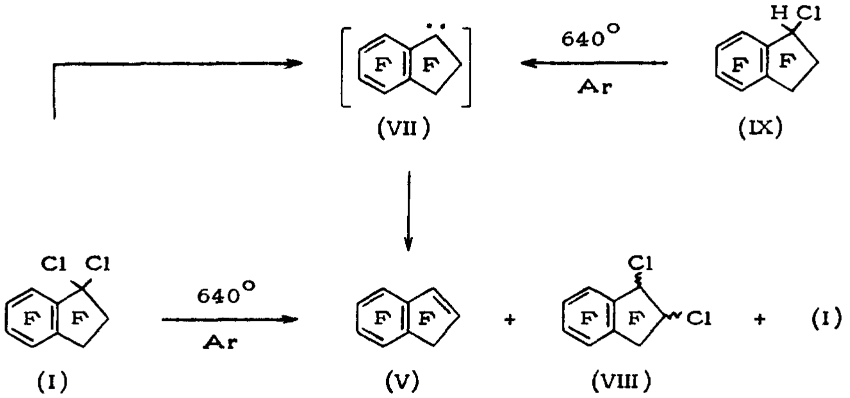


(II)

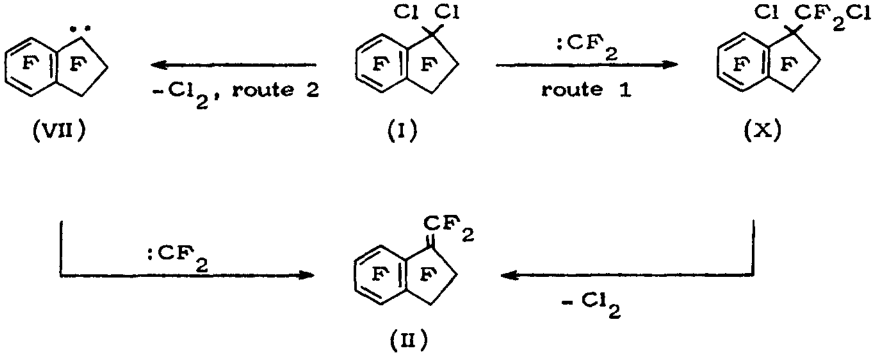
(V) (III) (IV)

~2 : 1

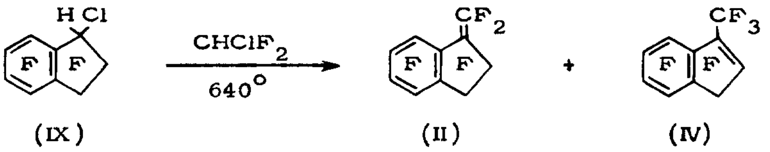
The formation of indene (V), probably, proceeds through isomerization of carbene (VII) generated from indan (I). Indeed, indan (I) under the reaction conditions, in the absence of a $:CF_2$ source, undergoes partial transformation into indene (V) and its derivative - 1,2-dichlor-octafluoroindan (VIII). With a temperature rise to 680°, the yield of compound (V) is increased. The supposition put forward is not in contradiction to the data obtained by us on the thermal transformation of 1-hydro-1-chloroctafluoroindan (IX) into indene (V). In the dehydrochlorination of compound (IX), evidently, carbene (VII) is generated, similarly to the case with haloforms [4, 7, 8] and α-fluoro-benzylchloride [9]. Carbene (VII), in its turn, evidently, isomerizes into indene (V). Isomerization of fluorine-containing carbenes into olefins is described in the literature [10].



In conformity with our previous investigations on copyrolysis of pentafluorobenzotrichloride and its derivatives with haloforms and tetrahaloethylenes [2], as well as on the thermolysis of polyfluorophenylcyclopropanes [11], the formation of methyleneindan (II) in the reaction of indan (I) with $CHClF_2$ can be supposed as most likely to proceed by way of difluorocarbene insertion into the C-Cl bond of indan (I) with subsequent dechlorination of the insertion product (route 1) or/and as a result of recombination of carbene (VII) with difluorocarbene (route 2).

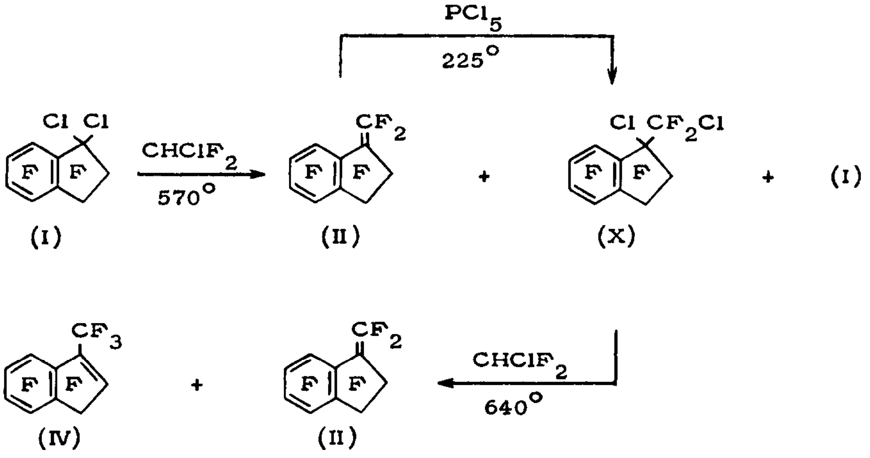


The formation of indene (V) in the pyrolysis of compound (I) under argon, as well as in its copyrolysis with $CHClF_2$ is not in contradiction with route 2 of the reaction. In addition , in the interaction of indan (IX) with $CHClF_2$, as in the reaction of compound (I) with $CHClF_2$, the main product is methyleneindan (II).

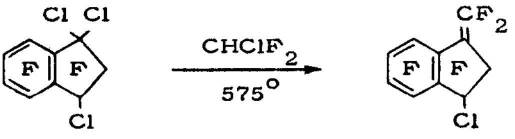


In this case, however, one cannot exclude the possibility of compound (II) being formed by way of difluorocarbene insertion into the C-Cl bond of indan (IX) with subsequent dehydrochlorination of the insertion product (cf. [12]).

Should route 1 of the reaction be realized, with lowering of the temperature one could expect the presence in the reaction mixture of the product of difluorocarbene insertion into the C-Cl bond of the initial compound. As a matter of fact, in the interaction of indan (I) with $CHClF_2$ at 570°, 1-chloro-1-difluorochloromethyloctafluoroindan (X) is formed. Indan (X) obtained from compound (II) by heating with PCl_5, in its turn, under the conditions of indan (I) reacting with $CHClF_2$, gives methyleneindan (II) in a high yield.



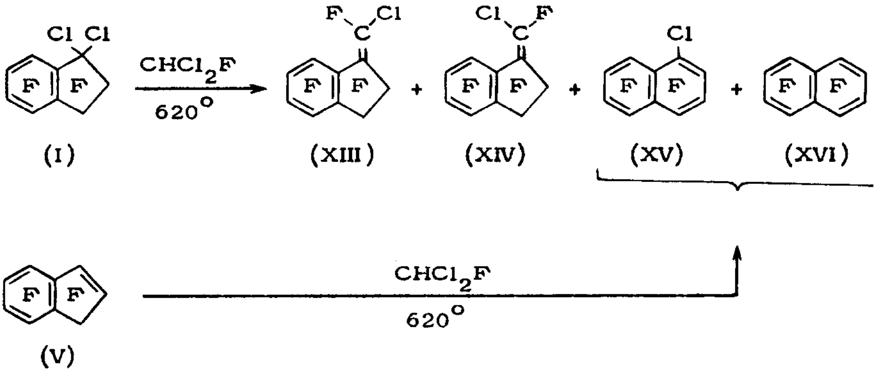
In accordance with the fact that copyrolysis of indan (I) with $CHClF_2$ gives methyleneindan (II), it appeared reasonable to extend this reaction, on the one hand, to other 1,1-dichloropolyfluoroindanes and, on the other hand, to other haloforms, so as to determine whether it was possible to synthesize other polyfluoro-1-methyleneindanes in such a manner. We have shown, that in copyrolysis of 1,1,3-trichloroheptafluoroindan (XI) with $CHClF_2$ at 575° the main product is 3-chloroperfluoro-1-methyleneindan (XII).



(XI) (XII)

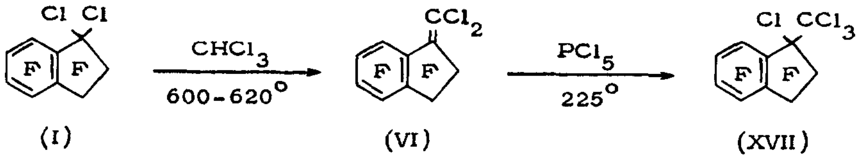
With the temperature rising to 640° the yield of methyleneindan (XII) drops. Copyrolysis of 1,1,3,3-tetrachlorohexafluoroindan with $CHClF_2$ leads to a very complicated mixture of products.

Formation of polyfluoro-1-methyleneindanes takes place also in the interaction of indan (I) with other haloforms. But the yield of the corresponding methyleneindanes is lower than in the case of $CHClF_2$. In copyrolysis of indan (I) with $CHCl_2F$ as a source of fluorochlorocarbene [7], isomeric 1-fluorochloromethyleneoctafluoroindanes (XIII) and (XIV) are formed in a ratio ~ 2:1 alongside of 1-chloroheptafluoronaphthalene (XV) and a small quantity of octafluoronaphthalene (XVI).



Compounds (XV) and (XVI) at least partially can be products of interaction of indene (V), which is formed from indan (I), with $CHCl_2F$. Indeed, in copyrolysis of indene (V) with $CHCl_2F$ the main product is naphthalene (XVI) alongside of naphthalene (XV).

In the interaction of indan (I) with chloroform as a source of dichlorocarbene [8] at ~600° 1-dichloromethyleneoctafluoroindan (VI) is formed.

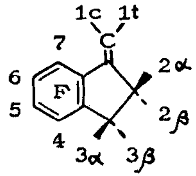


When the temperature is lowered to 525°, there takes place not only the formation of methyleneindan (VI), but also reduced elimination of one chlorine atom in the initial compound, leading to indan (IX). 1-Chloro-1-trichloromethyloctafluoroindan (XVII), the product of dichlorocarbene insertion into the C-Cl bond of compound (I), has not been detected (^{19}F NMR spectrum of the mixture). Authentic indan (XVII) has been synthesized from compound (VI) and PCl_5.

The ratio of methyleneindanes (XIII) and (XIV) in the reaction of compound (I) with $CHCl_2F$ has been determined from the ^{19}F NMR spectrum of their mixture. A distinctive feature of the spectra of these compounds is a large coupling constant of the fluorine atom of the fluorochloromethylene group, which is in the cis-position to the aromatic ring, with the fluorine atom in position 7 (see Table 2). In Tables 1 and 2 chemical shifts of the signals and coupling constants in the ^{19}F NMR spectra of the methyleneindanes described in this paper are presented. Signals were assigned by comparing the spectra of these compounds in the same manner as it was done for polyfluorochlorindanes [2c]. In the assignment of the signals of vinyl fluorine atoms, it was assumed that the value of the coupling constant of fluorine nuclei was materially dependent on the spatial proximity of the interacting nuclei [13]. It should be noted , that in the methyleneindanes described, the signal of the atom F^5 which is in para-position to the double bond is less shifted down-field than the signal of F^6. A similar situation is observed in the ^{19}F NMR spectrum of octafluoroindene (V) [14].

TABLE 1

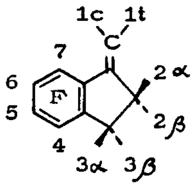
Chemical shifts (ppm down-field from C_6F_6 as an internal standard) of signals in ^{19}F NMR spectra of polyfluoromethyleneindanes



Compound	F - 1c	F - 1t	F - 2	F - 3	F - 4	F - 5	F - 6	F - 7
(II)	98.2	90.5	48.4	53.1	22.8	12.6	17.0	26.9
(VI)	-	-	47.7	52.5	22.5	14.7	17.3	41.0
(XII)	98.2	89.6	51.9 (α) 59.1 (β)	48.6 (α)	22.9	12.5	15.6	26.4
(XIII)	112.2	-	47.4	53.9	22.6	13.7	17.2	31.3
(XIV)	-	104.4	48.6	52.7	22.6	13.7	17.2	35.2

TABLE 2

Moduli of the coupling constants (Hz) for polyfluoromethyleneindanes



J_{ij} \ Compound	(II)	(VI)	(XII)*	(XIII)	(XIV)
1c2	2.5		3	4	
1c5	8		8	8	
1c7	73		71	97	
1t2	16		17 (α) 21 (β)		24
1t5	8		8		8
1t7	8		8		16
34	7	8	7	7	8
45	17	21	17	17**	17**
46	8	7	8	8**	8**
47	16	17	16	16	16
56	16	19	16	16**	16**
57	5	8	5	6	6
67	17	19	17	17	17

* $J_{2\alpha 2\beta}$ = 234 Hz

** Approximate values, since signals 4, 5 and 6 of compounds (XIII) and (XIV) are pairwise mutually superimposed.

TABLE 3

Elemental analysis data, IR and UV spectra of compounds

Compound	Found, %			Required, %			IR spectrum (cm^{-1}), fluorinated arom. ring	UV spectrum λ_{max}, nm (lg ε)
	C	Cl	F	C	Cl	F		
$C_{10}F_{10}$* (II)							1754 (C=C), 1530, 1513	241 (4.16), 281 (2.84), 285 (2.82, sh.)
$C_{10}F_{10}$* (IV)							1700 (C=C), 1515, 1500	278 (3.15, sh.), 305 (3.43)
$C_{10}Cl_2F_{10}$ (X)	31.3	18.6	49.4	31.5	18.6	49.9	1525	270 (3.01)
$C_{10}ClF_9$ (XII)	36.7	10.4	52.2	36.8	10.9	52.4	1756 (C=C), 1532, 1516	242 (4.19), 284 (2.86)
$C_{10}ClF_9$ (XIII+XIV)	36.5	10.6	52.4	36.8	10.9	52.4	1688 (C=C), 1532, 1516	255 (4.29), 287 (3.13, sh.)
$C_{10}Cl_4F_8$ (XVII)	29.2	34.6	36.9	29.0	34.3	36.7	1525	270 (3.26)

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* Elemental composition of compounds (II) and (IV) is determined by means of high-resolution mass spectrometry.

TABLE 4

Pyrolysis of compounds (I), (II), (IX), (X) and their copyrolysis with $CHClF_2$

Initial compound, g	Gas (15 l/h)	Temperature, °C	Yield of mixture, g	Content of main products in mixture, %[*]
(I) - 2	Ar	640	1.27	(I) - 54, (V) - 6, (VIII)[**] - 10
(I) - 1	Ar	680	0.40	(I) - 21, (V) - 18
(I) - 1	$CHClF_2$	570	0.53	(I) - 5, (II) - 51, (X) - 27
(I) + (II) - 0.5 + 0.5	Ar	570	0.48	(I) - 41, (II) - 26, (IV) - 17[***]
(I) - 1	$CHClF_2$	640	0.51	(II) - 65, (IV) - 5
(II) - 1	$CHClF_2$	640	0.64	(II) - 66, (IV) - 9
(IX) - 0.6	$CHClF_2$	640	0.29	(II) - 60, (IV) - 8
(IX) - 0.7	Ar	640	0.14	(V) - 57
(X) - 1	$CHClF_2$	640	0.52	(II) - 69, (IV) - 4
(X) + (I) - 0.5 + 0.5	$CHClF_2$	640	0.56	(II) - 69, (IV) - 4

[*] According to GLC and ^{19}F NMR spectroscopy data.

[**] Authentic product (VIII) is prepared by known method [16].

[***] Content of each of other products does not exceed 3%.

EXPERIMENTAL

^{19}F NMR spectra were recorded on a Varian A-56/60A at 56.4 MHz for solutions in CCl_4 (11 mol.%). Chemical shifts are quoted in δ ppm down-field from C_6F_6 as an internal standard. IR spectra were recorded on a UR-20 spectrometer for solutions in CCl_4. UV spectra were recorded on a Specord UV-VIS for solutions in heptane, $10^{-4}-10^{-3}$ mol/l. Mass spectra were recorded on an AEI-MS 902. Elemental analysis data, IR and UV spectra of novel compounds are presented in Table 3.

Interaction of 1,1-dichloroctafluoroindan (I) with $CHClF_2$

311 g of indan (I) were passed through a quartz tube (400x20 mm) at 630-640° in a stream of $CHClF_2$ (15 l/h) for 16.5 h. Distillation with steam gave 300 g of a mixture (dried over $MgSO_4$) which, according to GLC data, contained ~65-68% of methyleneindan (II). The mixture was subjected to vacuum distillation in a stream of argon on a rectification column; as a result, 156 g of perfluoro-1-methyleneindan (II) (nc) were isolated, b.p. 109.8-110°/75 mm Hg, containing no admixtures (^{19}F NMR spectrum). In addition, fractions were obtained, enriched with compounds (II) - (V) (^{19}F NMR spectra, GLC).

The reaction carried out with smaller quantities of compound (I) gave a mixture of the same composition, but in a smaller yield (see Table 4). The results of pyrolysis of some other compounds are also presented in Table 4.

Reaction of indan (I) with $CF_2=CF_2$

By following a similar procedure, from 5 g of indan (I) and $CF_2=CF_2$ (15 l/h) at 630-640° (15 minutes) 4.75 g of a mixture were obtained, which, according to the GLC and ^{19}F NMR data, contained 47% of methyleneindan (II) and 15% of indene (IV).

3-Chloroperfluoro-1-methyleneindan (XII) (nc)

By following a procedure similar to that described above, from 10.1 g of indan (XI) and $CHClF_2$ at 575° (30 minutes) 7 g of a mixture were obtained, which, according to GLC data, contained 33% of methyleneindan (XII). The latter was isolated by preparative GLC (175°, SKTFT-50 on chromaton W, N_2).

Copyrolysis of indan (I) with $CHCl_2F$

In a similar manner, from 2g of indan (I) and $CHCl_2F$ (15 l/h) at 620° (6 minutes) 4 g of a mixture were obtained. A part of low-boiling products with b.p. to 110° was distilled off from the mixture. The residue (1.6 g) contained according to GLC data, 30% of methyleneindanes (XIII) and (XIV), 10% of (XV), 3% of (XVI), 10% of the initial compound. Naphthalene (XV) and the mixture of methyleneindanes (XIII) (nc) and (XIV) (nc) were isolated by preparative GLC (200°, SKTFV-803 on celite, N_2). The ^{19}F NMR spectrum of the obtained naphthalene (XV) and its m.p. coincide with those of the authentic sample [15].

Interaction of indan (I) with $CHCl_3$

(a) At 620°

A solution of 1 g of indan (I) in 4.2 g of $CHCl_3$ was passed through a quartz tube (400x20 mm) at 620° for 4 minutes. Distillation with steam and drying over $MgSO_4$ gave 1.5 g of a mixture which, according to GLC data, contained 4% of methyleneindan (VI), 16% of initial (I), 11% of CCl_4, 62% of C_2Cl_4. In the ^{19}F NMR spectrum of the mixture signals of authentic compounds (I) and (VI) were observed.

(b) At 525°

In a similar manner from 1 g of indan (I) and 4.2 g of $CHCl_3$ at 525° 2.87 g of a mixture were obtained. The fraction with b.p. to 130° was distilled off. The residue (1.08 g) contained, according to GLC data, 4% of methyleneindan (VI), 17% of indan (IX), 41% of the initial compound (I). In the ^{19}F NMR spectrum of the residue signals of the authentic compound (IX) [16] were observed.

Copyrolysis of octafluoroindene (V) with $CHCl_2F$ and $CHClF_2$

The process was carried out in the same manner as the copyrolysis of indan (I) with these haloforms. From 1 g of indene (V) and $CHCl_2F$ at 620°, after distilling-off the products with b.p. to 120°, 1.15 g of a mixture were obtained, containing, according to the GLC and ^{19}F NMR data, 30% of naphthalene (XVI) and 7% of naphthalene (XV).

From 1 g of indene (V) and $CHClF_2$ at 640° a complex mixture of products was obtained (0.44 g), containing, according to GLC data, 11% of indene (III), 6% of indene (IV) and 8% of the initial compound. In the ^{19}F NMR spectrum of the mixture signals of the above-mentioned compounds were observed.

Perfluoro-3-methylindene (IV) (nc)

(a) A mixture of 1 g of compound (VI) with 3.54 g of CsF was heated in a sealed ampoule at 235° for 2.5 h and then at 260° for 3 h. Distillation with steam gave 0.73 g of methylindene (IV).

(b) In a similar manner indene (IV) was obtained from 0.16 g of compound (II) and 0.02 g of CsF at 235°. In the absence of CsF the reaction does not take place.

^{19}F NMR spectrum of methylindene (IV): 99.0 (CF_3, $J_{F^2-CF_3} \sim \sim J_{F^4-CF_3} \sim 20$ Hz), 40.0 ($1F^2$), 37.7 ($2F^1$, $J_{F^1-F^2} \sim 14$ Hz), 24.1 (2F), 16.6 (1F), 10.8 (1F).

Interaction of methyleneindan (II) with PCl_5

6 g of compound (II) were heated in a sealed ampoule with 12.8 g of PCl_5 at 225° for 6.5 h. The contents were transferred into water, the organic layer (7.2 g) was dried over $MgSO_4$ and distilled in vacuum. 5.6 g of compound (X) (nc) were obtained, b.p. 75-77° (5 mm Hg). ^{19}F NMR spectrum: 106.4 (CF_2Cl), 56.9 ($2F^3$), 52.5 ($1F^2_A$), 39.6 ($1F^2_B$), 31.2 (1F), 23.6 (1F), 19.3 (1F), 17.4 (1F); $J^{AB}_{FF} = 237$ Hz (cf. [2c]).

1-Chloro-1-trichloromethyloctafluoroindan (XVII) (nc)

By following a procedure similar to the above, from 1 g of compound (VI) and 1.9 g of PCl_5 after sublimation (120°, 4 mm Hg) 0.86 g of compound (XVII) (viscous liquid) was obtained.
^{19}F NMR spectrum: 58.9 ($2F^3$), 59.5 ($1F^2_A$), 44.2 ($1F^2_B$), 38.0 (1F), 23.1 (1F), 19.3 (1F), 17.0 (1F); $J^{AB}_{FF} = 230$ Hz.

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