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FLUOROINDENES

6.* REACTION OF PERFLUORO-2-METHYLINDENE WITH ALUMINUM CHLORIDE

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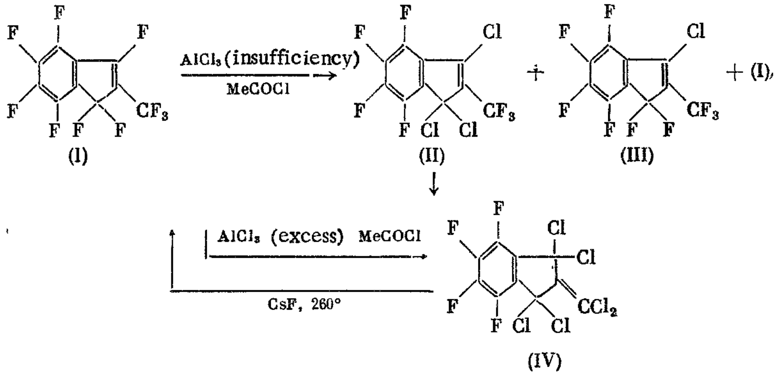
We have recently shown that polyfluoroindenyl cations are formed during the reaction of polyfluoroindenes with SbF_5 [2]. In the case of perfluoro-2-methylindene (I), breaking off of an F atom from the geminal site of the molecule also takes place with the formation of the perfluoro-2-methylindenyl cation. Breaking off of an F atom from the CF_3 group was not observed in this case. On the basis of these results, the suggestion has been expressed of aromatic character of the last ion, unlike the antiaromatic unfluorinated indenyl cations [2]. For confirmation of the generality of the observed phenomenon, it was of interest to study the relative reaction capability of the geminal site and the CF_3 group in compound (I) during its reaction with other Lewis acids. Behavior of the indene (I) with $AlCl_3$ has been studied in this work.

It has been shown that, during the reaction of compound (I) with insufficient $AlCl_3$ in acetyl chloride, 1,1,3-trichloroperfluoro-2-methylindene (II) is formed along with 3-chloroperfluoro-2-methylene (III). In this case, the unreacted compound (I) remains. Upon increase of the amount of $AlCl_3$, the indene (II) is obtained along with 2-dichloromethylene-1,1,3,3-tetrachlorotetrafluoroindan (IV). The indan (IV) is formed with good yield during the action of $AlCl_3$ on the indenes (I) and (II):



Structures of the compounds (II) and (IV) have been confirmed by the results of elemental analysis, measurement of molecular weights, spectral results, and the chemical conversions. Thus, the reaction of the indan (IV) with CsF leads to the compound (I). In the ^{19}F NMR spectrum of the indan (IV) are two signals of equal intensity with δ −23.3 ($F^{4,7}$) and −14.8 ppm ($F^{5,6}$) (assignment of signals by analogy with those for symmetrical polyfluoroindans [3]). In the ^{13}C NMR spectrum of the indan (IV) exist signals with δ 144.5 and 144.1 ($C=CCl_2$), ~143.3 d ($C^{4,5,6,7}$; $^{1}J_{^{13}C-F} \sim 260$ Hz), 123.4 ($C^{3a,7a}$), and 77.4 ppm ($C^{1,3}$) (compare with chemical bonds of ^{13}C atoms in organic compounds having similar structural fragments [4]). The signals of atoms $C^{3a,7a}$ and components of the doublets of atoms $C^{4,5,6,7}$ are broadened as the result of spin–spin coupling with the F atoms not bonded with these atoms [5]. Signals of the rest of the carbon atoms are singlets.

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*See [1] for Communication 5.

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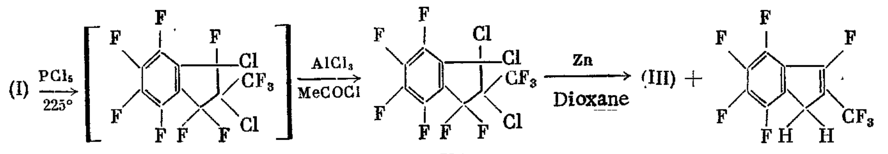
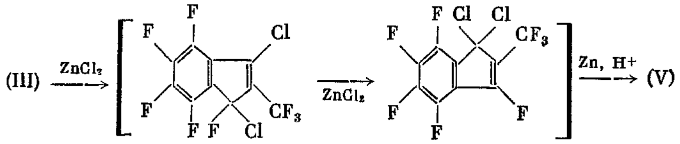
The indene (III) is prepared by reverse synthesis from (I) according to the scheme



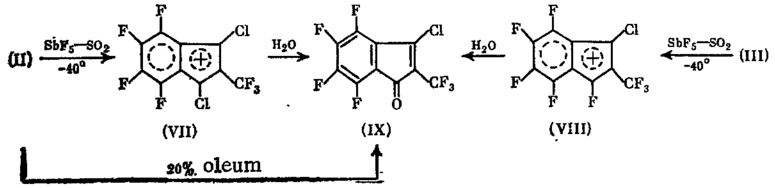
(VI) (V)

In this case, 1,1-H,H-perfluoro-2-methylindene (V) is obtained along with the compound (III). One of the possible paths of formation of the indene (V) may be the reaction of compound (III) with $ZnCl_2$, prepared during the dehalogenation of 1,1,2-trichloroperfluoro-2-methylindan (VI) according to the scheme



A similar type of conversion was suggested in [6, 7].

It is possible that the exchange of F atoms for Cl in the indene (I) under the action of $AlCl_3$, which leads to the compound (II), proceeds through the intermediate formation of 1-chloroperfluoro-2-methylindene, which later isomerizes to the indene (III) or is converted into 1,1-dichloroperfluoro-2-methylindene. Further reaction of these indenes with $AlCl_3$ leads to (II). The process probably proceeds in a manner analogous to that for octafluoroindene and $AlCl_3$ [6]. In this case it is evident that polyfluoroindenyl cations (or crypto-ions) are formed as intermediates. Actually perfluoro-2-methylindenyl [2], 1,3-dichloroperfluoro-2-methylindenyl (VII), and 1-chloroperfluoro-2-methylindenyl (VIII) cations, respectively, are formed during reaction of (I)-(III) with SbF_5:



(VII) (IX) (VIII)

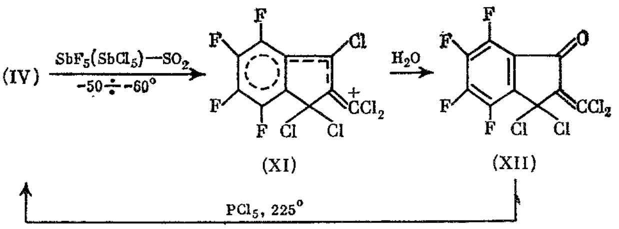
The ^{19}F NMR spectral data, as well as the formation of 3-chloroperfluoro-2-methylindenone (IX) upon the treatment of solutions of the salts of cations (VII) and (VIII) with water provides evidence of the formation of the cations (VII) and (VIII) during the reaction of the indenes (II) and (III) with SbF_5. The compound (IX) was obtained by reverse synthesis, the reaction of the indene (II) with oleum. In the ^{19}F NMR spectrum of the cation (VII) exist signals with δ −101.8, −63.8, and −37.3 ppm (3 : 2 : 2), and in the spectrum of the cation (VIII) with δ −150.0, −101.9, −73.7, −69.0, −41.4, and −37.7 ppm (1 : 3 : 1 : 1 : 1 : 1). The same regularities are observed in the spectra of the ions (VII) and (VIII) as in the spectra of other polyfluorinated indenyl cations [2].

The formation of compound (IV), and not 1,1,3-trichloro-2-trichloromethyltetrafluoroindene (X), in the reaction of the indenes (I) and (II) with $AlCl_3$ probably is caused by the greater thermodynamic stability of compound (IV), although the double bond in it likewise is not conjugated with the aromatic ring. In compound (IV), in comparison with the indene (X), reduction of the strain of the five-membered ring as the result of decrease in the number of sp^2 hybrid C atoms evidently occurs. In addition, in compound (IV) steric interactions of the atoms Cl−Cl and Cl−F probably should be lower than in the indene (X).

The formation of compound (IV) in the reaction of indenes (I) and (II) with $AlCl_3$ may be represented, for example, by a scheme which includes the intermediate formation of the 1,1,3-trichlorotetrafluoroindenyl-2-dichloromethyl cation (XI) (or a crypto-ion):

$$\text{(I) or (II)} \xrightarrow{AlCl_3} [(XI)] \xrightarrow{Cl^-} \text{(IV)}$$

This suggestion does not contradict the results which we obtained on the formation of the cation (XI) during the reaction of (IV) with SbF_5 or $SbCl_5$ in SO_2 at low temperature:



Evidence of the formation of the cation (XI) under these conditions is provided by ^{19}F NMR spectral data and some chemical conversions. In the ^{19}F NMR spectrum of the cation (XI) are four signals of equal intensities. Their fine structure was worked out in approximation to a spectrum of first order. Shifts of the signals for solutions in SbF_5-SO_2 and $SbCl_5-SO_2$ do not differ significantly ($\leqslant$ 0.8 ppm). In the spectrum of the cation (XI) are observed shifts of the signals in a weak field and increase in some spin–spin coupling constants of the F atoms in comparison with those for their precursors. However, these changes are less than the analogous changes observed earlier in the spectra of polyfluorinated benzyl cations [8]. Assignment of the signals was done by analogy with those for the polyfluorinated benzyl cations [8].

During reaction of a solution of a salt of the cation (XI) with water, 2-dichloromethylene-3,3-dichlorotetrafluoroindan-1-one (XII) is formed along with its precursor (IV). Structure of the compound (XII) was confirmed by the results of elemental analysis and measurement of the molecular weight, IR and ^{19}F NMR spectra, and chemical transformations. Thus, the reaction of (XII) with PCl_5 leads to the formation of the indan (IV). The similarity of the UV spectra of compound (XII) and the polyfluoroindans and the noticeable difference from the spectra of the polyfluoroindenones (see Experimental) also confirms the structure of the compound (XII) and rejects the alternative structure of 2-trichloromethyl-3-chlorotetrafluoroindenone.

Thus, we have shown that in compound (I), under the action of $AlCl_3$, the exchange of F atoms for Cl proceeds more easily in position 1 than in the CF_3 group. The possibility is not excluded that this is associated with the greater thermodynamic stability of the perfluoro-2-methylindenyl cation than of the perfluoro-2-indenylmethyl cation. This, in turn, probably is evidence in favor of the aromatic character of the perfluoro-2-methylindenyl cation [2].

EXPERIMENTAL

The ^{19}F NMR spectra were taken on Varian A-56/60A apparatus (56.4 MHz) for solutions of neutral compounds in CCl_4 (11 mole %) or for solutions of salts of the ions (VII), (VIII), and (XI) in SO_2. The internal standard was C_6F_6. The ^{13}C NMR spectrum of compound (IV) was taken on a Bruker Physik AG HX-90 pulse spectrometer (FRG) (22.63 MHz) with subsequent Fourier transformation on a B-NC 12 electronic computer. The internal standard was CCl_4 (96.0 ppm from TMS), taken as the solvent. The IR spectra were taken on UR-20 apparatus in CCl_4. The UV spectra were recorded on Specord UV-VIS apparatus in heptane. The mass spectra were taken on AEI MS-902 apparatus.

3-Chloroperfluoro-2-methylindene (III). A mixture of 0.6 g of (I) and 1.2 g of PCl_5 was heated in a sealed ampul at 225-230° for 6 h. It was put into water, extracted with CH_2Cl_2, washed with a solution of $NaHCO_3$, and dried with $MgSO_4$. After partial evaporation of the solvent, 0.95 g of product was obtained which was dissolved in 4 ml of AcCl, and 0.26 g of $AlCl_3$ was added to it at ~20°. Then the mixture was stirred 4 h at 45° and treated in a manner analogous to the preceding. The amount of 1.05 g of a mixture was obtained which contained the indan (VI) along with a small amount of solvent. The ^{19}F NMR spectrum of (VI) (external standard C_6F_6, δ, ppm): −99.4 (3F), −54.1 and −51.4 (AB system, $J^{gem}_{F-F} = 266$ Hz), −25.4, −23.1, −19.5, −16.9 (3 : 1 : 1 : 1 : 1 : 1 : 1).

Later, during boiling, to 1.27 g of activated Zn powder in 5 ml of dioxane was added a solution of the mixture obtained in 5 ml of dioxane and was boiled with stirring for 2.5 h. The mixture was steam distilled, extracted with CH_2Cl_2, dried with $MgSO_4$, and the solvent partly distilled. The amount of 1.4 g of a mixture was obtained which contained, according to the results of GLC (LKhM-7A, 70-270°, 4000 × 4 mm, SE-30 on Chromosorb W, 15 : 100, He, 60 ml/min), about ~10% of the compounds (III) and (V) and 74% dioxane along with unidentified impurities. The compounds (III) and (V) were separated by preparative GLC (135°, SKTFT-50 on Celite, N_2).

The indene (III), mp 54-55° (from alcohol, in a sealed capillary): Found: $C_{10}ClF_9$ (high-resolution mass spectrometry). The ^{19}F NMR spectrum (δ, ppm): −101.5 (CF_3), −45.4 (CF_2), −23.5, −19.2, −15 (3 : 2 : 1 : 1 : 2); the signal of the CF_3 group is a triplet with $J_{CF_3-F^1} = 3.4$ Hz (compare with spectrum of compound (I) [1]). IR spectrum (ν, cm^{-1}): 1625 (C=C), 1510 (fluorinated aromatic ring), 1430, 1420. UV spectrum [λ_{max}, nm (log ε)]: 301 (3.60), 309 (3.54, plateau), compare [1].

Indene (V), found: $C_{10}H_2F_8$ (high-resolution mass spectrometry). PMR spectrum: doublet (J = 7 Hz for multiplets), δ 3.7 ppm, compare [7]. The ^{19}F NMR spectrum (δ, ppm): −102.3 d (CF_3, $J_{CF_3-F^3}$ = 15 Hz, compare [1]), −45.3 (F_3), −19.3, −16.2, −9.6, −8.1 (3 : 1 : 1 : 1 : 1 : 1). IR spectrum (ν, cm^{-1}): 2965 (C−H), 1680 (C=C), 1535, 1520, 1506 (fluorinated aromatic ring), 1430.

Reaction of Perfluoro-2-methylindene (I) with $AlCl_3$. a) To a stirred solution of 0.85 g of the indene (I) in 3 ml of AcCl at ~20° was added dropwise a solution of 0.69 g of $AlCl_3$ in 7 ml of AcCl for 1 h. Then the mixture was stirred 4 h at 45-50° and left overnight. The reaction mass was poured onto ice, extracted with CH_2Cl_2, washed with a solution of $NaHCO_3$, and dried with $MgSO_4$. The solvent was distilled off, and the mixture was held at −8° for a week, and then filtered. Obtained was 0.23 g of 2-dichloromethylene-1,1,3,3-tetrachlorotetrafluoroindan (IV), mp 135.5-136.2° (from alcohol, in a sealed capillary). Found: C 29.29; Cl 51.63; F 18.57%; mol. wt. 403 (isothermal distillation). Calculated for $C_{10}Cl_6F_4$: C 29.38; Cl 52.03; F 18.59%; mol. wt. 409. The ^{19}F and ^{13}C NMR spectra are given in total. IR spectrum (ν, cm^{-1}): 1606 (C=C), 1649, 1522 (fluorinated aromatic ring), 1402.

The liquid (0.8 g) was distilled in vacuum in a current of argon. Obtained was 0.6 g of 1,1,3-trichloroperfluoro-2-methylindene (II), bp 83-85° (~2 mm). Found: $C_{10}Cl_3F_7$ (high-resolution mass spectrometry). The ^{19}F NMR spectrum of (II), (δ, ppm): −103.1 s, −23.8, −17.1, −14.0, −13.1 (3 : 1 : 1 : 1 : 1). IR spectrum (ν, cm^{-1}): 1609 (C=C), 1516 (fluorinated aromatic ring), 1413. UV spectrum: λ_{max} 306 nm (log ε 3.57), compare [6].

b) In a manner analogous to the preceding, from 0.2 g of the indene (I) and 0.08 g of $AlCl_3$ was obtained 0.2 g of a mixture containing, according to ^{19}F NMR spectral data, the compounds (I), (II), and (III) in the ratio ~2.6 : 2 : 1.

c) In an analogous manner, from 0.06 g of the indene (I) and 0.16 g of $AlCl_3$ was obtained 0.07 g of a compound, the IR and ^{19}F NMR spectra of which were identical to the spectra of (IV), obtained in the experiment a.

d) In an analogous manner, from 0.065 g of the indene (II) and 0.11 g of $AlCl_3$ was obtained 0.07 g of (IV), the IR and ^{19}F NMR spectra of which coincided with the spectra of the product obtained in the previous experiment.

Reaction of the Indan (IV) with CsF. The amount of 0.13 g of the indan (IV) with 0.58 g of CsF was heated in a sealed ampul for 2 h at 235° and 4 h at 260°. By distillation, 0.06 g of a substance was isolated, the IR and ^{19}F NMR spectra of which coincided with the spectra of the indene (I).

3-Chloroperfluoro-2-methylindenone (IX). A solution of 0.14 g of the indene (II) in 0.3 ml of CCl_4 was stirred with 0.5 ml of 20% oleum 0.5 h at ~20°, then 15 min at 50°, and 1.5 h at ~20°. The reaction mass was poured into water, extracted with CH_2Cl_2, and dried with $MgSO_4$. From the extract was isolated 0.1 g of the indenone (IX), which was purified by sublimation, mp 74-75.3° (in a sealed capillary). Found: $C_{10}ClF_7O$ (high-resolution mass spectrometry). The ^{19}F NMR spectrum (δ, ppm): −101.5 s, −27.0, −21.1, −18.8, −17.0 (3 : 1 : 1 : 1 : 1). IR spectrum (ν, cm^{-1}): 1737, 1607 (C=O, C=C), 1503 (fluorinated aromatic ring), 1411. UV spectrum [λ_{max}, nm (log ε)]: 313 (3.23 sh), 327 (3.42), 3.40 (3.44), 355 (3.20 sh), compare [2, 6].

Formation of 1,3-Dichloroperfluoro-2-methylindenyl Cation (VII). To a solution of 0.24 g of SbF_5 in SO_2 (~0.5 ml) in an ampul for NMR was added 0.1 g of the indene (II) at −50°, stirred (an intense green coloration of the solution appeared), and the ^{19}F NMR spectrum recorded at −40° (see general part). Then the solution was poured into water, extracted with CH_2Cl_2, dried with $MgSO_4$, and the solvent was distilled off. Obtained was 0.08 g of a mixture containing, according to ^{19}F NMR spectral data, the indenone (IX) and its precursor (II) in the ratio ~2 : 1.

Solution of a Salt of the 1-Chloroperfluoro-2-methylindenyl Cation (VIII). In an analogous manner, from 0.04 g of the indene (III) and 0.11 g of SbF_5 in SO_2 (^{19}F NMR spectrum at −40° is presented in the general part) was obtained (VIII). Then hydrolysis of the salt was carried out in a manner analogous to the previous one. Obtained was 0.026 g of a compound, the IR spectrum of which coincided with the spectrum of the indenone (IX).

Formation of 1,1,3-Trichlorotetrafluoroindenyl-2-dichloromethyl Cation (XI). a) In a manner analogous to the preceding, from 0.15 g of the compound (IV) and 0.32 g of SbF_5 in SO_2 at −60° was obtained a red solution of a salt of the cation (XI). In the ^{19}F NMR spectrum of the ion (XI) at −50° were four well-resolved signals of equal intensity (δ, ppm): −53.6 (F^6), −43.8 (F^4), −29.9 (F^7), −21.4 (F^5); $J^{4,5}_{F-F}$ = 20.5, $J^{4,6}_{F-F}$ = 28.5, $J^{4,7}_{F-F}$ = 13.5, $J^{5,6}_{F-F}$ = 20, $J^{5,7}_{F-F}$ = 9, $J^{6,7}_{F-F}$ = 21.5 Hz.

b) In a manner analogous to the preceding, from 0.11 g of the compound (V) and 0.37 g of $SbCl_5$ in SO_2 at −60° was obtained a red solution of a salt of the cation (XI). In the ^{19}F NMR spectrum of (XI) at −50° were four well-resolved signals of equal intensity (δ, ppm): −54.4 (F^6), −44.5 (F^4), −30.1 (F^7), −21.8 (F^5). The fine structure of the signals coincided with that in case a.

Hydrolysis of a Salt of the Cation (XI). The solution of the salt of the ion (XI) obtained in experiment a was poured into water, extracted with CH_2Cl_2, dried with $MgSO_4$, and the solvent was distilled off. Obtained was 0.13 g of a solid product containing, on the basis of ^{19}F NMR spectral data, 2-dichloromethylene-3,3-dichlorotetrafluoro-1-indanone (XII) and its precursor (IV) in ratio ~1 : 1. By column chromatography (silica gel, CCl_4), from 0.4 g of the mixture, obtained in three parallel experiments, was isolated 0.19 g of the precursor (IV) and 0.18 g of the compound (XII), mp 107-107.5° (from alcohol, in a sealed capillary). Found: $C_{10}Cl_4F_4O$ (high-resolution mass spectrometry).

In the ^{19}F NMR spectrum of the indanone (XII) were four signals of equal intensity (δ, ppm): −25.1, −23.2, −21.4, −13.9. IR spectrum (ν, cm^{-1}): 1737 (C=O), 1585 (C=C), 1640, 1517, 1510 (fluorinated aromatic ring), 1400, 1380. UV spectrum [λ_{max}, nm (log ε)]: 280 (4.34), 292 (4.23), compare with the spectra of polyfluorinated indanones [3] and indenone (IX).

Reaction of the Indanone (XII) with PCl_5. The amount of 0.04 g of the indanone (XII) with 0.12 g of PCl_5 was heated in a sealed ampul for 2 h at 140° and 4.5 h at 225°. After distillation of the solvent, 0.04 g of product was obtained, the IR and ^{19}F NMR spectra of which coincided with the spectra of (IV).

CONCLUSIONS

1. In perfluoro-2-methylindene during reaction with $AlCl_3$, the reaction capability of the geminal site is higher than for the CF_3 group. In the reaction of perfluoro-2-methylindene with insufficient $AlCl_3$, 1-chloro- and 1,1,3-trichloroperfluoro-2-methylindenes are obtained, and with excess $AlCl_3$, 2-dichloromethylene-1,1,3,3-tetrachlorotetrafluoroindan.

2. From 1-chloro- and 1,1,3-trichloroperfluoro-2-methylindenes during reaction with SbF_5 and from 2-dichloromethylene-1,1,3,3-tetrachlorotetrafluoroindan during reaction with SbF_5 or $SbCl_5$, 1-chloro- and 1,3-dichloroperfluoro-2-methylindenyl and 1,1,3-trichlorotetrafluoroindenyl-2-dichloromethyl cations, respectively, are formed. Upon quenching of solutions of salts of the first two ions with water, 3-chloroperfluoro-2-methylindenone is formed, and, from the last, 2-dichloromethylene-3,3-dichlorotetrafluoro-1-indanone.

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