FLUOROINDENES

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COMMUNICATION 3. * PREPARATION OF 1,1,3-TRICHLOROPENTAFLUOROINDENE AND REACTION OF OCTAFLUORO- AND POLYFLUOROTRICHLOROINDENES WITH OLEUM V. M. Karpov, V. E. Platonov,

UDC 542.91:547.665'121

Recently it was shown by us that electrophilic agents react with octafluoroindene (I) either at the double bond or at the CF_2 group [1]. As a continuation of studying the reaction of polyfluoroindenes with electrophilic agents it seemed expedient to us to study the relation between the reactivity of the double bond and the geminal node in these compounds with the same electrophilic agent (20% oleum) as a function of the substituents in the five-membered ring. For this purpose we studied the behavior of the 3-chlorohepta-fluoro- (II) and 1,1,3-trichloropentafluoroindenes (III) in comparison to the behavior of indene (I). To synthesize indene (III) we studied the reaction of indene (I) with $AlCl_3$.

Indene (I) reacts easily with $AlCl_3$; indene (III) is formed along with indene (II) at a 2:1 ratio of indene (I) and $AlCl_3$. In addition, the reaction mixture contains unreacted indene (I).



The reaction of indene (I) with excess $AlCl_3$ gives indene (III) in good yield. The structure of indene (III) is confirmed by its transformation under the influence of PCl_5 to 1,1,2,3,3-pentachloropentafluoroindan (IV).



It is possible that the exchange of fluorine atoms by chlorine in indene (I) when it is reacted with $AlCl_3$ proceeds via the perfluoroindenyl cation[†] (or the cryptoion). Here the intermediately formed poly-fluorochloroindenes, with either one or two chlorine atoms in the geminal node, evidently enter into the allylic type of rearrangement, which is observed, for example, in the reaction of perfluoropropulene with $AlCl_3$ [3]. It is not excluded that the intermediately formed indenes (A) and (B), which contain fluorine and chlorine atoms in the geminal node, disproportionate to give indenes that contain either two fluorine



*See [1, 2] for Communications 1 and 2.

[†]The perfluoroindenyl cation was generated recently [1].

Novosibirsk Institute of Organic Chemistry, Siberian Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 7, pp. 1593-1596, July, 1975. Original article submitted July 30, 1974.

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or chlorine atoms in the geminal node. A similar disproportionation of the 3-fluoro- and 3,3-difluoroperchloropropylenes in the presence of AlCl₃ is known [4].

Indene (I) dissolves readily in 20% oleum to give heptafluoro-1-indanone-2-sulfonic acid (V). Indene (II) reacts less vigorously with oleum. Besides sulfonic acid (V), 3-chloropentafluoroindenone (VI) is formed in this reaction. In the case of indene (III) the reaction goes mainly at the geminal node and leads to indenone (VI). The structure of indenone (VI) was confirmed by its transformation under the influence of PCl_5 to indan (IV).



The entrance site of the electrophilic agent in the reaction of indene (I) with oleum is found to be in agreement with the stability of the intermediately formed cation, and also with the charge distribution in indene (I) [1]. The orientation in the reaction of 20% oleum at the double bond of indene (II) is also found to be in agreement with the stability of the intermediately formed cation. However, it is possible that in indene (II), when compared with indene (I), a decrease in the electron density occurs in the 2 position (similar to what takes place when going from tetrafluoro- to trifluorochloroethylene [5]), which leads to a decrease in the reactivity of the double bond in the reactions with electrophilic agents. The data on the orientation in the reactivity of the double bond of indene (II) raises the possibility of drawing the geminal node into reaction with the oleum. The additional introduction into the geminal node of the more labile chlorine atoms* in place of the fluorine atoms [indene (III)] changes the relation between the reac-tivity of the double bond in favor of the latter.

EXPERIMENTAL

The ¹⁹F-NMR spectra were taken on a Varian A-56/60A instrument at a frequency of 56.4 MHz using CCl_4 solutions. The concentration was 11 mole %. The other conditions will be specified. Hexafluorobenzene was used as the internal standard. The IR spectra were taken on a UR-20 instrument using either CCl_4 solutions or KBr pellets. The UV spectra were recorded on a Specord UV-VIS instrument using hep-tane solutions. The molar concentration was $10^{-4}-10^{-3}$. The molecular weights were determined by mass spectrometry on MS-902 and MX-1303 instruments. The temperature of the admission system and ionization chamber was 100° C, and the nominal electron energy was 70, 13.5, and 11 eV.

Reaction of Octafluoroindene (I) with $AlCl_3$. a) To a stirred solution of 10.3 g of $AlCl_3$ in 35 ml of freshly distilled AcCl at ~20° was added in drops a solution of 10.0 g of indene (I) in 15 ml of AcCl in 1 h. Then the mixture was stirred at ~20° for 1 h, then at 50° for 7 h, and let stand overnight. The mixture was poured on ice, and the organic layer was washed with NaHCO₃ solution. We obtained 13.2 g of a mixture that was dried over MgSO₄. Vacuum-distillation in a nitrogen stream gave 10.7 g of 1,1,3-trichloropentafluoroindene (III) with bp 108-109° (9 mm). Found: C 34.56; Cl 34.36; F 30.69%; mol. wt. 308. $C_9Cl_3F_5$. Calculated: C 34.93; Cl 34.37; F 30.70%; mol. wt. 308 (35 Cl).

The ¹⁹F-NMR spectrum of indene (III) has four signals at δ -28.2, -22.8, -13.1, and -8.7 ppm, with a respective intensity ratio of 1:1:2:1. Infrared spectrum (ν , cm⁻¹): 1668 (C=C), 1516, 1501 (fluorinated aromatic ring). Ultraviolet spectrum, λ_{\max} 309 nm (log ε 3.24). †

b) To a stirred solution of 0.50 g of indene (1) in 2.5 ml of AcCl at $\sim 20^{\circ}$ was added in drops a solution of 0.14 g of AlCl₃ in 2.5 ml of AcCl. Then the mixture was stirred at $\sim 20^{\circ}$ for 1.5 h and worked up as

^{*}See, for example, the hydrolysis of 1,1,1-trichloro-4,4,4-fluorobutene [6]. †See [2] for the UV spectra of the other polyfluoroindenes.

described in the preceding experiment. We obtained 0.46 g of a mixture that, based on the data of the 19 F--NMR and IR spectra, contains indenes (I), (II), and (III) in an ~4:1:2 ratio (from the 19 F--NMR spectra), respectively.

<u>Heptafluoro-1-indanone-2-sulfonic Acid (V).</u> Indene (I) (0.20 g) was stirred with 0.2 ml of 20% oleum at ~20°. Indene (I) dissolved completely in 5-10 min to give sulfonic acid (V). The ¹⁹F-NMR spectrum of the obtained solution was recorded, and then the reaction mass was poured into water. The aqueous solution was worked up in the usual manner to give 0.31 g of the S-benzylthiuronium salt of sulfonic acid (V) with mp 163-164° (from water). Found: C 40.48; H 2.14; F 26.65; N 5.28; S 12.95%. $C_{17}H_{11}F_{7}N_{2}O_{4}S_{2}$. Calculated: C 40.48; H 2.20; F 26.37; N 5.56; S 12.71%. The IR and ¹⁹F-NMR spectra of the salt are given in [1].

The ¹⁹F-NMR spectrum of sulfonic acid (V) (in oleum) has seven signals of equal intensity at δ -68.6 and 57.6 (AB system, $J_{F-F}^{gem} = 283 \text{ Hz}$); +1.0 (F²), -33.3, -31.8, -27.7, -21.8 (fluorine atoms of aromatic ring).

<u>3-Chloropentafluoroindenone (VI)</u>. A mixture of 7.0 g of indene (III) and 7 ml of 20% oleum was stirred at ~20° for 1 h and then poured on ice. The mixture was extracted with ether, the extract was dried over $MgSO_4$, and the solvent was distilled off. We obtained 5.7 g of a yellow product, which was purified by sublimation, mp 97.5-98.5° (in a sealed capillary). Found: C 42.17; Cl 13.87; F 37.31%; mol. wt. 254. C₉ClF₅O. Calculated: C 42.46; Cl 13.93; F 37.31%; mol. wt. 254 (³⁵Cl).

The ¹⁹F-NMR spectrum of indenone (VI) has five signals of equal intensity at δ -28.1, -21.0, -18.9, -16.7, and -11.9 ppm. Infrared spectrum (ν , cm⁻¹): 1748 (C=O), 1656 (C=C), 1500 (fluorinated aromatic ring). Ultraviolet spectrum, λ_{max} , nm (log ϵ): 310 (3.37), 324 (3.50), 338 (3.39), 382 (2.83).

<u>Reaction of 3-Chloroheptafluoroindene (II) with 20% Oleum.</u> A mixture of 0.25 g of indene (II) and 0.25 ml of 20% oleum was stirred at 50°. Indene (II) dissolved completely in 25-30 min to give sulfonic acid (V) and indenone (VI). The ¹⁹F-NMR spectrum of the obtained solution was recorded, and then the reaction mass was poured into water. The mixture was extracted with CH_2Cl_2 and dried over MgSO₄. From the extract we isolated 0.07 g of indenone (VI). The IR and ¹⁹F-NMR spectra of the indenone are identical with the spectra of the product obtained in the preceding experiment. The aqueous portion was worked up in the usual manner to give 0.27 g of the S-benzylthiuronium salt of sulfonic acid (V) with mp 163-164° (from water). The IR spectrum of the salt is identical with the spectrum of the sulfonic acid (V) that was obtained from indene (I).

Based on the ¹⁹F-NMR spectral data, sulfonic acid (V) and indenone (VI) (identified in a parallel experiment by the addition of the authentic product) were obtained in a respective ratio of $\sim 2:1$.

<u>1,1,2,3,3-Pentachloropentafluoroindan (IV)</u>. A mixture of 0.62 g of indene (III) and 1.25 g of PCl_5 was heated in a sealed ampule at 225° for 7.5 h. The reaction mass was transferred to water extracted with CH_2Cl_2 , and dried over MgSO₄. The solvent was distilled off. We obtained 0.67 g of indan (IV) with mp 80.4-81° (from ethanol). Found: C 28.45; Cl 46.30; F 24.51%. $C_9Cl_5F_5$. Calculated: C 28.42; Cl 46.61; F 24.97%. The ¹⁹F-NMR spectrum of indan (IV) has three signals at δ -71.3 (F²), -23.2 (F^{4,7}), and -15.6 ppm (F^{5,6}), with a respective intensity ratio of 1:2:2.

Infrared spectrum (ν , cm⁻¹): 1645, 1520, 1510 (fluorinated aromatic ring), 1398. Ultraviolet spectrum, λ_{max} , nm (log ϵ): 270 (2.91 sh), 275 (2.95).

Reaction of Indenone (VI) with PCl_5 . A mixture of 0.10 g of indenone (VI) and 0.25 g of PCl_5 was heated in a sealed ampule at 150° for 7 h and at 225° for 7.5 h. The mixture was worked up as described in the preceding experiment. We obtained 0.14 g of indan (IV). The IR and ¹⁹F-NMR spectra of indan (IV) are identical with the spectra of the product obtained in the preceding experiment.

CONCLUSIONS

1. The reaction of octafluoroindene with aluminum chloride gives 1,1,3-trichlorobentafluoroindene.

2. The reaction of 20% oleum with octafluoroindene leads to heptafluoro-1-indanone-2-sulfonic acid, with 3-chloroheptafluoroindene to a mixture of heptafluoro-1-indanone-2-sulfonic acid and 3-chloropenta-fluoroindenone, and with 1,1,3-trichloropentafluoroindene to 3-chloropentafluoroindenone.

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