FORMATION OF PERFLUORO-1,1,3-TRIMETHYLINDANE IN THE REACTION OF TRIMETHYLSILYLPENTAFLUOROBENZENE WITH PERFLUORO-4-METHYL-2-PENTENE

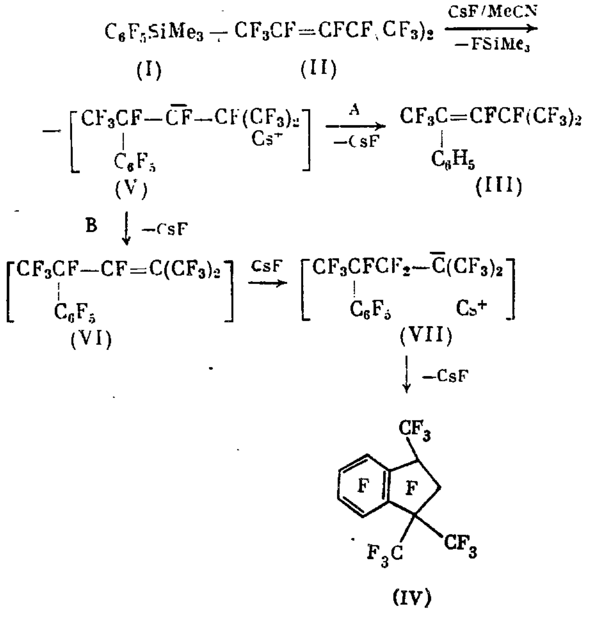
V. V. Bardin, V. A. Petrov,
I. V. Stennikova, G. G. Furin,
and L. S. German

UDC 542.91:547.665'161

The intramolecular cyclization of pentafluorobenzene derivatives by the action of base is commonly used in the synthesis of polyfluorinated heteroatomic compounds [1]. Several syntheses have been reported for polyfluorinated carbocyclic compounds with the intermediate generation of a carbanion site in the side chain [2]. However, perfluorinated benzocycloalkenes could not be obtained by this procedure. In the present work, the first example is reported for the formation of a perfluoroindane derivative by intramolecular nucleophilic cyclization.

In previous work [3], we showed that trimethylsilylpentafluorobenzene (I) reacts with polyfluoroalkenes in the presence of CsF by the replacement of vinyl fluorine atoms by C_6F_5. The reaction of arylsilane (I) with perfluoro-4-methyl-2-pentene (II) unexpectedly led to the formation of approximately equal amounts of perfluoro-1,1,3-trimethylindane (IV) and perfluoro-4-methyl-2-phenyl-2-pentene (III). Furthermore, a high-boiling fraction was isolated, which was shown to be a mixture of the products of the pentafluorophenylation of (III) and (IV) as indicated by ^{19}F NMR spectroscopy [3].

Heating of isomers (III) and (IV) with CsF in acetonitrile does not lead to their interconversion. Thus, these compounds are not the products of consecutive reactions and, apparently, are formed by parallel pathways. We may assume that the first step is nucleophilic pentafluorophenylation of olefin (II) by a complex composed of arylsilane and cesium fluoride, leading to perfluorinated carbanion (V). The elimination of F^- from this carbanion directly gives perfluorinated arylolefin (III) (pathway A) and its isomer (VI) (pathway B). The addition of a fluoride ion to olefin (VI) proceeds preferentially at C^3 to give the more stable tertiary carbanion (VII), which, in turn, cyclizes with intramolecular replacement of an aromatic ring fluorine atom to form fluorinated indane (IV).



Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. A. N. Nesmeyanov Institute of Heteroorganic Compounds, Academy of Sciences of the USSR, Moscow. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 2, pp. 477-479, February, 1989. Original article submitted May 24, 1988.

0568-5230/89/3802-0420 $12.50

EXPERIMENTAL

The ^{19}F NMR spectra of solutions of compounds in $CDCl_3$ were recorded on a Bruker CXP-200 spectrometer at 188.31 MHz (the duration of the major pulse was 2 μsec at 45°C). The external standard was CF_3CO_2H. The IR spectra were taken neat on a UR-20 spectrometer. The mass spectra were taken on a Finnigan MAT MS-8200 mass spectrometer. The gas-liquid chromatographic analysis was carried out on an LKhM-80MD chromatograph using a column packed with FS-1265 on Chromosorb W. The injector temperature was 250°C. The column temperature was 100°C. The helium gas carrier flow rate was 10 ml/min. Products (III) and (IV) were isolated by preparative gas-liquid chromatography under the conditions of the analytical determination.

Reaction of Arylsilane (I) with Olefin (II). A sample of 18.7 g arylsilane (I) was added over 10 min to a stirred mixture of 0.5 g fused cesium fluoride, 10 ml anhydrous acetonitrile, and 35 g fluoroolefin (II). The mixture was stirred for 4 h at 40°C and cooled. A sample of 50 ml pentane was added to dilute the mixture, which was then filtered, washed with water, and dried over $CaCl_2$. Distillation gave 11 g of a mixture of (III) and (IV) (bp 160-180°C) and 3.2 g of a fraction with bp 120-125°C (10 mm). Pure (III) and (IV) were isolated by preparative gas-liquid chromatography.

Perfluoro-4-methyl-2-phenyl-2-pentene (III), bp 154-156°C (by the Sivolobov Method). ^{19}F NMR spectrum (δ, ppm): −16.2 ($3F^1$), −2.8 ($3F^5 + 3F^{4'}$), 20.6 ($1F^3$), 60.0 ($2F_o$), 70.7 ($1F_p$), 82.1 ($2F_m$), 105.4 ($1F^4$), $J_{13} = 22$, $J_{34} = 13$, $J_{45} = 8$ Hz. IR spectrum (ν, cm^{-1}): 1708, 1660, 1517, 1454, 1352, 1328, 1306, 1269, 1227, 1177, 1070, 1005, 988, 860, 832, 793, 754, 744. Mass spectrum, m/z (rel. intensity, %): 448 (76) [$C_{12}F_{16}^+$], 429 (38) [$C_{12}F_{15}^+$], 279 (44) [$C_9F_9^+$], 241 (31) [$C_9F_7^+$], 69 (100) [CF_3^+]. Found: C, 31.9; F, 68.0%. Calculated for $C_{12}F_{16}$: C, 32.1; F, 67.9%.

Perfluoro-1,1,3-trimethylindane (IV), bp 175-176°C (according to the Sivolobov Method). ^{19}F NMR spectrum (δ, ppm): −14.3 (CF_3^3), −11.0 and −5.0 ($2CF_3^1$), 35.9 ($1F^{2A}$), 37.5 ($1F^{2B}$), 51.1 and 53.8 ($2F^{5,6}$), 63.5 and 65.7 ($2F^{4,7}$), 76.7 ($1F^3$), $J_{2A,2B} = 272$, $J_{3,3\alpha} = 24$ Hz. IR spectrum (ν, cm^{-1}): 1649, 1520, 1418, 1320, 1296, 1270, 1246, 1206, 1177, 1142, 1108, 1075, 1011, 986, 823, 800, 766, 749, 738, 700. Mass spectrum, m/z (rel. intensity, %): 448 (36) [$C_{12}F_{16}^+$], 429 (45) [$C_{12}F_{15}^+$], 379 (99) [$C_{11}F_{13}^+$], 291 (32) [$C_{10}F_9^+$], 241 (33) [$C_9F_7^+$], 69 (100) [CF_3^+]. Found: C, 31.8; F, 67.9%. Calculated for $C_{12}F_{16}$: C, 32.1, F, 67.9%.

Reaction of Cesium Fluoride with (III) and (IV). A mixture of 0.4 g (III), 0.1 g cesium fluoride, and 2 ml anhydrous acetonitrile was stirred for 4 h at 40-45°C. Gas-liquid chromatography indicated that (III) remained unchanged under these conditions. Similar behavior was found for (IV).

CONCLUSIONS

The reaction of pentafluorophenyltrimethylsilane with perfluoro-2-methyl-2-pentene in the presence of cesium fluoride gives perfluoro-1,1,3-trimethylindane in addition to the product of the pentafluorophenylation.

LITERATURE CITED

1. G. G. Yakobson, T. D. Petrova, and L. S. Kobrina, Fluorine Chemistry Reviews, Vol. 7, Marcel Dekker, New York (1974), p. 115.
2. V. M. Vlasov, T. D. Petrova, and G. G. Yakobson, J. Fluor. Chem., 2, No. 3, 373 (1972/1973).
3. V. V. Bardin, G. G. Furin, and I. V. Stennikova, Second Soviet–West German Symposium on Fluorine Chemistry, Novosibirsk (1988), p. 37.