Chemistry

Academician I. L. KNUNYANTS and E. G. BYKHOVSKAYA

1960

SovietRxiv

Abstract

Full Text

Chemistry

Academician I. L. KNUNYANTS and E. G. BYKHOVSKAYA

INTERACTION OF FLUOROOLEFINS WITH HYDRAZOIC ACID AND REARRANGEMENT OF PERFLUOROALKENYL AZIDES

In reactions of various compounds with perfluoroolefins, along with addition at the multiple bond, substitution of fluorine atoms also takes place in the vinylic and, in some cases, in the allylic position (¹). The processes of addition and substitution are independent and are the result of conjugation of bonds in φ-olefins. The initial act of the reaction is interpreted as attack by an anion; the intermediate carbanion formed (I) is stabilized either by capture of a proton to give a saturated simple ether (II), or, from the carbanion, as a result of conjugation of bonds in it, a fluoride anion is eliminated and a vinyl alkyl ether (III) is formed (²).

$$CF_2{=}CF_2 + \overline{O}R \longrightarrow CF_3{-}\overline{CF}{-}CF_2OR \begin{array}{l} \xrightarrow{H^+} CF_3{-}CFH{-}CF_2OR \quad (II) \\ \longrightarrow CF_3{-}CF{=}CF{-}OR \quad (III) \end{array}$$

(I)

However, it is equally legitimate to assume that the electrophilic molecule of the fluoroolefin adds the undissociated molecule of the nucleophilic reagent at the expense of an unshared pair of electrons, with formation of a transient tetracoordinate complex (IV); the latter is stabilized by intramolecular formation of a hydrogen H ... F bond, which simultaneously facilitates the elimination of hydrogen fluoride with formation of the product of vinylic substitution

$$CF_3{-}CF{=}CF_2 + ROH \longrightarrow CF_3{-}CF{=}CF{-}OR \longrightarrow [-HF]CF_3{-}CF{=}CF{-}OR$$

This interpretation also accommodates well other experimental data on the addition of alcohols to φ-olefins. Thus, addition of wine alcohol to trifluorochloroethylene in the presence of sodium ethylate leads entirely to trifluorochlorodiethyl ether, whereas in a reaction carried out by passing trifluorochloroethylene through a suspension of sodium ethylate in sulfuric ether, ethyldifluorochlorovinyl ether is formed (³).

These same regularities are confirmed by the example of the reaction of φ-olefins with hydrazoic acid, which until now has remained unstudied. Thus, on interaction of φ-propylene and φ-isobutylene with a suspension of sodium azide in alcohol, saturated β-monohydroperfluoropropyl and β-monohydroperfluoroisobutyl azides are formed:

$$CF_2{=}CF{-}CF_3 \cdots \overline{N}_3 \longrightarrow CF_3{-}\overline{CF}{-}CF_2N_3 + H^+ \longrightarrow CF_3{-}CFH{-}CF_2N_3$$

In this case, only in the case of φ-isobutylene is the formation of a small amount of the product of vinylic substitution observed. Replacement of the solvent —polar alcohol—by nonpolar symmetrical tetrachloroethane, in which the triethylammonium salt of hydrazoic acid was dissolved, led, also in the case of φ-propylene, to formation of the product of vinylic-

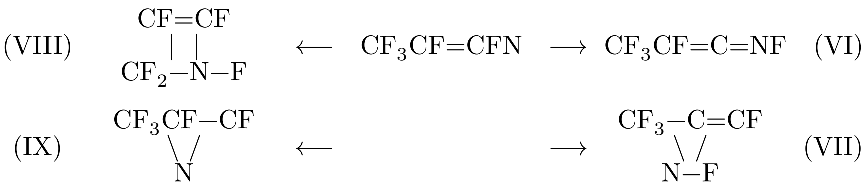
substitution (V) in appreciable yield. Perfluoroalkenyl azides (products of vinyl substitution) are extremely unstable and at room temperature spontaneously eliminate nitrogen, while the "azacarbene" formed then rearranges

$$CF_3{-}CF{=}CF_2 + [(C_2H_5)_3NH]N_3 \longrightarrow$$

$$\longrightarrow CF_3{-}CF{=}CF{-}N{-}N_2 \longrightarrow [CF_3{-}CF{=}CFN_3] \xrightarrow[-N_2]{} CF_3{-}CF{=}CFN \longrightarrow$$

$$\longrightarrow C_3F_5N$$

This rearrangement of the "azacarbene" may occur through migration to the nitrogen atom of fluorine from the α- (VI), β- (VII), and γ-position (VIII), and also through "unpairing" of the electrons of the π-bond (IX).



As a result of the reaction between ϕ-propylene and HN_3, a colorless gaseous compound with b.p. $-17°$ is formed. In order to choose the structure of this compound, its IR spectrum was studied. In the region of stretching vibrations of double bonds, a broad intense band with a maximum at 1724 cm^{-1} was observed. It is known that substances containing cumulated bonds have a high

Fig. 1

Figure 1: Fig. 1

vibrational frequency. Thus, in allene =C=C=C= there corresponds to them a strong band at 1980 cm^{-1}. On this basis, structure (VI) must be excluded from consideration. As is known, the characteristic frequencies of C=C and C=N shift into the short-wavelength region of the spectrum as the number of fluorine atoms on the carbon atoms increases. Thus in C_2H_4 $\nu_{C=C}$ is 1626, $CH_2{=}CHF$ 1650, $CH_2{=}CF_2$ 1728, $CFH{=}CF_2$ 1788, $CF_2{=}CF_2$ 1872 cm^{-1}.

In imino compounds not containing fluorine, the vibrational frequency of C=N practically coincides with the vibrational frequency of an olefinic bond and lies in the region 1620-1680 cm^{-1}. In fluorine-containing compounds of the same type it also rises sharply and, for example, in $CF_3N{=}CF_2$ reaches 1809 cm^{-1}. Hasseldine's data (^{4}) show that in compounds containing the group −CF=CF−, the vibrational frequency of =C=C= has an approximately constant value of 1733 cm^{-1}.

Fig. 1

The characteristic frequency for the double bond of the compound under investigation is close to the olefinic-bond frequency found in (^{4}) in the grouping −CF=CF−. At the same time, structure (VII) contains a =C=C= bond loaded with only one fluorine atom, and according to the available data one would expect a significantly lower frequency for this double bond.

Thus, structures (VIII) and (IX) are the most probable. However, structure (VIII) is more plausible, owing to the presence of an additional strong absorption near 1000 cm^{-1}, which apparently is caused by vibrations of the N−F bond. The nuclear magnetic spectrum of this substance also agrees with this*. Indeed, structure (VIII), in contrast to all the other proposed structures, has 4 nonequivalent positions of the fluorine atom, which appears in the nuclear magnetic resonance spectrum in the form

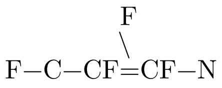
4 signals. In accordance with the literature data, the observed lines are characteristic of the following fluorine-containing groups: = NF, = CF_2, = CF− (Fig. 1).

Thus, the nuclear magnetic resonance data and the IR spectrum show that the gaseous compound formed, with b.p. −17°, is perfluoroazacyclobutene-2 (structure VIII), and consequently the "perfluoropropenylazacarbene" is stabilized through migration to nitrogen of a fluorine atom from the γ-position.

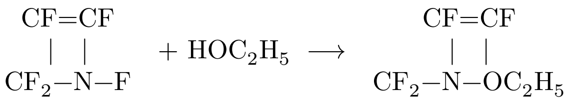
This process, analogous to the usual allylic rearrangement, is a consequence of conjugation of bonds in the "azacarbene."

---

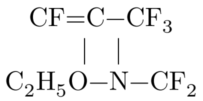
* The IR spectra and the nuclear magnetic resonance spectrum were taken by S. S. Dubov.



The fluorine atom attached to nitrogen in perfluoroazacyclobutene is very mobile: it is saponified by $1/10\,N$ alkali in the cold and is exchanged for an ethoxy group in absolute alcohol at −10°, giving 1-ethoxyazacyclobutene-2, a liquid with b.p. 96°



Analogous processes also occur in the interaction of φ-isobutylene with sodium azide in alcohol. In this case, along with the principal reaction product, β-monohydroperfluoroisobutyl azide, there is formed in small amount a product with b.p. 112°, which is 1-ethoxy-3-trifluoromethylazacyclobutene-2,



The structure of this compound is confirmed by its IR spectrum, identical with the spectrum of compound (VIII). Consequently, perfluoroalkenyl azides are extremely unstable compounds, spontaneously losing a molecule of nitrogen; in the free state they evidently cannot be isolated.

In contrast to them, β-monohydroperfluoroalkyl azides are stable, readily distillable liquids, unchanged on heating with water and with $1/10\,N$ alkali. These facts once again confirm that the formation of perfluoroalkenyl azides occurs as a result of substitution of the vinylic fluorine atom of φ-olefins, and not as a result of elimination of hydrogen fluoride from saturated monohydroperfluoroalkyl azides.

Experimental Part

Interaction of φ-propylene with a suspension of sodium azide in alcohol. Into a three-necked flask fitted with a stirrer and gas inlet and outlet tubes were placed 40 ml of ethyl alcohol and 3.3 g of activated sodium azide. Then, at room temperature and with vigorous stirring, dry φ-propylene (2.5 liters) was passed through. The precipitate was filtered off, and the filtrate was distilled on a rectification column. Two fractions were obtained:

1) Monohydroperfluoropropyl azide—a colorless, readily mobile liquid, b.p. 51°; d_4^{20} 1.4962; n_D^{20} 1.3100; MR_D found 24.86, calculated 24.64.

Found, %: C 18.89; H 0.53; N 21.46; F 59.32
$C_3HF_6N_3$. Calculated, %: C 18.65; H 0.52; N 21.76; F 59.06.

2) Ethyl 2-monohydroperfluoropropyl ether, b.p. 64°; d_4^{20} 1.3050; n_D^{20} 1.2963. Literature data (^{4}): b.p. 64°; d_4^{20} 1.2990; n_D^{20} 1.2960.

Interaction of φ-isobutylene with a suspension of sodium azide in alcohol. To a suspension of 6.5 g of sodium azide in ethyl–

in alcohol while cooling with ice, 2.5 liters of perfluoroisobutylene was passed through. Vigorous evolution of nitrogen was observed. The reaction mass was allowed to stand at room temperature until nitrogen evolution ceased. The precipitated sodium fluoride (found F 43.5%, calculated 45%) was filtered off, and the reaction mass was distilled on a rectification column. The fraction boiling from 71 to 76° was collected. The latter was thoroughly washed with water, dried over calcium chloride, and redistilled. Three products were obtained.

1) Ethyl 2-hydroperfluoroisobutyl ether—a colorless liquid with b.p. 82–83° (739 mm); d_4^{23} 1.3039; n_D^{23} 1.2940. Contains no nitrogen. According to literature data (^{1}), b.p. of ethyl 2-hydroperfluoroisobutyl ether 83.5–84°; d_4^{20} 1.4061; n_D^{20} 1.2950. 2) β-Monohydroperfluoroisobutyl azide (it could not be isolated in analytically pure form because its boiling point is close to the b.p. of ethyl 2-hydroperfluoroisobutyl ether). Colorless liquid with b.p. 71° (739 mm), d_4^{33} 1.5840, n_D^{23} 1.3020.

$C_4HF_8N_3$. Found %: C 20.20; H 0.91; F 61.60; N 14.25
Calculated %: C 19.85; H 0.51; F 62.55; N 17.32.

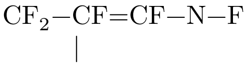
3) 1-Ethoxy-3-(trifluoromethyl)-perfluoroazacyclobutene-2. Colorless liquid with a faint pleasant odor, b.p. 112° (740 mm), d_4^{22} 1.4350, n_D^{22} 1.3172; molecular weight, found 214, calculated 221.

$C_6H_5F_6ON$. Found %: C 32.44; H 2.21; F 52.52; N 5.65
Calculated %: C 32.52; H 2.26; F 51.59; N 6.33.

Reaction of perfluoropropylene with triethylammonium hydrazoate. Dry propylene (2.5 liters) was passed at 0° into a solution of 14 g of the triethylammonium salt of hydrazoic acid in 80 ml of symmetrical tetrachloroethane. The reaction mixture was washed with dilute hydrochloric acid and water and dried over magnesium sulfate. The solution was placed in a Favorskii flask, the outlet of which was connected to an ampoule cooled with an acetone-“dry ice” mixture. At a residual pressure of 50–30 mm, 7 ml of liquid collected in the ampoule. The latter was transferred to a distillation flask fitted with a condenser and a spider receiver, the end of which was connected to an ampoule immersed in the cooling mixture. As soon as the liquid in the flask reached room temperature, nitrogen evolution began, and a gaseous substance condensed in the ampoule. After nitrogen evolution ceased, the residue was distilled on a rectification column. β-Monohydroperfluoropropyl azide—a colorless liquid with b.p. 51°; d_4^{20} 1.4967; n_D^{20} 1.3105; MR_D found 24.88; calculated 24.64.

$C_3HF_6N_3$. Found %: N 21.96; F 59.08
Calculated %: N 21.76; F 59.06.

The gas collected in the ampoule has b.p. −17°. Molecular weight, found 143.2, calculated 145,



$CF_2{-}CF{=}CF{-}N{-}F$ Found %: F 65.77
Calculated %: F 65.50.

Hydrolysis of perfluoroazacyclobutene-2. A solution of 1/10 *N* alkali and a weighed portion of perfluoroazacyclobutene-2 were placed in a bottle fitted with a stopper and stopcock. The bottle was evacuated and the ampoule containing the weighed portion was broken; it was allowed to stand for 30 min, and then the excess alkali was titrated and the fluorine content in the solution was determined (12.87%).

Received
30 I 1960

CITED LITERATURE

[1] I. L. Knunyants, L. S. German, B. L. Dyatkin, *Izv. AN SSSR, OKhN*, 1956, No. 11, 1353.
[2] W. Miller, *J. Am. Chem. Soc.*, 70, 431 (1948).
[3] R. Meier, F. Bohler, *Ber.*, 90, 2342 (1957).
[4] R. N. Haszeldine, *J. Chem. Soc.*, 1955, 1881; 1953, 3559.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.