

REACTION OF 1,4-DIBROMOHEXAFLUORO-2-BUTENE WITH O- AND N-NUCLEOPHILES*

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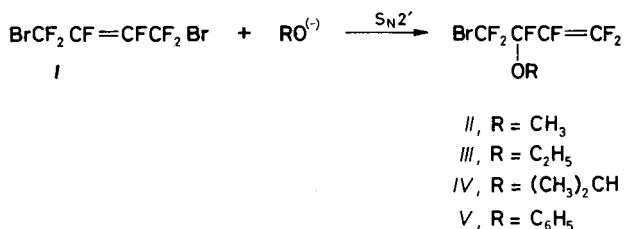
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Reaction of 1,4-dibromohexafluoro-2-butene (*I*) with sodium methoxide, ethoxide or isopropoxide in the corresponding alcohols proceeds with allylic rearrangement under formation of 3-alkoxy-4-bromohexafluoro-1-butenes *II–IV*. A kinetic study has proven the S_N2' mechanism for reaction of *I* with potassium phenoxide leading to 4-bromo-3-phenoxyhexafluoro-1-butene (*V*). Also the reaction of *I* with ammonia, affording 3-amino-4-bromo-2,4,4-trifluoro-2-butenenitrile (*IX*), is compatible with the allylic rearrangement by S_N2' mechanism. On the contrary, reaction of *I* with diethylamine gave no rearrangement product and, after hydrolysis, afforded *N,N*-diethyl-4-bromo-2,3,3,4,4-pentafluorobutanamide (*XVI*) and *N,N*-diethyl-4-bromo-2,3,4,4-tetrafluoro-2-butenamide (*XVII*) in the ratio 85 : 15.

In our previous communications we reported^{1–3} that nucleophilic reagents react with 3-chlorononafluoro-1,5-hexadiene at the perfluoroallyl chloride grouping with allyl rearrangement according to S_N2' mechanism whereas at the perfluoroallyl fluoride grouping only addition of the reagent takes place via a carbanion whose existence has been proven by formation of the hydryl derivative after neutralization.

The present communication studies the perfluoroallyl system using as model 1,4-dibromohexafluoro-2-butene (*I*) prepared by addition of bromine to perfluoro-1,3-butadiene⁴. Compound *I* has been described to react with alkali metal fluorides and chlorides with allylic rearrangement⁵. We have found that on treatment with an

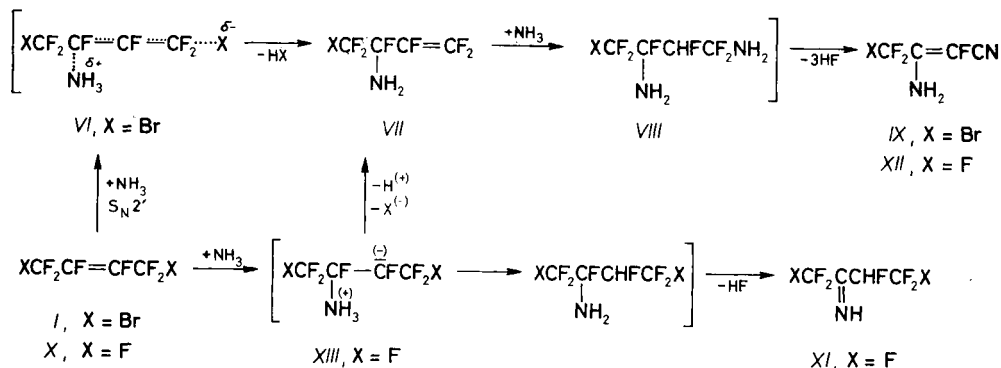


SCHEME 1

* Part XXXI in the series Chemistry of Organic Fluorine Compounds; Part XXX: J. Fluorine Chem. 31, 363 (1986).

equivalent of sodium alkoxide in the corresponding alcohol the butene *I* eliminates bromide anion already at -15° to -10°C to give products of allylic rearrangement, i.e. 3-alkoxy-4-bromohexafluoro-1-butenes *II-IV* (Scheme 1). The allylic substitution proceeds by the $\text{S}_{\text{N}}2'$ mechanism as evidenced by a study of reaction of compound *I* with potassium phenoxide whose rate allowed monitoring by gas-liquid chromatography. The amount of the arising 4-bromo-3-phenoxyhexafluoro-1-butene (*V*) was proportional to that of the reacted *I* and no side product, indicating reaction via carbanion, was observed.

Reaction of butene *I* with excess of ammonia in diethyl ether in the range -70° to -10°C afforded 3-amino-4-bromo-2,4,4-trifluoro-2-butenenitrile (*IX*) as the sole product. According to its ^{19}F NMR spectrum, only one stereoisomer was formed which was assigned *E*-configuration of the bromodifluoromethyl group and the fluorine atom at the double bond. The found unusually low coupling constant (2.8 Hz) corresponds to values known for an *E*-arrangement⁶ (2.3–5 Hz) whereas for a *Z*-configuration the published values^{7,8} are much higher (22–27 Hz).

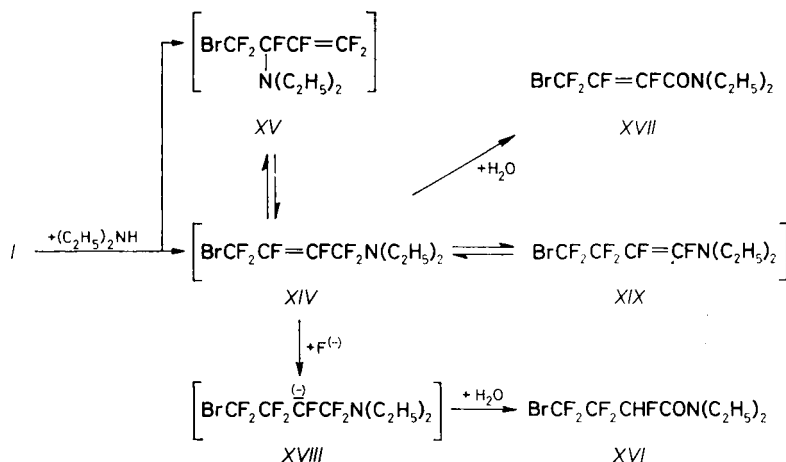


SCHEME 2

As shown in Scheme 2, the structure of the enamionitrile *IX* is compatible with loss of bromide anion from the perfluoroallyl bromide grouping in the starting butene *I* by $\text{S}_{\text{N}}2'$ mechanism via the transition state *VI* and reaction of the rearrangement product, 3-amino-4-bromohexafluoro-1-butene (*VII*), with ammonia at the terminal trifluorovinyl group to give the unstable diamine *VIII*. Elimination of 3 molecules of hydrogen fluoride from *VIII* in the ammonia medium affords the enamionitrile *IX*. Reaction of ammonia under the same conditions with octafluoro-2-butene (*X*), which has an analogous perfluoroallyl fluoride grouping, has been reported⁹. Contrary to our case, the principal reaction product was 2-imino-1,1,1,3,4,4,4-heptafluorobutane (*XI*) beside 3-amino-2,4,4,4-tetrafluoro-2-butenenitrile (*XII*) whose amount in the product increased with increasing reaction temperature. This

fact is in accord with the known lower reactivity of a fluorine atom in perfluoroallyl systems as compared with the reactivity of a bromine atom and also agrees with our previous results obtained in the studies of 3-chloro-1,5-hexadiene¹⁻³. The formation of the imino derivative *XI* with hydrogen atom on the C-3 carbon atom indicates that with octafluorobutene no S_N2' allylic rearrangement takes place but instead there is an addition to the double bond under formation of carbanion *XIII* (Scheme 2) which after neutralization and elimination of hydrogen fluoride is converted into the imino derivative *XI*. In a competitive reaction, the carbanion *XIII* loses fluoride anion and, as in the case of *I*, is transformed into the enamionitrile *XII*.

On the other hand, reaction of butene *I* with excess of diethylamine in diethyl ether at -30°C had a different course than with ammonia. Since the arising 4-bromo-1-diethylaminohexafluoro-2-butene (*XIV*) or 4-bromo-3-diethylaminohexafluoro-1-butene (*XV*) were too unstable to allow isolation, the reaction mixture was hydrolyzed. In the product we identified N,N-diethyl-4-bromo-2,3,3,4,4-pentafluorobutanamide (*XVI*) and N,N-diethyl-4-bromo-2,3,4,4-tetrafluoro-2-butenamide (*XVII*) in the ratio 85 : 15 (Scheme 3). The formation of amides *XVI* and *XVII* indicates either a direct substitution of bromine with diethylamine or a double rearrangement at the perfluoroallyl system. An analogous observation has been made by us¹⁰ with 6-bromooctafluoro-1,4-hexadiene which also contains a perfluoroallyl bromide grouping with the double bond inside the chain. Since reaction mixtures of fluoroalkylamines always contain a considerable amount of fluoride anions¹¹ (thanks to the lability of the C—F bonds at the α-carbon atom), the preponderance of the amide *XVI* over amide *XVII* may be ascribed to the addition of fluoride anion to the unsaturated amine *XIV*. The thus-arising carbanion *XVIII* is then neutralized



SCHEME 3

and hydrolyzed to give the amide *XVI*. It cannot also be excluded that the amide *XVI* results from hydrolysis of 4-bromo-1-diethylamino-1,2,3,3,4,4-hexafluoro-1-butene (*XIX*) formed by isomerization of 4-bromo-1-diethylamino-1,1,2,3,4,4-hexafluoro-2-butene (*XIV*) with fluoride anion (Scheme 3).

EXPERIMENTAL

The temperature data are uncorrected. All the prepared compounds were characterized by their NMR (^1H and ^{19}F) and IR spectra and by elemental analyses. The NMR spectra were measured in deuteriochloroform on a Varian XL-100/15 (100 MHz, CW) instrument. Chemical shifts are given in the δ -scale (ppm) using tetramethylsilane (^1H) and chlorotrifluoromethane (^{19}F) as internal standards. Upfield shifts in the ^{19}F NMR spectra are denoted as negative values. Infrared spectra were recorded on a Perkin-Elmer 325 spectrometer in chloroform. Gas-liquid chromatographic analyses were performed on Chrom 4 and Chrom 5 instruments (Laboratorní přístroje, Prague) with flame ionization detector; carrier gas nitrogen, 370×3 mm columns packed with 20% polypropylene sebacate or 10% silicone elastomer SE-30 on Chromaton N-AW-DMCS.

1,4-Dibromohexafluoro-2-butene (*I*) was obtained by addition of bromine to hexafluoro-1,3-butadiene in dichloromethane at low temperature using a modified procedure¹². Hexafluoro-1,3-butadiene was prepared by the procedure described by us previously¹³. Diethylamine was dried over solid potassium hydroxide and distilled. Potassium phenoxide was obtained by reaction of equimolar amounts of potassium hydroxide and phenol.

TABLE I
Yields and elemental analyses

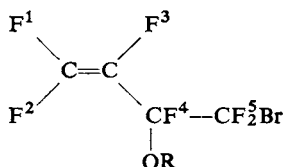
| Compound | Formula (mol. wt.) | Yield % | Calculated/found | | | | |
|------------|--|------------|------------------|------|-------|-------|-------|
| | | | % C | % H | % Br | % F | % N |
| <i>II</i> | $\text{C}_5\text{H}_3\text{BrF}_6\text{O}$ (273.0) | 48 | 22.00 | 1.11 | 29.27 | 41.76 | — |
| | | | 21.90 | 1.30 | 29.42 | 41.55 | |
| <i>III</i> | $\text{C}_6\text{H}_5\text{BrF}_6\text{O}$ (287.0) | 56 | 25.11 | 1.76 | 27.84 | 39.72 | — |
| | | | 25.35 | 1.92 | 27.52 | 39.55 | |
| <i>IV</i> | $\text{C}_7\text{H}_7\text{BrF}_6\text{O}$ (301.0) | 62 | 27.93 | 2.34 | 26.54 | 37.87 | — |
| | | | 28.27 | 2.64 | 26.53 | 38.27 | |
| <i>V</i> | $\text{C}_{10}\text{H}_5\text{BrF}_6\text{O}$ (335.1) | 29 | 35.84 | 1.50 | 23.85 | 34.02 | — |
| | | | 36.16 | 1.67 | 23.75 | 33.83 | |
| <i>IX</i> | $\text{C}_4\text{H}_2\text{BrF}_3\text{N}_2$ (215.0) | 54 | 22.35 | 0.94 | 37.17 | 26.51 | 13.03 |
| | | | 21.97 | 0.80 | 36.70 | 26.64 | 12.65 |

3-Alkoxy-4-bromohexafluoro-1-butenes I–IV

A solution of sodium alkoxide (prepared from 0.32 g, 14 mmol, of sodium) in the corresponding alcohol was added at -10 to -15°C to a stirred solution of I (5 g; 15 mmol) and a small amount of phenolphthalein in the same alcohol (30 ml) at a rate allowing decolorization of the phenolphthalein. The mixture was allowed to warm to room temperature during 1/2 h and poured into an excess of ice-cold water. The separated lower layer was washed with water and dried over molecular sieves. According to gas-liquid chromatography, the purity of the products was higher than 95%. They decomposed on attempted distillation under diminished pressure. Yields, elemental analyses, and spectral characteristics of the products are summarized in Tables I and II.

TABLE II

Spectral characteristics of alkoxybromohexafluorobutenes II–V



| Comp. | IR $\nu(\text{C}=\text{C}), \text{cm}^{-1}$ | $^1\text{H NMR}$ $\delta(J, \text{Hz})$ | $^{19}\text{F NMR}$ | | | | | J, Hz |
|-------|--|--|----------------------|----------------------|----------------------|----------------------|----------------------|---|
| | | | $\delta(\text{F-1})$ | $\delta(\text{F-3})$ | $\delta(\text{F-3})$ | $\delta(\text{F-4})$ | $\delta(\text{F-5})$ | |
| II | 1 780 vs | 3.61 s | -90.3 dd | -106.8 m | -183.8 m | -130.2 dm | -65.7 d | $J(1, 2) = 52.5$ $J(1, 3) = 37.5$ (<i>cis</i>) $J(2, 3) = 115$ (<i>trans</i>) $J(3, 4) = 37.5$ $J(4, 5) = 10$ |
| III | 1 777 vs | 1.32 t 4.05 q ($^3J = 7$) | -90.5 dd | -106.7 m | -182.8 m | -127.1 dm | -65.7 d | $J(1, 2) = 54$ $J(1, 3) = 37.5$ (<i>cis</i>) $J(2, 3) = 115$ (<i>trans</i>) $J(3, 4) = 39$ $J(4, 5) = 10$ |
| IV | 1 775 vs | 1.33 m 6 H 4.25 m 1 H | -90.9 dd | -106.6 m | -181.4 m | -123.1 dq | -65.7 d | $J(1, 2) = 55$ $J(1, 3) = 37.5$ (<i>cis</i>) $J(2, 3) = 115$ (<i>trans</i>) $J(3, 4) = 42.5$ $J(4, 5) = 10$ |
| V | 1 780 vs | 7.20 m | -90.0 dd | -105.6 m | -182.3 dm | -120.1 dq | -65.3 d | $J(1, 2) = 52.5$ $J(1, 3) = 37.5$ (<i>cis</i>) $J(2, 3) = 115$ (<i>trans</i>) $J(3, 4) = 40$ $J(4, 5) = 10$ |

4-Bromo-3-phenoxyhexafluoro-1-butene (*V*)

The title compound was prepared according to ref.¹⁴. A stirred mixture of *I* (3.2 g; 10 mmol), potassium phenoxide (1.32 g; 10 mmol), and diethyl ether (35 ml) was refluxed and the reaction was monitored by gas-liquid chromatography of samples washed with water. After 25 h all the starting compound reacted and the mixture was decomposed with dilute (1 : 3) hydrochloric acid (20 ml). The separated ethereal layer was washed successively with water, 10% solution of sodium hydroxide and again with water. After drying over anhydrous magnesium sulfate the ether was evaporated and the residue distilled in vacuo, affording 0.95 g (29%) of *V*, b.p. 67°C/2.35 kPa.

3-Amino-4-bromo-2,4,4-trifluoro-2-butenitrile (*IX*)

Ammonia (2.45 g; 144 mmol) was distilled during 30 min to a stirred solution of *I* (5 g; 15 mmol) in diethyl ether (16 ml) cooled to -70°C. After warming to -15°C further ether (50 ml) was added and the mixture was stirred at 20°C for 1 h. The insoluble salts were filtered and ether was evaporated. Distillation of the residue afforded 1.8 g (54%) of *IX*, b.p. 99°C/2.4 kPa. IR spectrum, cm⁻¹: 1 605 s (—NH₂); 1 670 vs (C=C); 2 220 s (CN); 3 320 ms, 3 370 s, 3 420 s, 3 510 s (—NH₂). ¹H NMR spectrum: 4.49 bs (—NH₂). ¹⁹F NMR spectrum: -52.8 d, 2 F (—CF₂Br), *J*(F, F) = 2.8 Hz; -164.05 t, 1 F (=CF—), *J*(F, F) = 2.8 Hz.

N,N-Diethyl-4-bromo-2,3,3,4,4-pentafluorobutanamide (*XVI*)and N,N-Diethyl-4-bromo-2,3,4,4-tetrafluoro-2-butenamide (*XVII*)

A solution of diethylamine (5.8 g; 80 mmol) in ether (10 ml) was added dropwise at -30°C to a stirred solution of *I* (6.44 g; 20 mmol) in diethyl ether (70 ml) during 30 min. The mixture was stirred at -30°C for 2 h and then refluxed for 3 h. After standing overnight the separated salts were filtered and ether was evaporated. The residue was steam-distilled, the organic layer separated, dried over anhydrous magnesium sulfate and distilled affording 4.2 g of the product, b.p. 95–102°C/1.70 kPa. Analysis of the ¹H and ¹⁹F NMR spectra has shown that the product consisted of *XVI* and *XVII* in molar ratio 85 : 15. IR spectrum (an 85 : 15 mixture of *XVI* and *XVII*) cm⁻¹: 1 665 s, 1 685 vs (C=C, C=O). ¹H NMR spectrum: 1.20 m, 6 H (2 × CH₃); 3.42 m, 4 H (2 × CH₂); 5.53 ddd, 1 H (CHF), ²*J*(H, F) = 47 Hz, ³*J*(H, F) = 17.8 and 4 Hz (amide *XVI*). ¹⁹F NMR spectrum: Amide *XVI*: -65.6 m, 2 F (—CF₂Br); -115.4 and -122.9 AB, 2 F (CF₂), ²*J* = 278 Hz; -198.9 dm, 1 F (CHF), ²*J*(H, F) = 47 Hz. Amide *XVII*: -54.3 dd, 2 F (—CF₂Br), ³*J*(3, 4) = 31 Hz, ⁴*J*(2, 4) = 17.5 Hz (*cis*); -144.4 dt, 1 F (F-3), ³*J*(2, 3) = 137.5 Hz (*trans*), ³*J*(3, 4) = 31 Hz; -160.2 dt, 1 F (F-2), ³*J*(2, 3) = 137.5 Hz, ⁴*J*(2, 4) = 17.5 Hz. The elemental analysis corresponded to a mixture of *XVI* and *XVII*.

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