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Bromination of the perfluoro-tert-butyl anion (I) occurs when gem-dibromides RR^1CBr_2 ($R,R^1 = CF_3$, CN, COOEt) are reacted with perfluoroisobutylene (PFIB) in the presence of CsF, in which connection the α -bromocarbanions $RR^1\overline{CBr}$, which are formed together with (CF₃)₃CBr (II), react with PFIB on the type of vinylic substitution, which in the final analysis leads to the adducts of bis(trifluoromethyl)allenes with CsF [1].

As it proved,* the reaction of anion (I) with CF_2Br_2 leads to a completely different result. Here, under mild conditions (~ 20°C), the product of replacing bromine in CF_2Br_2 by the $(CF_3)_3C$ group, namely, perfluoroneopentyl bromide (III), was obtained in good yield, while the impurities were identified to be monohydroperfluoroneopentane (IV), perfluoro-2,5,5-trimethyl-2-hexene (V), and only traces of bromide (II). The Br in bromide (III) could not be replaced by the $(CF_3)_3C$ group. The reaction of (III) with anion (I) goes at 150°, but leads only to reduction products, and specifically $(CF_3)_3CH$ and hydride (IV).

It may be assumed that the reaction of anion (I) with CF_2Br_2 proceeds by a scheme that involves difluorocarbene and the perfluoroneopentyl anion (VI) as intermediates. This is evidenced both by the character of the formed products and the data on the reactions of CF_2Br_2 with nucleophiles [3], including with the C-anion of the methyl ester of N-benzylideneglycine [4].

$$(CF_{8})_{2}C = CF_{2} \xrightarrow{\overline{F}} (CF_{3})_{3}\overline{C} \xrightarrow{Br-CF_{2}-Br} (CF_{3})_{3}CBr + : CF_{2}$$

$$(I) \qquad (II)$$

$$:CF_{2} \xrightarrow{(I)} (CF_{3})_{3}C - \overline{CF}_{2} \longrightarrow (CF_{3})_{3}C - CF_{2}Br (III)$$

$$\xrightarrow{H^{+}} (CF_{3})_{3}C - CF_{2}Br (IV)$$

$$(VI) \xrightarrow{(CF_{3})_{3}C - CF_{2}} (CF_{3})_{3}C - CF_{2}CF_{2}CF_{2}CF_{2} (V)$$

The initial attack of anion (I) on CF_2Br_2 leads to bromide (II)[†] and difluorocarbene, in which connection the CF_2Br anion is not formed as a kinetically independent particle (see [6]). In essence, this determines all of the differences in the reactions of anion (I) with CF_2Br_2 when compared with other gem-dibromides. Then anion (I) adds to difluorocarbene [4], while the carbanionic intermediate (VI) is stabilized either by capturing a bromine or a proton (from the medium) or by reaction at the multiple bond of PFIB. Here, in principle, the bromine source can be either CF_2Br_2 or bromide (II).[‡] The fact that bromide (II) does not accumulate in the reaction mixture can mean that it is formed only in the step of initiating the reaction, while the development of the chain is accomplished wholly via CF_2Br_2 [3], or it is completely consumed in the bromination step, preferably before CF_2Br_2 .

It should be mentioned that the presence of added cyclohexene has no effect on the yield of the reaction products of anion (I) with CF_2Br_2 and diffuoronorcarane is not formed at all. Evidently, anion (I) is a more efficient trap for diffuorocarbene than cyclohexene. At the same time, the yield of olefin (V) is somewhat dependent on the reaction conditions: when CF_2Br_2 is added to the PFIB and CsF, i.e. the fluoroolefin is present in excess during the entire process, more (V) is formed than when the reactants are mixed in the reverse order.

^{*} See [2] for preliminary communication.

[†]See [5] for mechanism of halogenating carbanions by polyhaloalkanes.

 $[\]ddagger$ See [7] for ability of $(CF_3)_3CBr$ to brominate various compounds.

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Olefin (V) was also obtained as a by-product when anion (I) is reacted with HCF_2Cl . It is obvious that also in this reaction, which leads mainly to hydride (IV), the carbene mechanism is realized with the intermediate formation of anion (VI) (see [4]).

$$(I) \xrightarrow{H-CF_2-Cl} : CF_2 \xrightarrow{(I)} (VI) - \xrightarrow{R_FH} (CF_3)_3C - CF_2H (IV) \xrightarrow{(CF_3)_3C - CF_2H} (V)$$

Fluorocarbanion (VIII), generated by the addition to \overline{F} to perfluoro-2-methyl-2-pentene (VII), could also be made to react with CF_2Br_2 . It is characteristic that also in this case, as in the reaction with anion (I), besides the main product, namely the primary bromide (IX), are formed small amounts of the tertiary bromide $(CF_3)_2CBrC_3F_7$. The reaction of CF_2Br_2 with perfluoropropylene and CsF in DMF also gives bromide (IX), i.e. the reaction with CF_2Br_2 precedes the dimerization of the fluoroolefin.

$$(CF_3)_3C = CFC_2F_5 \xrightarrow{F} (CF_3)_2\overline{C} - C_3F_7 \xrightarrow{CF_2BF_2} (CF_3)_2C$$

$$(VII) \qquad (VIII) \qquad (III) \qquad (IIX) \qquad CF_2BF_3$$

It should be mentioned that the reactions of anion (I) with CF_2Br_2 and HCF_2CI are convenient methods for the synthesis of bromide (III) and hydride (IV). The latter was obtained recently by the fluorination of neopentane using a special technique [8]. In this paper bromide (III) was synthesized in low yield from (IV) via perfluoroneopentyllithium. We established that perfluoroneopentylmagnesium bromide, which is easily obtained from bromide (III) by exchange reaction with EtMgBr, can also be used for the synthesis of compounds that contain the $(CF_3)_3CCF_2$ group, for example ester (X) and ketone (XI). In contrast, the reaction of bromide (III) with Zn in dioxane gives, instead of the corresponding organozine compound, perfluoroalkane (XII), i.e. the perfluoroneopentyl radicals are doubled.



EXPERIMENTAL

The ¹⁹F NMR spectra were taken on a Perkin-Elmer R-32 instrument (84.6 MHz) from CF₃COOH as the external standard. The IR spectra were recorded on a UR-20 instrument. The mass spectra were taken on a Varian MAT CH-8 spectrometer (70 eV). For the analytical and preparative GLC we used Krytox deposited on Chromosorb.

<u>Perfluoroneopentyl Bromide (III).</u> With stirring and cooling with ice, 40 g of PFIB was added in 3.5 h to a mixture of 29.7 g of freshly ignited CsF, 40 g of CF_2Br_2 , and 100 ml of abs. diglyme; after 3 h the volatile products were distilled at 10 mm of Hg into a trap (-78°); a fraction with bp up to 70°, which contained (NMR, GLC) CF_2Br_2 , bromide (II), and hydride (IV), was distilled from the condensate. The residue contained 40.5 g of bromide (III), contaminated with 2.5% of olefin (V) (GLC). Bromide (III) was freed of (V) by treatment with excess piperidine and vacuum-sublimation over conc. H_2SO_4 . The obtained (III) bromide was identical (melting point, NMR) with that described in [8].

<u>Reaction of Perfluoroisobutylene with HCF_2Cl in Presence of CsF.</u> With stirring and cooling with ice, HCF_2Cl was bubbled slowly into a mixture of 11.3 g of CsF, 14.4 g of PFIB, and 40 ml of abs. diglyme until the PFIB conversion was complete (checked by GLC). The volatile products were vacuum-distilled into a trap (-78°). We obtained 11.7 g of a mixture which contained 70% of hydride (IV) and 24% of olefin (V) (NMR, GLC). The pure (V) was isolated by preparative GLC, bp 118-120° (micro method), n_D^{20} 1.2960. Found:

C 23.97; F 75.69%. C₉F₁₈. Calculated: C 24.0; F 76.0%. Raman spectrum ($\Delta \nu$, cm⁻¹): 1676 (C=C).

¹⁹F NMR spectrum: -20.4 m (F²), -17.2 d.q (F¹), -14.6 d.t.q (F⁵), +16.9 m (F³), +21.5 m (F⁴); $J_{F^1-F^3} = 34.8; J_{F^3-F^5} = J_{F^4-F^5} = 12.5; J_{F^1-F^2} = 11.4; J_{F^2-F^5} = 1.9$ Hz. Mass spectrum (m/z, relative intensity, %): 450 (M⁺), < 1; 431 (M⁺ - F), 11.4; 231 (C₅F₉⁺), 70; 181 (C₄H₇⁺), 100; 69 (CF₃⁺), 96.

 $\frac{1-\operatorname{Bromo}-2,2-\operatorname{bis}(\operatorname{trifluoromethyl})\operatorname{perfluoropentane}(IX)}{15 \text{ g of olefin (VII), 13 g of CF}_2\operatorname{Br}_2, \text{ and 40 ml of abs. MeCN was heated in an autoclave for 45 h at 120-130°; the reaction mixture was poured on ice, and from the organic layer after distilling off the starting substances we isolated 6 g of a fraction with bp 80-125°, which contained 90% of bromide (IX); after preparative GLC, bp 118-120°, np²⁰ 1.3152. Found: C 18.54; F 63.18%. C₇BrF₁₅. Calculated: C 18.65; F 63.49% <math display="block">\stackrel{1}{\operatorname{Br}}\operatorname{CF}_2\operatorname{C}(\operatorname{CF}_3)_2\operatorname{CF}_2\operatorname{CF}_2\operatorname{CF}_3. \stackrel{19}{\operatorname{F}}\operatorname{NMR} \operatorname{spectrum:} -33.8 \operatorname{t.h}(\operatorname{F}^1), -16.9 \operatorname{t.t.t}(\operatorname{F}^2), +3.8 \operatorname{t}(\operatorname{F}^5), +25.8 \operatorname{m}(\operatorname{F}^3), +43.3 \operatorname{m}(\operatorname{F}^4); J_{\mathrm{F}^1-\mathrm{F}^4} = 17.9; J_{\mathrm{F}^2-\mathrm{F}^3} = 15; J_{\mathrm{F}^3-\mathrm{F}^5} = 14.1; J_{\mathrm{F}^1-\mathrm{F}^2} = J_{\mathrm{F}^2-\mathrm{F}^4} = 11.3; J_{\mathrm{F}^3-\mathrm{F}^4} = 2.8 \operatorname{Hz}.$

<u>2-Bromo-2-trifluoromethylperfluoropentane</u>. A mixture of 5 g of CsF, 9.4 g of olefin (VII), and 5.1 g of Br₂ in 30 ml of MeCN was stirred for 15 h at 40-50°, poured into HCl solution (1: 5), and the organic layer was distilled over conc. H₂SO₄. We obtained 9 g (75%) of the bromide with bp 95-97°, nD²⁰ 1.3055. Found:

C 18.00; F 60.70%. C₆BrF₁₃. Calculated: C 18.04; F 61.90%. $(CF_3)_2C = CF_2CF_3CF_3$. ¹⁹F NMR spectrum:

-12.0 t.t (F¹), +4.0 t (F⁴), +28.2 m (F²), +45.0 m (F³);
$$J_{F_{-}F_{-}}^{1} = 13$$
; $J_{F_{-}F_{-}}^{1} = 9.4$; $J_{F_{-}F_{-}}^{2} = 13.2$ Hz.

Ethyl Ester of Perfluoro- β , β -dimethylbutyric Acid (X). With stirring, 7 g of bromide (III) in 10 ml of ether was added in drops (-70°) to EtMgBr (from 2.5 g of EtBr and 0.6 g of Mg in 15 ml of abs. ether). After 2 h 2.6 g of ClCOOEt in 10 ml of ether was added, the mixture was stirred for 2 h, gradually warmed up to -10°, hydrolyzed with 1:5 HCl solution, and the ether layer was dried and evaporated. The residue was treated with an equal volume of conc. H₂SO₄, the mixture was kept at 100° until all of the ClCOOEt had de-composed (~ 0.5 h), and then it was distilled to give 2 g (29%) of ester (X), bp 63-65° (55 mm), nD²⁰ 1.3198. Found: C 28.20; H 1.47%. C₈H₅F₁₁O₂. Calculated: C 28.07; H 1.49%. Infrared spectrum: 1770 cm⁻¹. ¹⁹F NMR spectrum: -15.1 t (CF₃), +26.1 dec (CF₂); J = 11.5 Hz.

Phenyl Perfluoro (2,2-dimethyl) propyl Ketone (XI). To the Grignard reagent, obtained the same as the preceding from 11.2 g of bromide (III), was gradually added 3.6 g of PhCOF in ether, after which the mixture was stirred for 1 h at -70° , heated for 1 h up to 10° , hydrolyzed, and the ether solution was evaporated. Vacuum-distillation of the residue over conc. H₂SO₄ gave 4 g of a fraction with bp 70-80° (3 mm) containing 90% of ketone (XI) (GLC). Redistillation gave the pure (XI) with bp 68-70° (5 mm), nD²⁰ 1.4040. Found: C 38.0; H 1.42; F 56.36%. C₁₂H₅F₁₁O. Calculated: C 38.51; H 1.33; F 55.88%. Infrared spectrum: 1740 cm⁻¹. ¹³F NMR spectrum: -15.8 t (CF₃), +19.3 dec (CF₂), J = 11.3 Hz. Based on the data of the NMR spectra and chromatomass spectrometry, ketone (XI) is contaminated with (CF₃)₃CCFHCOPh; ¹⁹F NMR spectrum: -14.4 d (CF₃), +116.9 d.dec (CF); J_{F-H} = 43.5; J_{F-F} = 11.3 Hz; besides the ions with m/z 356 (M⁺) and 337 (M⁺ - F), the mass spectrum has intense peaks of the fragment ions with m/z 105 (C₇H₅O⁺) and 77 (C₆H₅⁺).

 $\frac{\text{Perfluoro-2,2,5,5-tetramethylhexane (XII).}}{\text{(III), and 15 ml of dioxane was heated up to 55°, where exothermic reaction was observed and the temperature rose to 85°, after which the mixture was kept at this temperature for 2 h. Then, with cooling, 25 ml of conc.} H_2SO_4 was added, and the mixture was heated in vacuo to sublime 1.4 g (30%) of (XII), mp 58-60° (identified via NMR with that described in [9]).}$

CONCLUSIONS

Fluorocarbanions, generated by the addition of fluorine anion to perfluoroisobutylene and perfluoro-2methyl-2-pentene, replace the bromine atom in difluorodibromomethane. A scheme is postulated with the intermediate involvement of difluorocarbene.

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THEORETICAL DISCUSSION OF CYCLODIMERIZATION OF NITRILE N-OXIDES TO FUROXANS

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The most characteristic reaction for nitrile N-oxides is the noncatalytic cyclodimerization to furoxans. Three hypotheses are given in the literature for the mechanism of this reaction [1]: the Huysgen synchronous mechanism (1), the zwitterion (2), and the nitrocarbene (3) (Scheme 1):



However, the experimental facts [1-4] on the cyclodimerization rate of nitrile N-oxides (NO), and on the heat isomerization and heat decomposition of furoxans, cannot be explained within the framework of any of these hypotheses.

The purpose of the present paper is to theoretically develop the hypotheses that come closest to the known experimental data on the rate and mechanism of the dimerization of NO to furoxans [1] and the reverse decomposition reaction [2] and also the isomerization of unsymmetrically substituted furoxans [3].

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