PERFLUORO-1,2-DIISOPROPYLIDENE-3,3-DIMETHYLCYCLOBUTANE – A NEW CROSS-CONJUGATED PERFLUOROTRIENE ISOMER

E. G. Ter-Gabrielyan and N. P. Gambaryan

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It was shown earlier that perfluorotrienes (I) under the action of cesium fluoride in diglyme form unstable salts containing substituted pentadiene anions (II) which readily rearrange to stable salts of cyclic carbanions having structure (IIIa) [1]. It was ascertained that in acetonitrile, salt (IIIa) also forms but isomerization proceeds much faster. Distillation of volatile components from the acetonitrile solution of salt (IIIa) (vacuum, 0-10°C) resulted in a new isomer of triene (I), the substituted cyclobutane (IV) with two exocyclic double bonds* (yield 90-95%). This cyclic diene (IV) is also obtained by dehydrofluorination of monohydroperfluoroolefins (Va, b) using $BF_3 \cdot NEt_3$ complex in ether.

The structure of cyclic diene (IV) is supported by the mass, IR, and NMR spectra. In the ^{19}F NMR spectrum three multiplets of equal intensity belonging to trifluoromethyl groups and an AB quartet due to the ring difluoromethylene group are observed. In the ^{13}C NMR spectrum the CF_3 carbons give quartets at δ 120.1, 119.9, 119.0, 118.8, 118.7, and 118.3 ppm with $^1J_{C-F}$ constants of 283.4, 283.4, 276.7, 278.0, 272.6, and 275.4 Hz, respectively. The ring carbons yield signals at 68.5 hept (C^3), $^2J_{C-CF}$ = 32.5, 133.3 s (C^2); 142.8 t (C^1), $^2J_{C-CF}$ = 21.7 and 116.3 t (C^4), $^1J_{C-CF}$ = 284.9. The isopropylidene carbons have signals at 125.7 hept (C^5), $^2J_{C-CF}$ = 36.6 Hz, and 130.7 hept (C^6), $^2J_{C-CF}$ = 37.9 Hz.

Isomer (IV) is a stable compound that does not change upon heating to 300°C in a sealed glass ampul. Upon pyrolysis (500°C) (IV) gives a mixture of five substances in which triene (I), diene (VI), and a small amount of perfluorotetramethylallene were identified using GLC and ^{19}F NMR. The content of the latter increases with slight increase of temperature and time of contact.

Isomer (IV), like the cyclodimer of perfluoro(3-methylbuta-1,2-diene) [2], adds halogen upon UV irradiation, forming dichloride (VII). The good yield of isomer (IV) obtained during distillation of volatile components from the solution of salt (III) in acetonitrile (vacuum, 0-10°C) was unexpected, since from the diglyme solution of this salt (vacuum, 40-50°C) mainly triene (I) was obtained [1] [an impurity previously unidentified by us turned out to be (IV)]. Upon distillation of volatile components from a diglyme solution of salt (III) at atmospheric pressure, i.e., at higher temperature, pure triene (I) was obtained. It is interesting that temperature also influences the decomposition of salt (III) in $BF_3 \cdot OEt_2$. At 0°C diene (VI) is formed [1], and at 35°C, together with (VI), approximately an equal amount of isomer (IV) and ∿20% of triene (I) are obtained. Formation of the initial triene indicates reversibility of all isomerization steps.

The terminal diene (VI) is a kinetically controlled reaction product. In fact, under the action of catalytic amounts of CsF in acetonitrile or diglyme it quickly is transformed into isomer (IV) with internal double bonds. Perfluorotriene (I) upon catalysis with CsF under the same conditions also transforms into (IV), but significantly slower. Isomer (IV) under the same conditions does not change (Scheme 1).

The influence of temperature on the decomposition of salt (III) is possibly explained by the presence of reverse fluorotropy, which leads to transformation of anion (IIIa) into anion (IIIb). Elimination of F^- from anion (IIIa) can lead to both isomer (IV) and (VI). Isomer (VI) cannot be obtained from (IIIb) and only (IV) is formed. Temperature increase apparently increases the content of isomeric anion (IIIb) in the mixture,† which leads to

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* Dienes of this type are obtained by dimerization of fluoroallenes or cycloaddition of compounds with multiple bonds to $(CF_3)_2C=C=C=CPh_2$ [2, 3].

† The ^{19}F PMR spectrum ascribed earlier to the anion with structure of (IIIa) possibly belongs to the mixture of (IIIa) and (IIIb).

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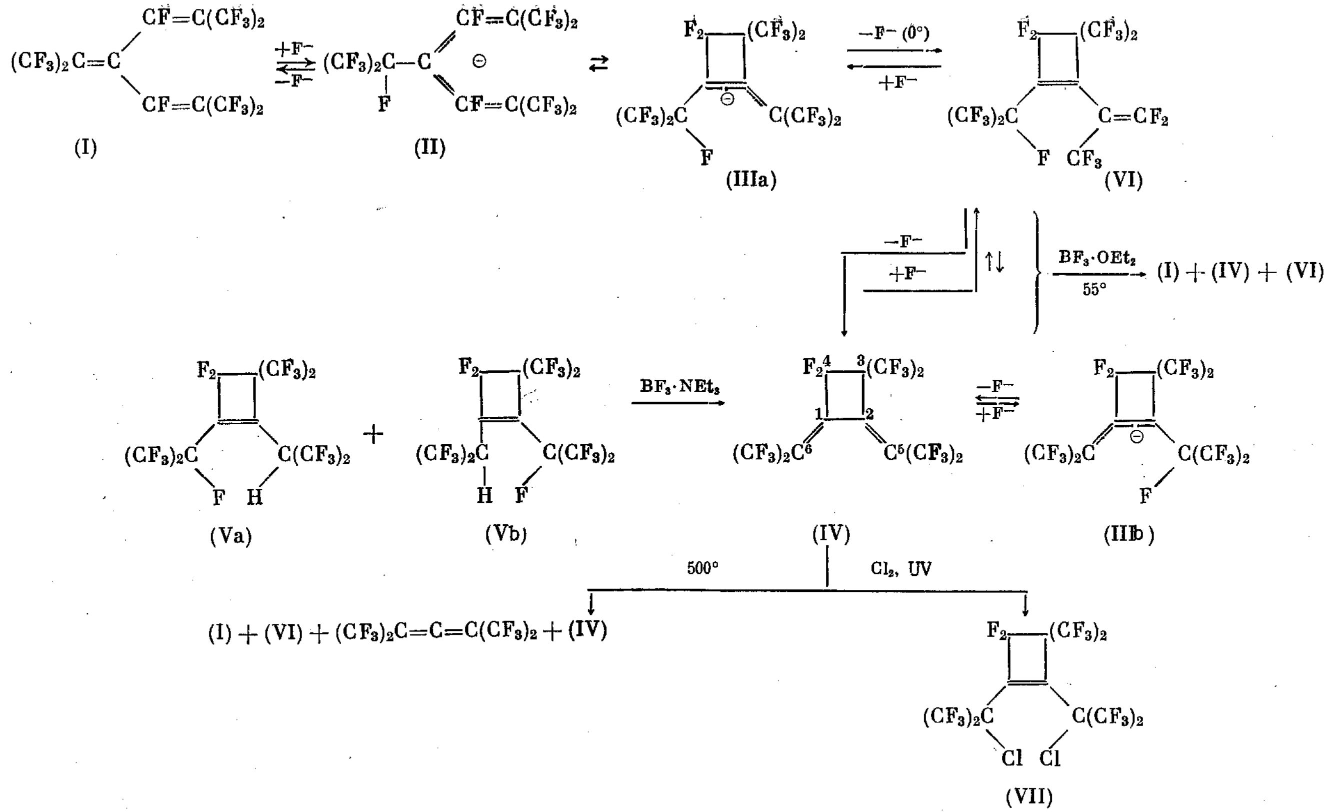

Scheme 1

an increase in yield of (IV). In favor of this assumption is also the fact that increase of protonation temperature of salt (III) increases the content of hydrofluoride (Vb) [4] corresponding to the isomeric anion (IIIb).

EXPERIMENTAL

The ^{19}F NMR spectra were recorded on a Perkin–Elmer R-32 (84.6 MHz) instrument, and the ^{13}C NMR spectra on a Brucker WP-200 SY (50, 31 MHz) with the internal standards being CF_3COOH and CD_3OD, respectively. The Raman spectra were taken on a Ramanor HG-25 spectrophotometer, (with excitation by an Ar laser), the IR spectra on a UR-20 instrument, and the mass spectra on a Varian MAT CH-8 (70 eV) instrument.

Perfluoro-1,2-diisopropylidene-3,3-dimethylcyclobutane (IV). a) To a freshly roasted CsF (3.4 g) in 20 ml absolute CH_3CN in an Ar atmosphere 10.6 g of triene (I) was added dropwise with stirring. After ∿20 h the ^{19}F NMR spectrum of the mixture contained signals due to salt (III). The mixture was evaporated into a trap (−78°C) under vacuum (2 mm) at 0-10°C. By distillation of the lower layer of condensate from concentrated H_2SO_4 there was obtained 10.1 g (95%) of isomer (IV) with bp 52.5-54°C (25 mm). Found: C 27.7; F 72.7%. $C_{12}F_{20}$. Calculated: C 27.5; F 72.5%. Mass spectrum: 524 M^+. Raman spectrum (ν, cm^{-1}): 1688 s, 1672 m, 1665 m. IR spectrum (ν, cm^{-1}): 1740 m, 1690 w, 1665 m. ^{19}F NMR spectrum (ppm); −15.3 m (CF_3, 6F), −13.5 m (CF_3, 6F), −12.2 m (CF_3, 6F), 19.7 (F_A), and 35.5 (F_B, CF_2, AB quartet, J = 225.84 Hz).

b) To a mixture of hydrofluorides (V) (1.4 g) $BF_3 \cdot NEt_3$ complex (0.45 g) in 1.5 ml absolute ether was added. The mixture was refluxed for 10 h. Volatile components were evaporated under vacuum (2 mm) into a trap (−78°C). The lower layer of condensate was separated (1,2 g) and distilled from concentrated H_2SO_4, yielding 0.8 g of isomer (IV) (59%), identical with an authentic sample by GLC and ^{19}F NMR.

Pyrolysis of Cyclobutane (IV). Pyrolysis was carried out in an argon flux. Products were collected in a trap (−78°C). A quartz tube of 0.6 cm diameter packed with crushed quartz was heated in a 20-cm-long cylindrical furnace (the temperature was measured on the outer wall of the tube). Argon was bubbled through isomer (IV). The rate of gas flow was 60 ml/min, the temperature was 500-520°C, and the time was 2 h. The obtained mixture (∿0.5g) was shown by GLC and ^{19}F NMR to contain ∿5% tetrakis(trifluoromethyl)allene, ∿20% triene (I), ∿20% isomer (VI), ∿10% unidentified impurities, and 45% unchanged cyclobutane (IV).

Chlorination of Cyclobutane (IV). Into 1.5 g of (IV) Cl_2 was bubbled with ultraviolet exposure for 6 h. By vacuum distillation 0.6 g (35.5%) of dichloride (VII) with bp 47-49°C (5 mm) was obtained. Found: C 24.2; F 64.0; Cl 11.3%. $C_{12}F_{20}Cl_2$. Calculated: C 24.2, F 63.9; Cl 11.9%. Mass spectrum 595 M^+. ^{19}F NMR spectrum (ppm): −14.0 m (CF_3, 6F), −10.4 m (CF_3, 6F), −8.0 m (CF_3, 6F), 28.0 (CF_2, 2F).

Decomposition of Salt (III) by Boron Trifluoride Etherate. To a solution of salt (III) obtained from 3.0 g triene (I) and 0.9 g CsF in 6 ml diglyme, 0.8 g of $BF_3\cdot OEt_2$ was added with stirring at 55-60°C. After 3 h the lower layer (2.5 g), contained ∿19% triene (I), ∿37% isomer (IV), and ∿44% isomer (VI) by GLC and ^{19}F NMR.

Reaction of Isomers (IV) and (VI) with CsF. To a suspension of freshly roasted CsF in abs. diglyme in an Ar atmosphere at 20°C an equimolar amount of isomer (IV) or (VI) was added with stirring. In both cases, a homogeneous solution of salt III was obtained (^{19}F NMR data).

Reaction of Cyclobutene (VI) with a Catalytic Amount of CsF. To 0.04 g CsF in 0.5 ml abs. acetonitrile (or diglyme) in an Ar atmosphere 0.4 g of isomer (VI) was added at ∿20°C. After 30 min the lower layer of the mixture contained only isomer (IV) (GLC, ^{19}F NMR data).

Reaction of Triene (I) with a Catalytic Amount of CsF. Treatment of triene (I) as above yielded only isomer (IV) after 10 h (GLC, ^{19}F NMR data).

Reaction of Isomer (IV) with a Catalytic Amount CsF. Isomer (IV) was unchanged after treatment with CsF as above. The lower layer of the mixture after ∿24 h contained only isomer (IV) (GLC, ^{19}F NMR data).

CONCLUSIONS

In the reaction of perfluoro-α,α-bis(isobutenyl)isobutylene with CsF a new cyclic isomer — perfluoro-1,2-diisopropylidene-3,3-dimethylcyclobutane — was obtained.

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TELOMERIZATION OF ISOPRENE WITH N-METHYLANILINE ON COMPLEX PALLADIUM CATALYSTS

L. I. Zakharkin and E. A. Petrushkina

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The preparation of acyclic terpene amines by telomerization of isoprene with secondary amines with catalysis by transition metal complexes is of great interest due to their possible use as fungicides, insecticides, herbicides, and juvenile hormone analogs [1]. Telomerization of isoprene (I) with dialkylamines, piperidine, and morpholine on complex palladium catalysts was studied in [1-5]. It was shown in [4] that all four possible telomers are formed in the telomerization of (I) with dialkylamines; in the telomers, two molecules of (I) are bound "head-to-head," "head-to-tail," "tail-to-tail," and "tail-to-head," and the ratio of the telomers is a function of the solvent, the use of acid cocatalysts, and the structure of the

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