HYDRATION OF 2,3-BIS(TRIFLUOROMETHYL)PERFLUORO-1,3-BUTADIENE

N. B. Kaz'mina, G. S. Krasnikova,
É. P. Lur'e, E. I. Mysov,
and I. L. Knunyants

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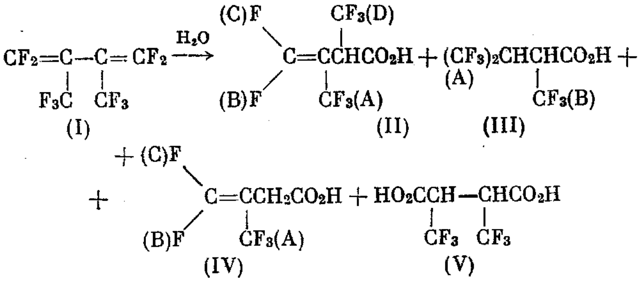
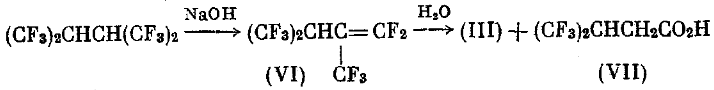
An examination of the Dewar model of the 2,3-bis(trifluoromethyl)perfluoro-1,3-butadiene (I) molecule [1] reveals that the angle between the planes of the double bonds is close to 90°, while rotation around the C—C bond is hindered by the presence of the two CF_3 groups. However, this does not exclude the possibility of a partial conjugation of the double bonds. The bromination results could give an answer to the question of conjugation, but (I) does not react with bromine. The nucleophilic addition to conjugated perfluorodienes described in the literature is restricted to the reaction of the perfluorobutadiene with an alcohol [2].

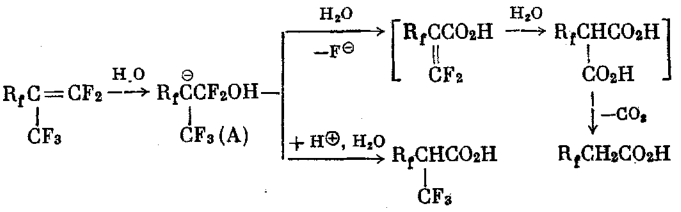
The hydration of (I), which was studied in the present paper, represented interest for elucidating the problem of the conjugation, and also from the standpoint of studying the properties of the hydration products. It proved that (I) does not react with water even on long heating in an autoclave at 100°C. In a homogeneous medium (aqueous acetone) reaction takes place at room temperature to give a mixture of acids, in which the 1,4-addition products could not be detected. The main hydration product of (I) is acid (II). Acid (III) is a side product that is formed by the addition of HF to either (I) or (II). To identify acid (III) we synthesized and hydrated 2,3-bis(trifluoromethyl)-3-hydroperfluoro-1-butene (VI).





$$(CF_3)_2CHCH(CF_3)_2 \xrightarrow{NaOH} \underset{(VI)\quad CF_3}{(CF_3)_2CH\underset{|}{C}=CF_2} \xrightarrow{H_2O} (III) + \underset{(VII)}{(CF_3)_2CHCH_2CO_2H}$$

The formation of acids (IV) and (VII) in the hydration of (I) and (VI) can be explained by the fact that the anions (A) are partially stabilized by the ejection of F^- anion (with subsequent hydrolysis of the substituted difluoroacrylic acid and decarboxylation).



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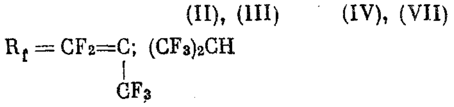
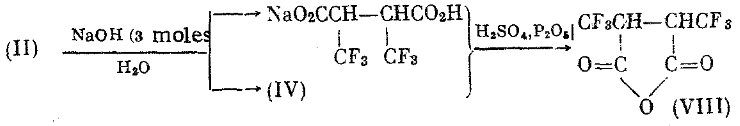


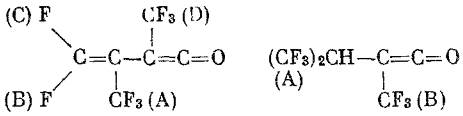
$R_f = CF_2{=}C(CF_3);\ (CF_3)_2CH$ — (II), (III); (IV), (VII)

The pure (IV) and (VII) acids were obtained by treating (II) and (III) with the calculated amount (3 moles) of $NaHCO_3$.

1,2-Bis(trifluoromethyl)succinic acid (V) was isolated from a mixture of acids (II), (III), (IV), and (V) by recrystallization from $CHCl_3$, while its anhydride (VIII) was obtained by treating the mixture of acids, formed by the alkaline hydrolysis of acid (II), with P_2O_5.

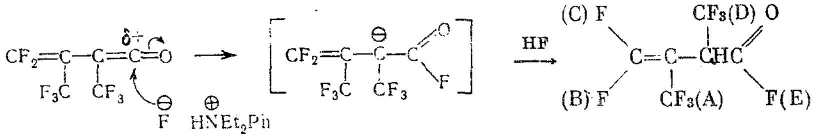


A study of the properties of the obtained products revealed that acids (II) and (III), similar to α-hydroperfluoroisobutyric acid [3], react with P_2O_5 to form stable ketenes (IX) and (X).



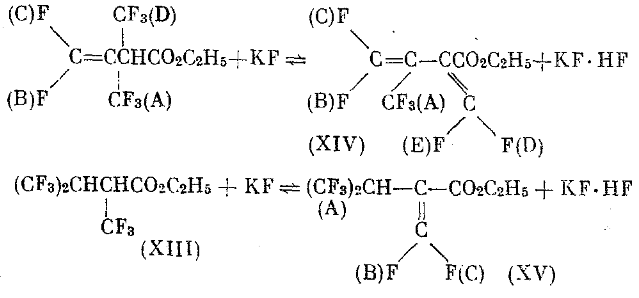
(IX) (X)

Ketenes (IX) and (X) are easily converted to the corresponding acids and esters. Acid fluoride (XI) was obtained from ketene (IX) and HF in the presence of catalytic amounts of diethylaniline.

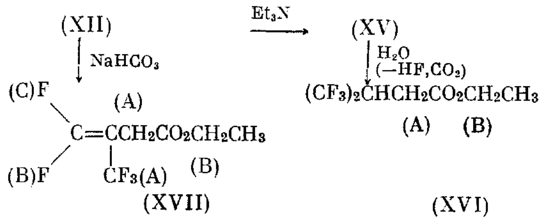


(XI)

Previously it was shown that the esters of α-hydroperfluoroisobutyric acid are dehydrofluorinated by NaF only at high temperatures(~600°) [4]. Refluxing with KF leaves then unchanged. It proved that esters (XII) and (XIII) easily undergo reversible dehydrofluorination when refluxed with KF. The equilibrium can be shifted completely to the right by distilling off the mixture of esters and repeating its treatment with anhydrous KF.



The esters of α-hydroperfluoroisobutyric acid remain practically unchanged when treated with Et_3N in the absence of a third component. The dehydrofluorination is reversible, and the equilibrium is shifted almost completely to the left [5]. When ester (XII) is reacted with Et_3N the role of the third component is played by double bonds [of ester (XII) and the intermediately formed ester (XIV)], which are capable of irreversibly adding the HF that is cleaved by the Et_3N. For this reason the hydrolysis of the α-CF_3 group in the presence of Et_3N [6] leads to ester (XVI) [and not (XVII)].



EXPERIMENTAL METHOD

The GLC method was used to analyze the mixtures and identify the obtained compounds: the column (5 m × 0.2 cm) was packed with 15% dioctyl phthalate deposited on Chromatone N-AW (0.250-0.315 mesh). The NMR spectra were taken on a Perkin—Elmer R-12 spectrometer (60 MHz), while the ^{19}F NMR spectra were taken on either a Hitachi or a Hitachi—Perkin—Elmer R-20 instrument (56.46 MHz). The chemical shifts are given in parts per million from the external standards, respectively TMS or CF_3COOH. The IR spectra were taken on a UR-20 spectrophotometer. The mass spectra were taken on a Varian CH-8 instrument.

The microanalysis results, yields, and the principal constants of the obtained compounds are summarized in Table 1.

2,3-Bis(trifluoromethyl-perfluoro-1,3-butadiene (I). To 604 g of 2,3-bis(trifluoromethyl)-2,3-dihydroperfluorobutane was added a suspension that had been prepared from 330 g of NaOH, 51 g of Al_2O_3, and 600 ml of water. The reaction mixture was stirred at 20°, checking the course of reaction by GLC. After ~48 h the products (mixture of 60% of diene (I) and 40% of butene (VI)) were distilled into a flask, cooled with Dry Ice. The obtained mixture was stirred with a suspension of 26 g of Al_2O_3, 165 g of NaOH, and 300 ml of water. The products (220-340 g) were distilled when the amount of butene (VI) reached 5-10% (after 48 h). The distilled mixture was again stirred with a suspension, obtained from 26 g of Al_2O_3, 165 g of NaOH, and 300 ml of water, until butene (VI) disappeared (~48 h). The product was distilled, and the yields of (I) were 180-210 g (35-40%), bp 49-51°, cf. [1]. The amount of (VI) reached 1%.

1-Perfluoroisopropenyl-2,2,2-trifluoropropionic Acid (II). A homogeneous mixture of 230 g of diene (I), 40 g of water, and 500 ml of acetone was sealed in two ampuls with SiO_2 (30-40 g in each) and let stand at ~20°. After a week the ampuls were opened, the reaction mixture was filtered, and the low-boiling components were distilled into cold water. The lower layer was separated from the water and represented 63 g of unreacted diene (I) (GLC). The residue from distilling off the diene and acetone contained (II), and the 1,2-bis(trifluoromethyl)-3,3,3-trifluorobutyric (III), perfluoroisopropenylacetic (IV), and 1,2-bis(trifluoromethyl)succinic (V) acids (^{19}F NMR). The mixture of acids was distilled, collecting the fraction with bp 120-170° (93 g); it was mixed with 15 ml of conc. H_2SO_4 and distilled at 140-170° to give 79 g of product. To 79 g of the mixed acids was added a 10-fold excess of P_2O_5 and distillation at 56-60° gave 52 g of ketene (IX). To 52 g of the ketene was added 3.9 g of water; the formed acid was distilled. We obtained 50 g of (II). The amount of acid (III) reached 5%. Infrared spectrum: 1750 cm^{-1}. NMR spectrum (δ, ppm): 13.67 s (OH); 4.46 g (CH), $J_{H-CF_3(D)} \sim 10$ Hz. ^{19}F NMR spectrum: −17.14 d.d.q. [CF_3(A)]; −8.00 d.q. [F(B)]; −5.29 m [F(C)]; − 9.86 m [CF_3(D)]; $J_{CF_2(A)-F(B)} \simeq 17.7$, $J_{CF_3(A)-F(C)} \sim 9.7$, $J_{CF_3(A)-CF_3(D)} \simeq 4$, $J_{F(B)-F(C)} \simeq 4$ Hz.

2,3-Bis(trifluoromethyl)-3-hydroperfluoro-1-butene (VI). A mixture of 400 g of 2,3-bis(fluoromethyl)-2,3-dihydroperfluorobutane and a solution of 53 g (1 mole) of NaOH in 150 ml of water was stirred vigorously for 1 h. The products were distilled into a flask, cooled with Dry Ice. We obtained 315 g of a mixture, which contained 10% of (I), 50% of (VI), and 40% of the starting butane. The mixture was fractionally distilled through a column that was packed with copper packing and equipped with a total reflux head. We collected the fraction with bp 56.5-57°; yield 63 g. NMR spectrum: 3.5 ppm (CH).

1,2-Bis(trifluoromethyl)-3,3,3-trifluorobutyric Acid (III). A homogeneous mixture of 63 g of butene (VI), 20 g of water, and 160 ml of acetone was sealed in an ampul with 20 g of SiO_2, and then let stand at ~20° for three days. The ampul was opened, the contents were filtered, and the low-boiling components were distilled into cold water. The lower layer was separated from the water to give 14.5 g of unreacted butene (VI) (GLC).

TABLE 1

Compound	Yield, %	T. bp., °C (T. mp., °C)	Empirical formula	Found, %			Calculated, %		
				C	H	F	C	H	F
(II)	30	165—166	$C_6H_2O_2F_8$	27,91	0,86	58,40	27,52	0,74	58.91
(III)	53	162—164	$C_6H_3O_2F_9$	25,89	0,94	61,21	25,90	1,09	61,51
(IV)	40	166	$C_5H_3O_2F_5$	31,04	1,62	50,15	31,58	1,58	50,00
(V)	19	(170—171)	$C_6H_4O_4F_6$	28,08	1,72	44,59	28,34	1,57	44.88
(VI)	26	56,5—57	C_6HF_{11}	25,73	0,40	74,09	25,53	0,35	74,11
(VII)	63	156	$C_5H_4O_2F_6$	28,51	1,90	53,32	28,57	1,90	54,28
(VIII)	24	(54—56)	$C_6H_2O_3F_6$	30,27	0,88	48,56	30.51	0,85	48,30
(IX)	80	56—57	C_6OF_8	29,90	—	63,10	30,00	—	63,33
(X)	65	59—60	C_6HOF_9	27,89	0,36	64,72	27,70	0,33	65,79
(XI)	73	81—82	C_6HOF_9	28,00	0,32	65,68	27,70	0,33	65,79
(XII)	78	133—134	$C_8H_6O_2F_8$	33,49	2,13	53,25	33,56	2,10	53,15
(XIII)	85	138—139	$C_8H_7O_2F_9$	31,86	2,40	55,80	31,37	2,28	55,89
(XIV)	71	126—127	$C_8H_5O_2F_7$	35,83	2,06	50,31	36,08	1,88	50,00
(XV)	71	128—129	$C_8H_6O_2F_8$	33,55	2,16	52,76	33,56	2,10	53,14
(XVI)	45	127—128	$C_7H_8O_2F_6$	35,48	3,48	47,64	35,29	3,36	47,90
(XVII)	56	127—129	$C_7H_7O_2F_5$	38,60	3,07	43,73	38,53	3,21	43,58

The residue from the distillation was filtered, and the water was separated. The mixture of acids (III) and (VII) was distilled with 20 ml of conc. H_2SO_4, collecting the fraction with bp 100-152°; yield 43 g. To 43 g of the mixed acids was added a 10-fold excess of P_2O_5, and distillation at 54-58° gave 25 g of ketene (X). To 25 g of the ketene was added 1.7 g of water. Distillation gave 25.6 g of acid (III). NMR spectrum (δ, ppm): 12.09 s (OH); 3.50 m (CH). ^{19}F NMR spectrum: −12.07 m [CF_3(A)]; −13.78 m [CF_3(B)].

Perfluoroisopropenylacetic Acid (IV). A mixture of 32 g of acid (II) and 35 g (3 moles) of $NaHCO_3$ was heated with a burner, and the formed water and acid (IV) were distilled off. The water was separated, while the acid was distilled with 5 ml of conc. H_2SO_4. We obtained 9.6 g of (IV). NMR spectrum (δ, ppm): 12.12 s (OH); 4.04 d.d (CH), $J_{CH_2-F(B)} = 1.8$, $J_{CH_2-F(C)} = 2.6$ Hz. ^{19}F NMR spectrum: −15.07 d.d [CF_3(A)]; −1.47 d.t.g [F(B)]; + 2.11 d.t.g [F(C)]; $J_{F(A)-F(B)} = 19.9$, $J_{F(A)-F(C)} = 10.7$, $J_{F(B)-F(C)} = 16.1$, $J_{F(B)-H} = 1.9$, $J_{F(C)-H}$ − 2.2 Hz.

2-Trifluoromethyl-3,3,3-trifluorobutyric Acid (VII). In a similar manner, (VII) was obtained from acid (III). NMR spectrum (δ, ppm): 11.58 s (OH); 2.64 d (CH_2); 3.50 h.t (CH), $J_{CH-F} \simeq 8$, $J_{CH-CH_2} = 5.9$ Hz. ^{19}F NMR spectrum: −8.74 d (CF_3), $J_{(CF_3)_2C-CH} \simeq 8.1$ Hz.

1,2-Bis(trifluoromethyl)succinic Acid (V). A mixture of 14 g of diene (I), 19 g of water, and 100 ml of acetone was refluxed for 19 h. The acetone was distilled off, and the residue was extracted with ether. The ether solution was dried over $MgSO_4$, and the ether was distilled off. The oily residue (7.7 g) was treated with $CHCl_3$; the mixture was let stand in the refrigerator. The crystalline acid was filtered, and washed on the filter with $CHCl_3$. We obtained 2.4 g of (V). ^{19}F NMR spectrum: −11.29 m.

Anhydride of 1,2-Bis(trifluoromethyl)succinic Acid (VIII). With cooling in ice, to a mixture of 37.8 g of acid (II) and 100 ml of water was added a solution of 17.6 g (3 mole) of NaOH in 250 ml of water. The water was vacuum distilled. To the residue was added 70 ml of conc. H_2SO_4, and the mixture of products (anhydride (VIII) and acids (II) and (IV)) was distilled, and then distilled twice with P_2O_5 (100 and 20 g), collecting the fraction with bp 146-147°. We obtained 8.2 g of anhydride (VIII). NMR spectrum (δ, ppm): 3.70 m (CH). ^{19}F NMR spectrum: −10.93 m (CF_3).

Perfluoroisopropenyl(trifluoromethyl)ketene (IX). To 30 g of acid (II) was added a 10-fold excess of P_2O_5. The mixture was heated with a burner and 22.7 g of the ketene was distilled off. The ketene was distilled with a small amount of P_2O_5. We obtained 22 g of (IX). Infrared spectrum: (ν, cm^{-1}): 1730, 1740, 2170 ($>C=C=O$). ^{19}F NMR spectrum: −14.28 d.d.q [CF_3(A)]; −10.63 d.q [F(B)]; −9.20 d.q.q [F(C)]; −20.43 d.q [CF_3(D)], $J_{F(A)-F(C)} = 9.8$ $J_{F(A)-F(B)} = 22.9$, $J_{F(B)-F(C)} = 10.7$, $J_{F(A)-F(D)} \simeq 3$, $J_{F(C)-F(D)} \simeq 4.8$ Hz.

2-Hydrohexafluoroisopropyl(trifluoromethyl)ketene (X). Compound (X) was obtained in a similar manner from (III). Infrared spectrum: (ν, cm^-): 1730, 2178 ($>C-C-O$). NMR spectrum (δ, ppm): 2.91 h (CH), $J_{CH-CF_3(A)} = 7.4$ Hz. ^{19}F NMR spectrum: 7.28 d.q [$CF_3(A)$]; −20.71 h [$CF_3(B)$]; $J_{CF_3(A)-CH} = 7.3$, $J_{CF_3(A)-CF_3(B)} = 2$ Hz.

1-Perfluoroisopropenyl-2,2,2-trifluoropropionyl Fluoride (XI). With cooling in ice, HF(~0.4 g) was passed into a mixture of 4.8 g of ketene and two drops of diethylaniline. The reaction mixture was brought up to ~20°, and then 4.3 g of the acid fluoride was distilled off at 50-94°. Redistillation gave 3.8 g of (XI). NMR spectrum (δ, ppm): 4.6 d.q (CH); $J_{CH-CF_3(D)} = 7.8$, $J_{CH-F(E)} = 4.8$ Hz. ^{19}F NMR spectrum: −16.86 d.d.q [$CF_3(A)$]; −10.47 br. q [F(B)]; −6.57 m [F(C)]; −8.71 d.d.q [$CF_3(D)$]; −116.87 q [F(E)]; $J_{F_3(A)-F(B)} \simeq 19$, $J_{CF_3(A)-F(C)} \simeq 10$, $J_{CF_3(A)-CF_3(D)} \simeq 4$, $J_{F(E)-CF_3(D)} = 12.9$; $J_{CF_3(D)-CH} = 8$ Hz. Mass spectrum (m/e); 260 (M^+, C_6HOF_9), 240 (M − HF, C_6OF_8), 213 (M−COF, C_5HF_8), 191 (C_5HOF_6), 163 (C_4HF_6), 143 (C_4F_5), 125 (C_4HF_4), 113 (C_3HF_4), 93 (C_3F_3), 75 (C_3HF_2), 69 (CF_3), 56 (C_3HF), 51 (CF_2H), 31 (CF).

Ethyl 1-Perfluoroisopropenyl-2,2,2-trifluoropropionate (XII). With stirring, to 65.7 g of ketene (IX) was gradually added 12.6 g (1 mole) of abs. ethanol. The reaction mixture was refluxed for 30 min. After distillation we obtained 74.5 g of ester (XII). NMR spectrum (δ, ppm): 3.99 q (CH); 4.06 q (CH_2); 0.55 t (CH_3); $J_{CH_2-CH_3} \simeq 7.2$, $J_{CH-CF_3(D)} \simeq 7.9$ Hz. ^{19}F NMR spectrum: −17.21 d.d.q [$CF_3(A)$]; −9.95 d.q [F(B)]; −4.14 d.q.q [F(C)]; −6.87 d.d.q [$CF_3(D)$]; $J_{CF_3(A)-F(B)} = 18.3$, $J_{CF_3(A)-F(C)} = 10.4$, $J_{CF_3(A)-CF_3(D)} \simeq 4$, $J_{F(B)-F(C)} = 4.4$, $J_{F(C)-CF_3(D)} = 14.9$, $J_{CF_3(D)-CH} = 8$ Hz.

Ethyl 1,2-Bis(trifluoromethyl)-3,3,3-trifluorobutyrate (XIII). Compound (XIII) was obtained in a similar manner from ketene (X).

Ethyl 1-Perfluoroisopropenyl-2,2-difluoroacrylate (XIV). Here 16 g of ester (XII) was distilled twice with 20 g of fused KF through a column packed with glass packing. After distillation without the KF we obtained 10.5 g of ester (XIV). Infrared spectrum: 1710, 1745 cm^{-1}. ^{19}F NMR spectrum: −15.88 d.d.d.d [$CF_3(A)$]; −3.91 d.d.d.q [F(B)]; −3.03 d.d.d.q [F(C)]; −13.38 d.d.d.q [F(D)]; − 12.04 d.d.d.q [F(E)]; $J_{CF_3(A)-F(B)} = 18.2$, $J_{CF_3(A)-F(C)} = 10.6$, $J_{CF_3(A)-F(D)} = 0.9$, $J_{CF_3(A)-F(E)} = 3.6$, $J_{F(B)-F(C)} = 3.1$, $J_{F(B)-F(D)} = 1.5$, $J_{F(B)-F(E)} = 3.5$, $J_{F(C)-F(D)} = 3.3$, $J_{F(C)-F(E)} = 1.5$, $J_{F(D)-F(E)} = 25.8$ Hz. Mass spectrum (m/e): 266 (M^+, $C_8H_5O_2F_7$), 238 (M − C_2H_4, $C_6HO_2F_7$), 221 (C_6OF_7), 213 ($C_6O_2F_6$), 199 ($C_6O_2F_6$), 193 (C_5F_7), 190 (C_5OF_6), 174 (C_5F_6), 171 (C_5OF_5), 143 (C_4F_5), 124 (C_4F_4), 121 (C_4OF_3), 105 (C_4F_3), 93 (C_3F_3), 74 (C_3F_2).

Ethyl 1-(2'-Hydrohexafluoroisopropyl)-2,2-difluoroacrylate (XV). Compound (XV) was obtained in a similar manner from ester (XIII). NMR spectrum (δ, ppm): 4.48 d.h (CH); 4.06 q (CH_2): 1.05 t (CH_3); $J_{CH-CF_3(A)} = 8.5$, $J_{CH-F(B)} = 2.3$, $J_{CH_2-CH_3} = 6.9$ Hz. ^{19}F NMR spectrum: −11.61 d.d [$CF_3(A)$]; −16.01 d.h [F(B); −18.71 d, [F(C); $J_{CF_3(A)-CH} = 8.6$, $J_{CF_3(A)-F(B)} = 16.3$, $J_{F(B)-CH} \simeq 2$, $J_{F(B)-F(C)} = 20.6$ Hz.

Reaction of Ethyl 1-Perfluoroisopropenyl-2,2,2-trifluoropropionate (XII) with Triethylamine. To 11 g of ester (XII) was added 3 g of Et_3N. The mixture was let stand for two days, and then it was distilled twice (tarry residues). After distillation with a little P_2O_5 we obtained 5.2 g of a mixture (bp 132-134°), which analyzed 63% of ester (XIII) and 37% of ester (XV). The esters were identified by comparing with authentic specimens via GLC and NMR.

Ethyl 2-Trifluoromethyl-3,3,3-trifluorobutyrate (XVI). A) A mixture of 16.9 g of acid (VII), 3.8 g of ethanol, and 2 ml of conc. H_2SO_4 was refluxed for 30 min, and then it was distilled, collecting the fraction with bp 78-140°. After washing with water, drying, and distillation we obtained 8.6 g of ester (XVI).

B. To a solution of 8.5 g of ester (XII) and 5 ml of water in 35 ml of acetone was gradually added 9.1 g (3 moles) of Et_3N. At the end of exothermic reaction the upper (colored) layer was separated, the acetone was distilled from it, and 10 ml of water was added to the residue. The obtained lower layer was washed with conc. HCl (5 ml) and water. The distillation of 5.9 g of the compound gave 4.4 g (62%) of ester (XVI), which was identical with that obtained by method A. NMR spectrum (δ, ppm): 3.58 t.h. (CH); 2.48 d $[CH_2(A)]$; 3.88 g $[CH_2(B)]$; 0.98 t (CH_3); $J_{CH-CH_2(A)} = 5.4$, $J_{CH_2(B)-CH_3} \simeq 7$, $J_{CH-CF_3} = 8$ Hz. ^{19}F NMR spectrum: −8.71 d, $J_{CF_3-CH} \sim 8$ Hz.

Ethyl perfluoroisopropenylacetate (XVII). A mixture of 62 g of ester (XII), 30 g of Na_2CO_3, and 20 g of $NaHCO_3$ was heated with a burner, and the liquid products were distilled off. The operation was repeated. After distillation we obtained 26.5 g of ester (XVII). Infrared spectrum: 1785 cm^{-1}. NMR spectrum (δ, ppm): 3.64 d.d. $[CH_2(A)]$; 4.64 g $[CH_2(B)]$; 1.64 t (CH_3); $J_{CH_2(A)-F(B)} \simeq 1.8$, $J_{CH_2(A)-F(C)} \simeq 2.2$; $J_{CH_2(B)-CH_3} = 6.9$ Hz. ^{19}F NMR spectrum: −15.34 d.d. $[CF_3(A)]$; −0.19 d.t.g. [F(B)]; +3.14 d.t.g. [F(C)]; $J_{CF_3(A)-F(B)} = 19.6$, $J_{CF_3(A)-F(C)} = 10.3$, $J_{F(B)-F(C)} = 18/4$. $J_{F(B)-CH_2(A)} \simeq 2$, $J_{F(C)-CH(A_2)} \simeq 2.2$ Hz.

CONCLUSIONS

1. Due to upsetting the coplanarity, 2,3-bis(trifluoromethyl)perfluoro-1,3-butadiene is hydrated in the 1,2 position.

2. Perfluoroisopropenyl(trifluoromethyl)ketene and 2-hydrohexafluoroisopropyl(trifluoromethyl)ketene were obtained by the respective treatment of 1-perfluoroisopropenyl-2,2,2-trifluoropropionic acid and 1,2-bis(trifluoromethyl)-3,3,3-trifluorobutyric acid with P_2O_5.

3. The dehydrofluorination of the esters of the 1-perfluoroisopropenyl-2,2,2-trifluoropropionic and 1,2-bis(trifluoromethyl)-3,3,3-trifluorobutyric acids gave the esters of the 1-perfluoroisopropenyl-2,2-difluoroacrylic and 1-(2-hydrohexafluoroisopropyl)-2,2-difluoroacrylic acids.

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