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Highly electrophilic derivatives of pentafluoromethacrylic acid are of interest because of their diverse reactivity [1]. The most convenient method for the preparation of these compounds is dehydrofluorination of the corresponding derivatives of α -hydrohexafluoroisobutyric acid with Et₃N·BF₃ [2]. In this way various esters and amides of pentafluoromethacrylic acid have been prepared. However, esters of bis-pentafluoromethacrylic acid and diols are not known until now.*

The starting compounds for the preparation of bis-pentafluoromethacrylates, $bis-\alpha$ -hydro-hexafluoroisobutyrates (Ia-c), are easily prepared by reacting bis(trifluoromethyl)ketenes with diols: ethylene glycol, butylene glycol, or hydroquinone.

 $\begin{array}{l} 2(CF_{3})_{2}C = C = O + HOZOH \rightarrow (CF_{3})_{2}CHCOOZOCOCH(CF_{3})_{2} \\ (Ia - c) \\ Z = (CH_{2})_{2} (a), (CH_{2})_{4} (b), 1, 4 - C_{6}H_{4} (c). \end{array}$

Earlier, analogous derivatives of glycerin were prepared in a similar way [4]; from fluorosulfonyltrifluoromethylketene the corresponding derivatives of ethylene glycol, pinacol, and pentaerythritol were prepared [5].

Just as alkyl α -hydrohexafluoroisobutyrates [6], bis-esters (I) show properties of CH acids. Thus, ester (Ic) on bromination in the presence of pyridine yields dibromide (II) (alkyl α -hydrohexafluoroisobutyrates are brominated in the same way [7]), and partial hydrolysis of the trifluoromethyl group in the presence of triethylamine leads to bis- β , β , β -trifluoropropionate (III) (cf. [8]).



By dehydrofluorination of bis-esters (Ia-c) with $Et_3N \cdot BF_3$ bis-pentafluoromethacrylates (IVa-c) are prepared.



The esters of ethylene and butylene glycol (IVa, b) are isolated by vacuum distillation; generally, the samples obtained contain a small amount of the starting bis- α -hydrohexafluoroisobutyrates (Ia, b), the boiling points of which are close to the boiling points of unsaturated bis-esters (IVa, b). Hydroquinone ester (IVc) could only be isolated in low yield by repeated crystallization from pentane or hexane.

*The bis-trifluoroacrylic ester of ethylene glycol, $(CF_2=CFCOOCH_2)_2$, has been prepared by dehalogenation of the corresponding tetrachloro- or dichlorodibromo derivative [3].

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| INDE I. I MAN DECLIA OI OMSACUIACEG DIS ESCEIS (IV) | TABLE | 1. | 19F | NMR | Spectra | of | Unsaturated | Bis-Esters | (IV) |); |
|---|-------|----|-----|-----|---------|----|-------------|------------|------|----|
|---|-------|----|-----|-----|---------|----|-------------|------------|------|----|

| Com- pound | Cher | mical shift | , ppm | J, Hz | | | |
|---|----------------------------|----------------------------|----------------------------|---|---|--|--|
| | Fa | Fb | CF3 | Fa—Fp | Fa-CF3 | Fb-CF. | |
| (IVa) (IV ^b) (IV ^c) | -16,53 -16,71 -22,34 | -15,83 -17,91 -21,61 | -14,71 -18,48 -19,26 | $\begin{vmatrix} +29,7 \\ +28.3 \\ +37,2 \end{vmatrix}$ | $\begin{vmatrix} -11,5\\ -11,9\\ -10,2 \end{vmatrix}$ | $\begin{array}{ c c } -21.2 \\ -24.4 \\ -27.1 \end{array}$ | |

*Spectra were recorded on an SXP-200 (188.31 MHz) spectrometer in $CDCl_3$. Calculations were carried out with the iterative program PANIC on an Aspect-2000 till RMS = 0.01.

The structures of the prepared products were confirmed by NMR, IR, and mass spectroscopy.

It is known [1] that esters of pentafluoromethacrylic acid are easily dimerized with a catalytic amount of the anion F⁻ to give the diesters $(CF_3)_2C(COOR)CF=C(CF_3)COOR$ (V). It has been shown by preliminary experiments that bis-esters (IV) can react in the same way and are thereby converted to polymers (or oligomers) of probable structure (VI).



Formation of polymers or oligomers is also possible in the reaction of bis-pentafluoromethacrylates with bifunctional nucleophiles. Actually, reaction of bis-ester (IVa) with ethylene glycol led to a product that was assigned structure (VII).

$$(1Va) \xrightarrow{\text{HOCH}_{2}\text{CH}_{2}\text{OH}} - \left(\begin{array}{c} -\text{CF}_{2}-\text{CH}-\text{C}_{-}\text{OCH}_{2}\text{CH}_{2}\text{O}-\text{C}_{-}\text{CH}-\text{CF}_{2}\text{OCH}_{2}\text{CH}_{2}\text{O} \\ & & & & \\ & & & \\ & & & & \\ & & & \\ & & & & \\$$

EXPERIMENTAL

 $^{19}{\rm F}$ NMR spectra were recorded on Perkin-Elmer R-32 (84.6 MHz) and Bruker WP-200 SV (188.3 MHz) spectrometers; chemical shifts are reported in ppm relative to the external standard CF₃COOH. IR spectra were taken on a UR-20 instrument and mass spectra on a VG-7070E spectrometer (electron ionization energy 70 eV); listed are m/z (relative intensity, %).

 $\frac{1,2-\text{Bis}(\alpha-\text{hydrohexafluoroisobutyroxy})\text{ethane (Ia)}}{2}$ At 0°C, into a mixture of 12.35 g of ethylene glycol and 10 ml of absolute ether was led 80 g of bis(trifluoromethyl)ketene; the solvent and the excess of $(CF_3)_2C=C0$ were evaporated at ~20°C under vacuum, and the residue was vacuum distilled to yield 76.45 g (92%) of bis-ester (Ia), bp 96-97°C (10 mm), mp ~40°C. ¹⁹F NMR spectrum (ether): -11.8 d [(CF_3)_2CH], JF-H = 7.5 Hz. IR spectrum (v): 1765 cm⁻¹ (C=0). Mass spectrum: 223 (27) [M⁺ - C_3HF_6CO_2], 222 (4) [M⁺ - C_3HF_6CO_2H], 179 (100) [C_3HF_6CO⁺], 69 (21) [CF_3]⁺, 45 (32) [C_2H_5O⁺ (?)]. Found, %: C 28.5; H 1.35; F 53.9. C₁₀H₆F₁₂O₄. Calculated, %: C 28.7; H 1.44; F 54.5.

1,4-Bis(α -hydrohexafluoroisobutyroxy)butane (Ib). Prepared in the same way from 5.00 g of 1,4-butylene glycol and 21 g of (CF₃)₂C=C=O in 10 ml of absolute ether. Yield 17.92 g (72%) of bis-ester (Ib), bp 83-85°C (1 mm), mp 33-35°C. ¹⁹F NMR spectrum (ether): -12.0 d

 $[(CF_3)_2CH], J_{F-H} = 7.5 \text{ Hz. IR spectrum (v): } 1760 \text{ cm}^{-1} (C=0). \text{ Mass spectrum: } 251 (2) \\ [M^+ - C_3HF_6CO_2], 250 (2) [M^+ - C_3HF_6CO_2H], 237 (5) [M^+ - C_3HF_6CO_2CH_2], 222 (16) [C_3HF_6CO_2-C_2H_3^+ (?)], 179 (84) [C_3HF_6CO^+], 69 (38) [CF_3^+], 54 (100) [C_4H_6^+]. Found, %: C 32.1; \\ H 2.19; F 50.4. C_{12}H_{10}F_{12}O_4. Calculated, %: C 32.3; H 2.24; F 51.1.$

 $\frac{1,4-\text{Bis}(\alpha-\text{hydrohexafluoroisobutyroxy})\text{benzene (Ic)}}{\text{droquinone in 350 ml of absolute ether was bubbled 135 g of <math>(CF_3)_2C=C=0$; after 14 h the solvent was evaporated under vacuum, and the residue was recrystallized from benzene. Yield 105.8 g (75%) of bis-ester (Ic), mp 91-92°C. ¹⁹F NMR spectrum (ether): -14.2 d [$(CF_3)_2CH$], $J_{F-H} = 7.5$ Hz. IR spectrum (v): 1770 cm⁻¹ (C=0). Mass spectrum: 466 (10) [M⁺], 446 (1) [M⁺ - HF], 427 (1) [M⁺ - HF - F], 288 (21) [M⁺ - C_3F_6CO], 179 (18) [C_3HF_6CO⁺], 110 (100) [C_6H_4(OH)_2⁺], 109 (15) [C_3F_3O⁺ (?)], 91 (13), 69 (24) [CF_3⁺]. Found, %: C 36.2; H 1.31; F 48.9. C_{14}H_6F_{12}O_4. Calculated, %: C 36.1; H 1.29; F 48.9.

A mixture of bis-ester (Ic), water, and Et_3N in the molar ratio of 1:4:4 was stirred in a flask equipped with a reflux condenser; after termination of the exothermic reaction the mixture was refluxed for 4 h, poured out in water, and extracted with ether. The ethereal extract was washed with cold diluted HCl and with water, and dried over CaCl₂. The ether was evaporated, and from the residue was obtained, by vacuum distillation (>100°C, 1 mm) followed by crystallization from benzene, 1,4-bis(β , β , β -trifluoropropionyloxy)benzene (III), mp 105-107°C. ¹⁹F NMR spectrum (ether): -13.5 t (CF₃CH₂), J_{F-H} = 9.4 Hz. IR spectrum (v): 1765 cm⁻¹ (C=0). Mass spectrum: 330 (4) [M⁺], 220 (13) [M⁺ - C₃HF₃O], 111 (23) [CF₃CH₂CO⁺], 110 (100) [C₆H₄(OH)₂⁺], 109 (6) [C₃F₃O⁺ (?)]. Found, %: C 44.2; H 2.43. C₁₂H₈F₆O₄. Calculated, %: C 43.7; H 2.44.

<u>1,4-Bis(α -bromohexafluoroisobutyroxy)benzene(II)</u>. To a solution of 3.00 g of bis(α -hydrohexafluoroisobutyroxy)benzene (Ic) in 5 ml of absolute pyridine was added dropwise at 0°C 2.35 g of Br₂. The mixture was poured out in cold diluted HCl, the precipitate was filtered off, washed with water, and dried. Yield 2.35 g (59%) of dibromide (II), mp 88-90°C (hexane). PMR spectrum (C₆F₆): δ 7.16 (C₆H₄). ¹⁹F NMR spectrum (C₆F₆): -8.9 s (CF₃). Found, %: C 26.9; H 0.53; F 37.3; Br 26.0. C₁₄H₄Br₂F₁₂O₄. Calculated, %: C 26.9; H 0.64; F 36.5; Br 25.6.

<u>1,2-Bis(pentafluoromethacryloyloxy)ethane (IVa)</u>. A mixture of 30.0 g of 1,2-bis(α-hydrohexafluoroisobutyroxy)ethane (Ia), 25.5 g of Et₃N·BF₃, and 20 ml of absolute ether was refluxed for 28 h. The precipitate was filtered off, washed with absolute ether, and the filtrate was evaporated under vacuum. Distillation of the residue yielded 15.7 g (58%) of bis-ester (IVa), bp 70-73°C (1 mm). See Table 1 for the ¹⁹F NMR spectrum. IR spectrum (ν , cm⁻¹): 1710, 1760 (C=0, C=C). Mass spectrum: 203 (9) [M⁺ - C₃F₅COO], 174 (10) [C₅H₃-F₅O⁺ (?)], 159 (100) [C₃F₅CO⁺], 69 (17) [CF₃⁺]. Found, %: C 31.7; H 1.10; F 49.8. C₁₀H₄-F₁₀O₄. Calculated, %: C 31.8; H 1.07; F 50.2.

To a solution of bis-ester (IVa) in absolute MeCN was added a small amount of calcined CsF. ¹⁹F NMR spectrum of the solution: $-18.2 \text{ dm} (\text{CF}_3^{a})$, $-13.1 \text{ dm} (\text{CF}_3^{b})$, $11.3 \text{ m} (\text{CF}^{c})$, $J_{a-c} = 24.4$, $J_{b-c} = 12.2 \text{ Hz}$ (cf. the ¹⁹F NMR spectra of dimers (V), R = Me or Et [9]). The solvent was evaporated, the residue was heated under vacuum (100°C, 1 mm), dissolved in MeOH, treated with water, centrifuged, and the oily residue was dried under vacuum over P_2O_5 . Polymer (VIa) was obtained. IR spectrum (ν , cm⁻¹): 1680 (C=C), 1765 (C=O). Found, %: C 31.9; H 1.30; F 49.7. (C₁₀H_4F₁₀O₄)_n. Calculated, %: C 31.8; H 1.07; F 50.2.

A solution of bis-ester (IVa) in absolute ether was treated with a cooled equimolar amount of ethylene glycol. After termination of the exothermic reaction the solvent was evaporated, the residue was dissolved in MeOH, treated with water, centrifuged, the oil obtained was washed with water, again dissolved in MeOH, the solvent was evaporated, and the residue was dried under vacuum over P_2O_5 . Polymer (VII) was obtained. IR spectrum (v): 1765 cm^{-1} (C=O).Found, %: C 33.5; H 2.48; F 42.0. $(C_{12}H_{10}F_{10}O_6)_n$. Calculated, %: C 32.7; H 2.29; F 43.2.

<u>1,4-Bis(pentafluoromethacryloyloxy)butane (IVb)</u>. Prepared in the same way as (IVa) from 4.0 g of 1,4-bis(α -hydrohexafluoroisobutyroxy)butane (Ib) and 3.3 g of Et₃N·BF₃. Yield 2.1 g (58%) of bis-ester (IVb), bp 80-86°C (1 mm), containing ~10% of starting bis-ester (Ib). ¹⁹F NMR spectrum: see Table 1. IR spectrum (ν , cm⁻¹, CC1₄): 1730, 1780 (C=0, C=C). Mass spectrum: 406 (1) [M⁺], 231 (1) [M⁺ - C₃F₅CO0], 230 (2) [M⁺ - C₃F₅CO0H], 159 (100) [C₃F₅CO⁺], 69 (19) [CF₃⁺], 54 (80) [C₄H₆]⁺. Found, %: C 35.2; H 1.90; F 46.7. C₁₂H₈F₁₀O₄. Calculated, %: C 35.5; H 1.93; F 46.8. <u>1,4-Bis(pentafluoromethacryloyloxy)benzene (IVc)</u>. 1,4-Bis(α-hydrohexafluoroisobutyroxy)benzene (Ic) was dehydrofluorinated in the same way as esters (Ia, b) by refluxing with an excess of $Et_3N \cdot BF_3$ in absolute ether. The precipitate was filtered off, washed with absolute ether, and the filtrate was evaporated under vacuum. The residue was treated with boiling hexane, decanted while still hot, the solution was slightly cooled, decanted again from the precipitated oil, and stored at about $-5^{\circ}C$. The precipitated oil was treated again in the same way. Upon cooling to about $-5^{\circ}C$ a small amount of bis-ester (IVc), mp 80-82°C, was obtained from the precipitate. ¹⁹F NMR spectrum: see Table 1. IR spectrum (v, cm⁻¹): 1710, 1745 (C=0, C=C). Mass spectrum: 426 (11) [M⁺], 159 (100) [C₃F₅CO⁺], 69 (16) [CF₃⁺]. Found, %: C 39.4; H 1.14; F 44.5. C₁₄H₄F₁₀O₄. Calculated, %: C 39.5; H 0.95; F 44.6. On addition of a catalytic amount of CsF to a solution of bis-ester (IVc) in acetonitrile, a precipitate was formed, probably polymer (VIc).

CONCLUSIONS

By reacting bis(trifluoromethyl)ketene with ethylene glycol, l,4-butylene glycol, or hydroquinone the corresponding bis- α -hydrohexafluoroisobutyrates are obtained, which on de-hydrofluorination with Et₃N·BF₃ yield bis-pentafluoromethacrylates.

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