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Additive Kolbe Electrosynthesis in the Presence of Acetylene and Butadiene

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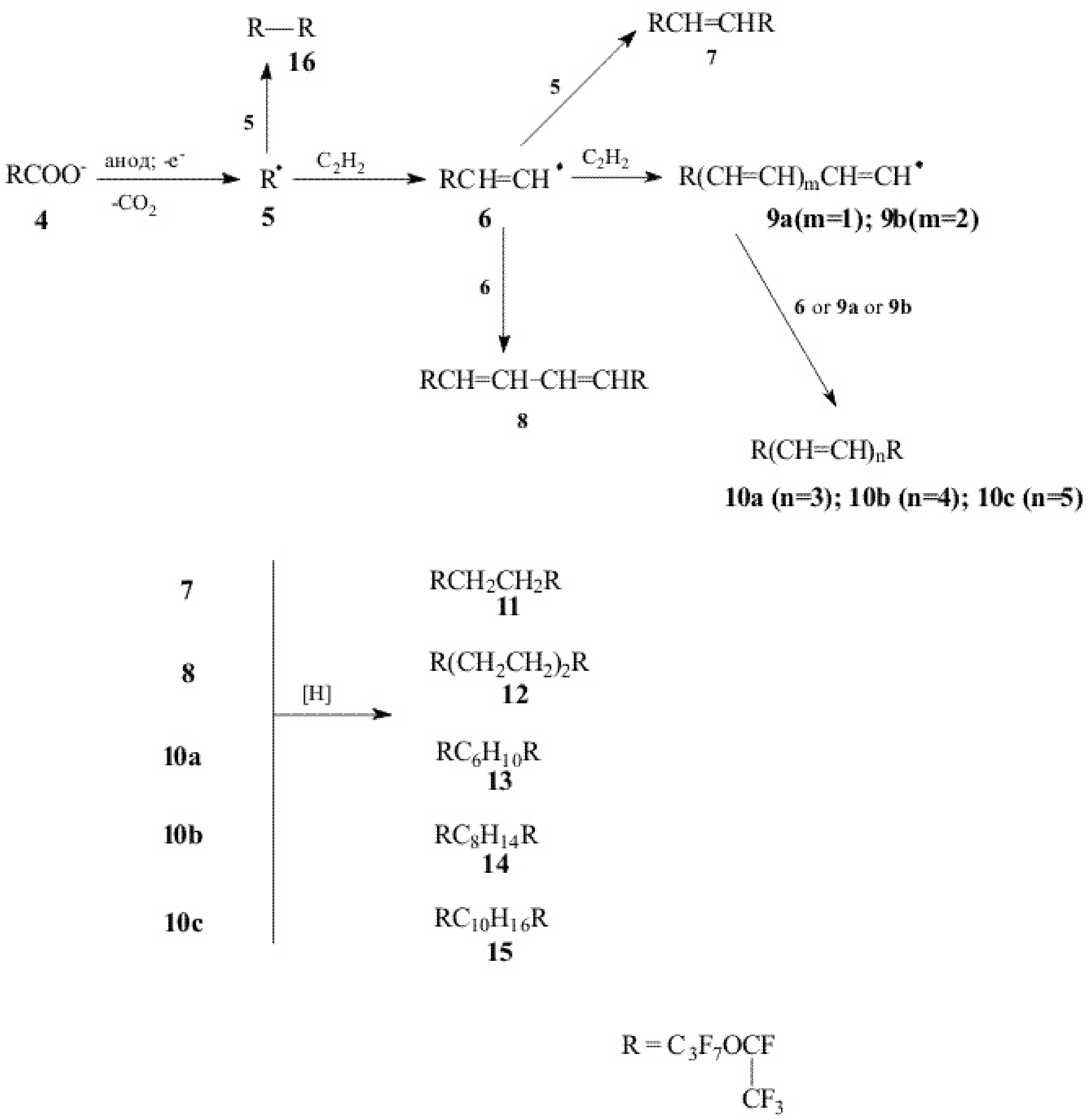
Partially fluorinated fluoroaliphatic compounds that combine physico-chemial properties specific both for fluoro- and hydrocarbons are of doubtless practical interest. Thus 1,2-dihydro-1,2-diperfluoroalkylethylenes (**1**) possessing high chemical stability and – in spite of the presence of vinylene fragment – high dissolving capability towards oxygen and carbon dioxide have been suggested as the components of gas transporting compositions (blood substitutes)[1-3].

Alkenes **1** were obtained by four-step synthesis from perfluoroalkyl iodides and ethylene. We have endeavoured to prepare these compounds by one-step reaction according to the scheme of additive Kolbe electrosynthesis in the presence of acetylene.

It is well known that acetylene polymerizes under the conditions of electrochemical process[4]. Nevertheless it is possible to compete with this process: the electrolysis of trifluoroacetic acid in the presence of acetylene afforded a mixture of 2,3-dihydrohexafluorobutene-2 (**2**) and 2,2,3-trihydro-3-trifluoromethylhexafluorobutane (**3**)[5]. Undoubtedly the formation of the latter is a result of CF_3-radical addition across the double bond of butene **2**and further hydrogen abstraction from the solvent.

It could be expected that further radical alkylation of the target alkenes **1** in the reactions with the participation of bulky fluoroalkyl radicals of iso-structure would be impeded. Indeed, the electrolysis of perfluoro-2-propoxypropionic acid (**4**) in the presence of acetylene led to the formation of olefine **7** and a mixture of compounds **8,11-15**(total percentage in the reaction products ~4%) but 4,7-dioxaperfluoro-5,6-dimethyldecane (**16**) appeared to be the main reaction product (96%). Besides these substances polymeric products were found both in the bulk of electrolyte and on the surface of electrodes (supposedly polyacetylene; the structure of polymers wasn't studied).

Scheme 1

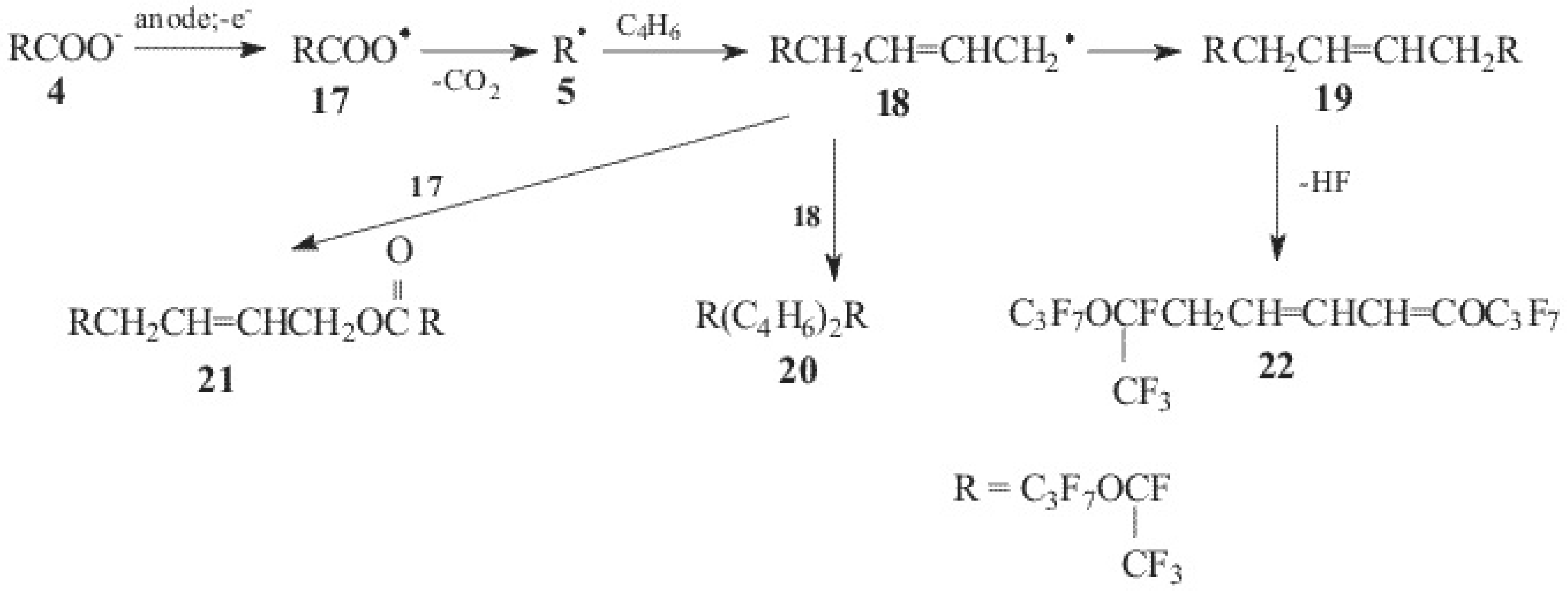


Considering the result of preparative-scale electrolysis one can conclude that electrolysis substantially comprises two parallel electrochemical reactions: Kolbe electrosynthesis affording the Kolbe-dimer **16** and electrochemical polymerization of acetylene. At the same time in spite of the low yield of the compounds **7,8,11-15** they are rather noticeable for their structures α-Diene **8** is the first example of diene preparation by the reaction of radical addition to acetylene (cf.[6]), and the compounds **13-15** were formed most likely by recombination of the radicals **6** and **9a** or by recombination of fluoroalkyl-α-di- and -trienyl radicals **9a,b** and further partial reduction of the polyenes **10a-c** formed. By the way not only the polyenes **10a-c** but their lower homologues **7** and **8** manifest the tendency to reduction forming the alkanes **11** and **12**. The easiness of the reduction - presumably of electrochemical nature - of olefine **7** and its vinylogs is connected with their increased electrophility induced by the presence of electron-withdrawing fluoroalkyl substituents located at the ends of vinylene or polyvinylenes chains.

Most probably the low yield of the products **7,8,11-15** is conditioned by the influence of several factors. It is an increased stability and, correspondingly, a reduced reactivity of perfluoro-α–propoxyethyl radical **5** (about the influence of α-fluoroalkoxi-groups on the reactivity of fluoroalkyl radicals see[7]) and higher reactivity of vinyl radicals – in comparison with the reactivity of their saturated analogues[8] – that determines high rate of acetylene polymerization. But first of all the composition of the reaction products reflects the low reactivity of acetylene in the radical addition reactions. Using the method of competitive reactions Tedder and co-workers demonstrated[6] that acetylene was at least by order of magnitude less active than ethylene in the reaction of photochemical addition of CF_3I.

The composition of the reaction products obtained by electrolysis of acid **4** in the presence of butadiene indicates at the decisive role of the reactivity of unsaturated organic substrate in the additive Kolbe electrosynthesis. In this case the share of adducts of radical **5** to butadiene increases up to 46.5%. It should be noted that in contrast to unsaturated compounds **7-8** obtained from acetylene olefine **19** and diene **20** have not been reduced under the conditions of electrolysis that is presumably connected with their less electrophility due to the presence of methylene bridge between fluoroalkyl substituent and double bond.

Scheme 2



Experimental

The mass spectra were recorded on VG ANALYTICAL 70-70E (70 eV) and Finnigan Polaris/GCQ Plus (70 eV) spectrometers.

Kolbe Electrosynthesis in the presence of acetylene

A mixture of 6.8 g (20.6 mmol) of acid **4**, 1.33 g (3.6 mmol) K-salt of acid **4**, 30 ml of acetone and 0.5 ml H_2O was electrolysed at 20°C in the presence of acetylene in undivided cell supplied with a water jacket, reflux condenser, magnetic stirrer, inlet tube and thermometer (acetylene was bubbled through electrolyte at the rate 30ml/min; anode – Pt-10%Ir alloy (15 cm^2); current density 13 mA/cm^2; 0.86 a.-h (1.62 F/mol) of electricity was passed). Then electrolyte was washed with diluted HCl-acid, organic layer was separated, the aq. solution was extracted with CH_2Cl_2, the organic solutions were combined, dried over $MgSO_4$, CH_2Cl_2 was evaporated, the products volatile up to 115-120°/2-3 Torr were evacuated into receiver (-78°). There was obtained 5.8 g of a mixture that contained 96% of 4,7-dioxaperfluoro-5,6-dimethyldecane **16** and 4% of a mixture **7,8,11-15** (according to chromatomass-spectroscopy data).

Mass-spectrum **16**(m/z, reference): 385 $[Ñ_7F_{15}O^+]$; 328 $[C_7F_{12}O^+]$; 285 $[C_5F_{11}O^+]$; 263 $[C_5F_9O_2^+]$; 219 $[C_4F_9^+]$; 197 $[C_4F_7O^+]$; 181 $[C_4F_7^+]$; 169 $[C_3F_7^+]$; 150 $[C_3F_6^+]$; 131 $[C_3F_5^+]$; 119 $[C_2F_5^+]$; 100 $[C_2F_4^+]$; 97 $[C_2F_3O^+]$; 69 $[CF_3^+]$ (100%).

Mass-spectrum **7**(mixture of isomers), isomer À(m/z, reference): 527 $[M\text{-}CF_3^+]$; 411 $[M\text{-}C_3F_7O^+]$; 339 $[C_8H_2F_{11}O_2^+]$; 245 $[C_6H_2F_9^+]$; 225 $[C_6HF_8^+]$; 195 $[C_5H_2F_7^+]$; 169 $[C_3F_7^+]$ (100%); 145 $[C_4H_2F_5^+]$; 119 $[C_2F_5^+]$; 100 $[C_2F_4^+]$; 69 $[CF_3^+]$. Isomer B (m/z, reference): 527 $[M\text{-}CF_3^+]$; 411 $[M\text{-}C_3F_7O^+]$; 339 $[C_8H_2F_{11}O_2^+]$; 245 $[C_6H_2F_9^+]$; 223 $[C_6H_2F_7O^+]$; 195 $[C_5H_2F_7^+]$; 173 $[C_5H_2F_5O^+]$; 169 $[C_3F_7^+]$ (100%); 151 $[C_5H_2F_3O_2^+]$; 119 $[C_2F_5^+]$; 100 $[C_2F_4^+]$; 69 $[CF_3^+]$; 57 $[C_3H_2F^+]$.

Mass-spectrum **8**(mixture of isomers) (m/z, reference): 622 $[M^+]$; 602 $[M\text{-}HF^+]$; 553 $[M\text{-}CF_3^+]$; 437 $[C_{11}H_4F_{15}O^+]$; 365 $[C_{10}H_4F_{11}O_2^+]$; 343 $[C_{10}HF_{10}O_2^+]$; 227 $[C_8H_4F_5O_2^+]$; 169 $[C_3F_7^+]$ (100%); 97 $[C_2F_3O^+]$; 69 $[CF_3^+]$; 43 $[C_2F^+]$.

Mass-spectrum **11** (m/z, reference): 529 $[M\text{-}CF_3^+]$; 413 $[M\text{-}C_3F_7O^+]$; 393 $[C_9H_3F_{14}O^+]$; 341 $[C_8H_4F_{11}O_2^+]$; 293 $[C_7H_3F_{10}O^+]$; 247 $[C_5F_9O^+]$; 227 $[C_6H_3F_8^+]$; 205 $[C_6H_3F_6O^+]$; 175 $[C_5H_4F_5O^+]$; 169 $[C_3F_7^+]$ (100%); 155 $[C_5H_3F_4O^+]$; 127 $[C_4H_3F_4^+]$; 100 $[C_2F_4^+]$; 77 $[C_5HO^+]$; 69 $[CF_3^+]$.

Mass-spectrum **12** (m/z, reference): 626 $[M^+]$; 456 $[C_{11}H_7F_{15}O_2^+]$; 387 $[C_{10}H_7F_{12}O_2^+]$; 325 $[C_8H_4F_{11}O^+]$; 271 $[C_8H_7F_8O^+]$; 199 $[C_7H_7F_4O_2^+]$; 169 $[C_3F_7^+]$ (100%); 159 $[C_4F_5O^+]$; 139 $[C_5H_6F_3O^+]$; 119 $[C_2F_5^+]$; 95 $[C_3H_2F_3^+]$; 69 $[CF_3^+]$; 59 $[C_2FO^+]$.

Mass-spectrum **13*** (mixture of isomers) (m/z, reference): 652 $[M^+]$; 569 $[C_{16}H_3F_{18}O_2^+]$; 452 $[C_{12}H_{10}F_{14}O_2^+]$; 383 $[C_{11}H_{10}F_{11}O_2^+]$; 353 $[C_{10}H_8F_{11}O^+]$; 293 $[C_{10}H_5F_8O^+]$; 267 $[C_8H_3F_8O^+]$; 243 $[C_6H_3F_8O^+]$; 195 $[C_5H_2F_7^+]$; 169 $[C_3F_7^+]$; 127 $[C_4H_3F_4^+]$; 100 $[C_2F_4^+]$; 73 $[C_3H_2FO^+]$; 69 $[CF_3^+]$; 57 $[C_3H_2F^+]$; 43 $[C_2F^+]$ (100%).

Mass-spectrum **14*** (mixture of isomers) (m/z, reference): 680 $[M^+]$; 661 $[M\text{-}F^+]$; 495 $[M\text{-}C_3F_7O^+]$; 475 $[C_{15}H_{13}F_{15}O^+]$; 395 $[C_{13}H_{14}F_{11}O^+]$; 365 $[C_{10}H_4F_{11}O_2^+]$; 343 $[C_{10}HF_{10}O_2^+]$; 309 $[C_7F_{11}O^+]$; 265 $[C_8H_4F_7O_2^+]$; 195 $[C_5H_2F_7^+]$; 169 $[C_3F_7^+]$; 159 $[C_4F_5O^+]$; 119 $[C_2F_5^+]$; 95 $[C_3H_2F_3^+]$; 69 $[CF_3^+]$; 58 $[C_3H_3F^+]$; 43 $[C_2F^+]$ (100%).

Mass-spectrum **15*** (mixture of isomers) (m/z, reference): 706 $[M^+]$; 667 $[C_{20}H_{15}F_{20}O_2^+]$; 629 $[C_{20}H_{15}F_{19}O_2^+]$; 579 $[C_{19}H_{15}F_{17}O_2^+]$; 521 $[M\text{-}C_3F_7O^+]$; 501 $[C_{17}H_{15}F_{14}O^+]$; 463 $[C_{17}H_{15}F_{12}O^+]$; 421 $[C_{15}H_{16}F_{11}O^+]$; 365 $[C_{11}H_8F_{11}O^+]$; 293 $[C_7H_3F_{10}O^+]$; 169 $[C_3F_7^+]$; 140 $[C_5H_4F_4^+]$; 119 $[C_2F_5^+]$; 69 $[CF_3^+]$; 58 $[C_3H_3F^+]$; 43 $[C_2F^+]$ (100%).

***** (The positions of double bonds have not been established)

Kolbe electrosynthesis in the presence of butadiene

A mixture of 6.4 g (19.4 mmol) of acid **4**,1.75 g (4.8 mmol) K-salt of acid **4**, 27 ml MeCN and 3 ml H_2O was electrolysed in the presence of butadiene in undivided cell described above (the rate of butadiene – 30 ml/min; current density 66 mA/cm^2; 0.8 a.-h (1.56 F/mol) of electricity was passed). The electrolyte was worked up as described in the previous example to give 6 g of a mixture that contained 53.5% of compound **16**, 32.3% of olefine **19**, 11% of diene **20**, 1.8% of compound **21**[**] and 3.4% of compound **22** (according to chromatomass-spectroscopy data).

Mass-spectrum **19** (mixture of isomers) (m/z, reference): 624 $[M^+]$; 555 $[M\text{-}CF_3^+]$; 439 $[M\text{-}C_3F_7O^+]$; 419 $[C_{11}H_5F_{14}O^+]$; 339 $[C_9H_6F_{11}O^+]$; 273 $[C_7H_2F_9O^+]$; 253 $[C_8H_5F_8^+]$; 233 $[C_8H_4F_7^+]$; 169 $[C_3F_7^+]$; 159 $[C_4F_5O^+]$; 119 $[C_2F_5^+]$; 95 $[C_3H_2F_3^+]$; 77 $[C_5HO^+]$; 69 $[CF_3^+]$; 59 $[C_2FO^+]$ (100%).

Mass-spectrum **20**[*] (mixture of isomers) (m/z, reference): 678 $[M^+]$; 659 $[M\text{-}F^+]$; 609 $[M\text{-}CF_3^+]$; 589 $[C_{17}H_{11}F_{18}O_2^+]$; 493 $[M\text{-}C_3F_7O^+]$; 473 $[C_{15}H_{11}F_{14}O^+]$; 393 $[C_{13}H_{12}F_{11}O^+]$; 379 $[C_{12}H_{10}F_{11}O^+]$; 365 $[C_{11}H_8F_{11}O^+]$; 353 $[C_{10}H_8F_{11}O^+]$; 339 $[C_9H_6F_{11}O^+]$; 225 $[C_9H_6F_5O^+]$; 193 $[C_8H_5F_4O^+]$; 173 $[C_8H_4F_3O^+]$; 169 $[C_3F_7^+]$; 153 $[C_9H_{10}FO^+]$; 127 $[C_4H_4F_3^+]$; 103 $[C_8H_7^+]$; 85 $[C_5H_6F^+]$; 79 $[C_5H_3O^+]$; 77 $[C_5HO^+]$; 69 $[CF_3^+]$; 59 $[C_2FO^+]$ (100%).

Mass-spectrum**21** (mixture of isomers) (m/z, reference): 668 $[M^+]$; 640 $[C_{14}H_6F_{22}O_3^+]$; 620 $[C_{14}H_5F_{21}O_3^+]$; 551 $[C_{13}H_5F_{18}O_3^+]$; 483 $[M\text{-}C_3F_7O^+]$; 454 $[C_{11}H_5F_{15}O_2^+]$; 355 $[C_9H_6F_{11}O_2^+]$; 339 $[C_9H_6F_{11}O^+]$; 318 $[C_9H_4F_{10}O^+]$; 269 $[C_8H_5F_8O^+]$; 225 $[C_8H_5F_4O_3^+]$; 169 $[C_3F_7^+]$; 153 $[C_6H_5F_4^+]$; 119 $[C_2F_5^+]$; 85 $[C_5H_6F^+]$; 69 $[CF_3^+]$; 59 $[C_2FO^+]$ (100%).

Mass-spectrum **22** (mixture of isomers) (m/z, reference): 604 $[M^+]$; 419 $[M\text{-}C_3F_7O^+]$; 339 $[C_{11}H_4F_9O_2^+]$; 325 $[C_8H_4F_{11}O^+]$; 293 $[C_7H_3F_{10}O^+]$; 273 $[C_7H_2F_9O^+]$; 253 $[C_7HF_8O^+]$; 233 $[C_8H_4F_7^+]$; 169 $[C_3F_7^+]$; 159 $[C_4F_5O^+]$; 127 $[C_4H_2F_4^+]$; 109 $[C_3F_3O^+]$; 95 $[C_3H_2F_3^+]$; 69 $[CF_3^+]$; 59 $[C_2FO^+]$ (100%).

[**] The addition of electrochemically generated acyloxy-radicals to butadiene was described in[9]

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