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> ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

# Pyrolytic Decarboxylation of Some Derivatives of Perfluorinated Mono- and Dicarboxylic Acids

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**Abstract**—Pathways of pyrolysis of perfluorinated carboxylic acids are considered in relation to the structure of the acids and reaction conditions. The reaction mechanism is discussed.

As shown in [1, 2], pyrolytic decarboxylation of salts of linear perfluorinated carboxylic acids gives terminal fluoroolefins in high yields, reaching 90 mol % in the case of sodium salts:

$$C_n F_{2n+1} CF_2 CF_2 CO_2 M \xrightarrow{250-300^{\circ}C} C_n F_{2n+1} CF = CF_2$$
  
+ CO<sub>2</sub> + MF; (M = Na<sup>+</sup>, K<sup>+</sup>, ..., Ca<sup>2+</sup>...).

Similarly, terminal perfluoroalkoxyalkenes are formed in high yields by pyrolysis of sodium salts of perfluoro- $\omega$ -alkoxyalkanoic acids (from butyric to caproic) [3].

Perfluorinated alkyl vinyl ethers have also been obtained in high yields [4] by pyrolysis of solutions of perfluoro-2-alkoxypropionic acid salts in diglyme:

$$CF_3$$

$$C_nF_{2n+1}OCFCO_2M$$

$$\xrightarrow{120-160^{\circ}C, \text{ diglyme}} C_nF_{2n+1}OCF=CF_2 + CO_2 + MF,$$

In this study, we examined in detail how the structure of perfluorinated carboxylic acid derivatives with various  $\alpha$ - and  $\beta$ -substituents affects the pyrolysis pathway.

The pathway of pyrolysis of perfluoro-2-alkoxypropionyl fluorides in absolute diglyme at 120°C in the presence of anhydrous sodium carbonate depended on the ratio of perfluoroacyl fluoride and sodium carbonate:

$$\mathbf{R}^{F} = CF_{3} - (\mathbf{a}), CF_{3}CF_{2}CF_{2} - (\mathbf{b}), CF_{3}O(CF_{2})_{3} - (\mathbf{c}), C_{3}F_{7}OCFCF_{2} - (\mathbf{d}).$$

The figure shows how the yields of perfluorinated alkyl vinyl ethers, their linear dimers, and the corresponding bis(perfluoro-1-methyl-2-oxaalkyl) ketones depend on the molar ratio of sodium carbonate and acyl fluoride. The first step of the reaction involves formation of sodium perfluoro-2-alkoxypropionate along with NaF and  $CO_2$ . The pyrolytic decarboxylation proper presumably involves formation of the reactive intermediate carbanion:



which, depending on the reactant ratio, can either eliminate the fluoride anion to form perfluorinated alkyl vinyl ether  $\mathbf{II}$  or react with the initial sub-

strate I to form ketone III. Also, we identified among the pyrolysis products small amounts of the dimers IV of perfluorinated alkyl vinyl ethers, which suggests the possibility of the reaction of the carbanion with II.

The structures of the products were confirmed by bromination across the double bond. The <sup>19</sup>F NMR data for the compounds identified are listed in the table.

Gubanov *et al.* [5] showed that dry pyrolysis of sodium perfluoro-3-methoxypropionate follows the scheme

$$\begin{array}{cccc} CF_{3}OCF_{2}CF_{2}COONa \xrightarrow[-CO_{2}]{\bigcirc} CF_{3}OCF_{2}CF_{2}]^{\bigcirc} Na^{\oplus} \xrightarrow[-NaF]{} 0.26 \ CF_{3}OCF=CF_{2} \\ V & \downarrow \\ 0.24F_{2}C=CF_{2} \ + \ [CF_{3}O]^{\bigcirc} Na^{\oplus} \xrightarrow[-NaF]{} COF_{2} \xrightarrow[-NaF]{} 0.35CF_{3}OCF_{2}CF_{2}COF_{$$

Experiments on pyrolysis of V in diglyme at 120°C showed that the perfluoro-3-oxaalkyl anion generated by decarboxylation can eliminate either the fluoride ion from the  $\beta$ -position or (major pathway) the perfluoromethoxide anion, with its subsequent transformation into carbonyl difluoride. The yields of perfluorinated methyl vinyl ether and tetrafluoroethylene were 30 and 60 mol %, respectively. With Na<sup>+</sup> replaced by K<sup>+</sup>, the yield of tetrafluoroethylene increases from 60 to 95 mol %, suggesting stabilization of the trifluoromethoxide anion with the potassium ion, in agreement with the data of [5, 6].

An unexpected result was obtained in pyrolysis of 2-bromotetrafluoropropionyl fluoride **VI** in dry diglyme at 120°C in the presence of anhydrous sodium carbonate. Instead of the expected trifluorobromoethylene, we detected 1,1-dibromotetrafluoroethane **VII** in the reaction products by <sup>19</sup>F NMR (see table) and mass spectroscopy. Apparently, the bromotetrafluoroethyl anion generated by decarboxylation of the 2-bromotetrafluoropropionate anion is stabilized by abstraction of the bromine cation from the second substrate molecule, rather than by elimination of the fluoride or bromide anion:



The formation of tetrafluoroethylene as the major product of pyrolysis of perfluoro-3-oxaalkanoic acid derivatives has been observed previously [7] in pyrolysis of sodium perfluoro-4-oxaheptanedioate at 250°C, when the monodecarboxylation product, perfluoro-3vinyloxypropionyl fluoride, was obtained in a less than 2% yield. This product isomerized at room tem-



Yield  $\alpha$  of pyrolysis products of perfluoro-2-alkoxypropionyl fluorides vs. the molar ratio *N* of sodium carbonate to acyl fluoride: (*1*) perfluorinated alkyl vinyl ether **II**, (2) perfluoro ketone **III**, and (3) dimer **IV** of perfluorinated alkyl vinyl ether.

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 78 No. 10 2005

10												
$^{19}F$	NMR	spectra	of	products	formed	in	pyrolysis	of	perfluorinated	carboxylic	acid	derivatives

Compound	Position	δ <sub>CCl3</sub> D, ppm	$J_{\mathrm{F}^{*}-\mathrm{F}^{*},\mathrm{Hz}}$	nF
Perfluorinated 4-oxaamyl vinyl ether <b>IIc</b> ${}^{5}F$ $C^{1}E_{2}OC^{3}E_{2}C^{6}E_{2}C^{2}E_{2}OC=C$	1 2 3	-55.5 -83.9 -84.2	$F^{1}-F^{3}$ , 10 $F^{2}-F^{1}$ , 10; $F^{2}-F^{5}$ ; 7, 6 $F^{3}-F^{1}$ , 10; $F^{3}-F^{2}$ , 10	3 2 2
7 <sup>7</sup> <sup>7</sup> <sup>4</sup>	4c 5t 6 7	-114.2 -121.5 -128.3 -134.8	$F^{4}-F^{5}$ , 87; $F^{4}-F^{7}$ , 67; $F^{5}-F^{7}$ , 112; $F^{5}-F^{4}$ , 87; $F^{5}-F^{2}$ , 6 s $F^{7}-F^{5}$ , 111; $F^{7}-F^{4}$ , 67; $F^{7}-F^{2}$ ,	1 1 2 6
Bis(perfluoro-1-methyl-2,6-dioxaheptyl) ketone <b>IIIc</b> $(C^{1}F_{3}OC^{5}F_{2}C^{6}F_{2}COC^{7}F)_{2}C=O_{4F}$	1 2 3 4 5 6 7	-54.6 -76.5 -79.7 -81.1 -84.6 -127.8 -135.2	$\begin{array}{c} F^{1}-F^{5}, \ 10\\ F^{2}-F^{4}, \ 150\\ s\\ F^{4}-F^{2}, \ 150\\ F^{5}-F^{1}, \ 10\\ s\\ m\end{array}$	3 1 3 1 2 2 1
Perfluoro-9-methyl-2,6,10,14-tetraoxapentadec- 7-ene <b>IVc</b> $C^{1}F_{3}OC^{5}F_{2}C^{6}F_{2}COC^{7}F_{4F}C^{-9t}F$ $C^{1}F_{3}OC^{5}F_{2}C^{6}F_{2}C^{5}F_{2}OC^{-8t}F$	1 2 3 4 5 6 7 8t 9t	-55.0 -76.7 -79.9 -81.3 -84.5 -127.8 -130.5 -133.1 -165.5	m $F^2-F^4$ , 148 s $F^4-F^2$ , 150 m m m $F^8-F^9$ , 120 $F^9-F^8$ 120	6 1 3 1 6 4 1 1
1,1-Dibromotetrafluoroethane VII $C^{2}F_{3}C^{1}FBr_{2}$ Perfluoro-2-methyloxalan-3-one $F^{3}F^{4}F^{4}F^{5}F^{-1}F^$	1 2 1 2 3 4 5	-76.6 -81.7 -79.1 -81.0 -92.5 -120.2 -120.9	$F^{1}-F^{2}$ , 10, q, $F^{2}-F^{1}$ , 10, d, $F^{1}-F^{3}$ 125; $F^{1}-F^{5}$ 10 s $F^{3}-F^{1}$ 125; $F^{3}-F^{4}$ 8 $F^{4}-F^{6}$ 280 $F^{4}-F^{3}$ 8 s	1 3 1 3 1 1 1
$C^2F_3$	6	-129.8	$F^6-F^4$ 280; $F^6-F^1$ 10	1

perature under the action of CsF into a cyclic ketone, perfluoro-2-methyloxalan-3-one **VIII**:

# NaOOCCF2CF2OCF2CF2COONa



Accordingly, we detected in the experiments on the pyrolysis of perfluoro-2-methyl-3-oxahexanedioic acid difluoride **IX** (its acyl moiety is isomeric to that of sodium perfluoro-4-oxaheptanedioate) in diglyme at 120°C in the presence of an equimolar amount of sodium carbonate, along with sodium trifluoroacetate and tetrafluoroethylene, also compound **VIII** formed in ~15 mol % yield:

$$\begin{array}{c} CF_{3} & {}^{60-140^{\circ}C,Na_{2}CO_{3}}, \\ FOCCFOCF_{2}CF_{2}COF \xrightarrow{diglyme}_{-CO_{2}, -NaF} NaOOCCFOCF_{2}CF_{2}COF \\ \hline \\ \hline \\ \hline \\ \hline \\ \hline \\ -CO_{2}, -NaF \end{array} 0.8CF_{2}=CF_{2} + 0.8CF_{3}COONa + O \\ \hline \\ VIII \\ F_{2}C \\ \hline \\ CF_{2} \\ CF_{2} \\ \hline \\ CF_{2} \\ \hline \\ CF_{2} \\ \hline \\ CF_{2} \\ CF_{2} \\ \hline \\ CF_{2} \\ CF_{2} \\ CF_{2} \\ \hline \\ CF_{2} \\ C$$

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 78 No. 10 2005

The product was identified by the characteristic <sup>19</sup>F NMR signals of magnetically nonequivalent geminal fluorine atoms with coupling constants of 125 Hz for the CH<sub>2</sub>O group and 280 Hz for the CF<sub>2</sub>CO group. The <sup>19</sup>F NMR spectrum with the signals of the -OCF< and  $-CF_3$  groups is given in the table; it is quite consistent with the data from [7].

### **EXPERIMENTAL**

The pyrolysis products were analyzed chromatographically with an LKhM-8MD chromatograph [model 5, thermal conductivity detector, programmed heating from 30 to 200°C at a rate of 6 deg min<sup>-1</sup>,  $3000 \times 3$ -mm columns, solid support Silokhrom-2 (0.16-0.2 mm, packing density  $0.30 \pm 0.01$  g cm<sup>-3</sup>), stationary phase 5F4E (15 wt %), carrier gas helium (40 ml min<sup>-1</sup>)].

The <sup>19</sup>F NMR spectra were recorded on a Bruker Spectrospin HX-90 spectrometer at a working frequency of 84.67 MHz; hexafluorobenzene or hexafluoro-*p*-xylene was used as internal reference. The <sup>19</sup>F chemical shifts were recalculated relative to CCl<sub>3</sub>F.

The <sup>1</sup>H NMR spectra were recorded on the same device at 90 MHz, with hexamethyldisiloxane as external reference.

The mass spectra were recorded on a Chromass Varian CH-7M device.

Perfluoro-2-(4-oxaamyloxy)propionyl fluoride **Ic** was prepared by electrochemical fluorination of methyl 3-methoxypropionate [8], followed by condensation of the resulting perfluoro-3-methoxypropionyl fluoride with hexafluoropropene oxide on KF in diglyme.

The synthesis of perfluoro-2-methyl-3-oxahexanedioic acid difluoride **IX** has been described previously [9].

Perfluoro-2-methoxypropionyl fluoride **Ia** was prepared by condensation of  $COF_2$  with hexafluoropropene oxide [10], and perfluoro-2-propoxypropionyl fluoride **Ib** and perfluoro-2-(2-methyl-3-oxahexyloxy)propionyl fluoride **Id**, respectively, by dimerization and trimerization of hexafluoropropene oxide under similar conditions [11].

Perfluoro-2-bromopropionyl fluoride **VI** was prepared from 67 g (0.4 mol) of hexafluoropropene oxide and 43 g (0.42 mol) of dry NaBr in 75 ml of absolute diglyme at  $-30^{\circ}$ C with stirring in a stainless steel autoclave. After warming up to room temperature, the lower organofluorine layer was separated, and 80 g of a product (yield 88 mol %) with bp ~20°C was obtained. It was identified as CF<sub>3</sub>CFBrCOOCH<sub>3</sub> by the <sup>19</sup>F NMR [ $\delta_{\rm F}$ , ppm: 77.1 d (3F, CF<sub>3</sub>, *J* 10 Hz), 134.1 q (1F, CFBrCOOCH<sub>3</sub>, *J* 10 Hz] and mass spectra [*m*/*z* (*I*<sub>rel</sub>, %): 209, 207 (5.4), *M*<sup>+</sup> – OCH<sub>3</sub>; 181, 179 (30.5), *M*<sup>+</sup> – 59 (CF<sub>3</sub>CFBr<sup>+</sup>); 162, 160 (3.7), C<sub>2</sub>F<sub>3</sub>Br<sup>+</sup>; 131, 129 (13.9), CF<sub>2</sub>Br<sup>+</sup>; 128 (4.8), C<sub>2</sub>F<sub>4</sub>CO<sup>+</sup>; 109 (6.6), C<sub>2</sub>F<sub>3</sub>CO<sup>+</sup>; 100 (7.2), C<sub>2</sub>F<sub>4</sub><sup>+</sup>; 81 (3.3), C<sub>2</sub>F<sub>3</sub><sup>+</sup>; 69 (119), CF<sub>3</sub>; 59 (100) COOCH<sub>3</sub><sup>+</sup>.

Pyrolysis of perfluoro-2-(4-oxaamyloxy)propionyl fluoride Ic. (a) A 250-ml four-necked round-bottomed glass flask equipped with a stirrer, thermometer, and water-cooled reflux condenser was charged with 31 g (0.3 mol) of dry  $Na_2CO_3$  and 30 ml of diglyme dehydrated over CaH<sub>2</sub>. The contents were heated on a water bath to 70°C, after which 50 g (0.15 mol) of **Ic** was added dropwise until the CO<sub>2</sub> evolution ceased. Then the reflux condenser was replaced with a descending condenser, the mixture [a suspension of  $Na_2CO_3$  in a solution of sodium perfluoro-2-(4-oxaamyloxy)-propionate in diglyme] was heated to 120°C, and 40 g of the product was collected in the receiver. According to GLC, the product consisted of 97.5% per-fluorinated 4-oxaamyl vinyl ether IIc (92 mol %) and 2.5% perfluoro-4-oxaamyl 1,3,3,3-tetrafluoroethyl ether. The following products were isolated by fractional distillation and characterized: CF<sub>3</sub>OCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>OCF=CF<sub>2</sub>, bp 64°C,  $d_4^{20}$  1.636; mass spectrum, m/z ( $I_{rel}$ , %): 332 (0.37), C<sub>4</sub>F<sub>12</sub>O<sub>2</sub><sup>+</sup> =  $M^+$ ; 169 (1.83),  $C_3F_7^+$ ; 147 (1.92),  $C_3F_5O^+$ ; 135 (1.39),  $C_2F_5O^+$ ; 131 (0.9),  $C_3F_5^+$ ; 119 (5.24),  $C_2F_5^+$ ; 100 (2.2),  $C_{2}F_{4}^{+}$ ; 97 (2.37),  $C_{2}F_{3}O^{+}$ ; 81 (3.35),  $C_{2}F_{3}^{+}$ ; 78 (4.29),  $C_2F_2O^+$ ; 69 (100),  $CF_3^+$ ;  $CF_3OCF_2CF_2CF_2OCFHCF_3$ , bp  $71-72^{\circ}$ C,  $d_4^{20}$  1.622.

(b) Similarly, a mixture of 8 g (0.075 mol) of dry  $Na_2CO_3$  and 30 ml of dry diglyme was heated to  $60^{\circ}C$ , and 50 g (0.15 mol) of **Ic** was added, after which the mixture was heated at 140-150°C for 2 h until the gas evolution ceased. Then the mixture was cooled to 80°C, the reflux condenser was replaced with the descending condenser, and the reaction products were distilled off in a vacuum (2-3 mm Hg). After the separation of the lower organofluorine layer, we obtained 43 g of the product containing, according to GLC, 93% bis(perfluoro-1-methyl-2,6-dioxaheptyl) ketone (90 mol %) and 7% of an impurity. We isolated by fractional distillation and characterized ketone **IIIc**, bp 74–75°C (18 mm Hg),  $d_{4}^{20}$  1.757,  $n_D^{20}$  1.2836. The impurity was identified by <sup>19</sup>F NMR as linear dimer IVc of perfluorinated 4-oxaamyl vinyl ether, CF<sub>3</sub>OCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>OCFCF=CFOCF<sub>2</sub>CF<sub>2</sub>CF<sub>2</sub>OCF<sub>3</sub> È₽₃

RUSSIAN JOURNAL OF APPLIED CHEMISTRY Vol. 78 No. 10 2005

bp 70–71°C (18 mm Hg),  $d_4^{20}$  1.736,  $n_D^{20}$  1.2805. Its structure was also confirmed by UV-induced bromination [characteristics of the dibromide: bp 73°C (2 mm Hg),  $d_4^{20}$  1.9811,  $n_D^{20}$  1.3443. The mass spectrum of the product was also consistent with the structure of the linear dimer, m/z ( $I_{rel}$ , %): 664 (6.4),  $C_{12}F_{24}O_3 = M^+$ ; 595 (0.63),  $M^+ - CF_3$ ; 579 (3.8),  $M^+ - CF_3O$ ; 498 (0.6),  $M^+ - C_3F_6O^+$ ; 479 (1.1),  $M^+ - C_3F_7O$ ; 413 (7.7), 498 – CF<sub>3</sub>O; 325 (2.4),  $C_7F_{11}O_2^+$ ; 275 (2.3),  $C_6F_9O_2^+$ ; 247 (2.7),  $C_5F_9O^+$ ; 219 (1.1),  $C_4F_9^+$ ; 178 (25.2),  $C_4F_6O^+$ ; 169 (98.9),  $C_3F_7^+$ ; 159 (33.0),  $C_4F_5O^+$ ; 150 (5.9),  $C_3F_6^+$ ; 147 (49.5),  $C_3F_5O^+$ ; 135 (30.3),  $C_2F_5O^+$ ; 119 (74.8),  $C_2F_5^+$ ; 100 (37.3),  $C_2F_4^+$ ; 69 (100),  $CF_3^+$ .

Similarly, we obtained by pyrolysis of perfluoro-2methoxypropionyl fluoride **Ia**, perfluoro-2-propoxypropionyl fluoride **Ib**, and perfluoro-2-(2-methyl-3oxahexyloxy)propionyl fluoride **Id** the corresponding symmetrical ketones **IIIa**, **IIIb**, and **IIId** with admixture of linear dimers **IV**.

Pyrolysis of perfluoro-3-methoxypropionyl fluoride. Similarly to the above-described procedure, a flask with the reflux condenser cooled by a dry ice/alcohol mixture was charged with 22.3 g (0.21 mol) of  $Na_2CO_3$  and 40 ml of dry diglyme; 46 g (0.2 mol) of CF<sub>3</sub>OCF<sub>2</sub>CF<sub>2</sub>COF was fed through a siphon until the refluxing and CO<sub>2</sub> evolution ceased. The resulting suspension of NaF in a solution of sodium perfluoro-3-methoxypropionate V in diglyme was heated to 120°C, with fractional distillation of the pyrolysis products. Carbonyl fluoride was taken up by a sodium carbonate solution, perfluorinated methyl vinyl ether was condensed in a coil trap at -50°C, and tetrafluoroethylene was taken up by liquid bromine in a trap, with conversion into dibromotetrafluoroethane. We obtained 10 g of CF<sub>3</sub>OCF=CF<sub>2</sub> (30 mol %) and 31 g of CF<sub>2</sub>BrCF<sub>2</sub>Br (60 mol %).

**Pyrolysis of perfluoro-2-bromopropionyl fluoride VI.** Similarly to the pyrolysis of perfluoro-3-methoxypropionyl fluoride, 45 g (0.2 mol) of **VI** was fed to a mixture of 22.3 g (0.21 mol) of Na<sub>2</sub>CO<sub>3</sub> and 40 ml of dry diglyme, until the refluxing and CO<sub>2</sub> evolution ceased. Then the reflux condenser was replaced with a water-cooled descending condenser, the flask was heated to 120°C, and 23 g (45 mol %) of perfluoro-1,1-dibromoethane **VII** was distilled off; bp ~5°C,  $d_4^{20}$  2.188,  $n_D^{20}$  1.364; mass spectrum, m/z ( $I_{rel}$ , %): 262, 260, 258 (47.8),  $C_2F_4^{79-81}Br_2^+ = M^+$ ; 193, 191, 189 (32.5),  $M^+ - CF_3$ ; 181, 179 (100),  $M^+ - Br$ ; 162, 160, 158 (17.5),  $M^+ - C_2F_4 = Br_2^+$ ; 131, 129,  $M^+ -$   $CF_2Br$ ; 112, 110,  $M^+ - CF_3Br = CFBr^+$ . In low-boiling gases, after the uptake of  $CO_2$  with an alkali, we identified tetrafluoroethylene and 1-hydro-1bromotetrafluoroethane, which was also detected as impurity in the main product by <sup>19</sup>F NMR spectroscopy.

Pyrolysis of perfluoro-2-methyl-3-oxahexanedioic acid difluoride IX. A similar flask equipped with a water-cooled refluxed condenser was charged with 10.6 g (0.1 mol) of dry Na<sub>2</sub>CO<sub>3</sub> and 50 ml of dehydrated diglyme. The mixture was heated on an oil bath to 60°C, and 31 g (0.1 mol) of IX was added dropwise from a dropping funnel over a period of 2 h. The mixture was stirred until the  $CO_2$  evolution ceased. Then the mixture was gradually heated with stirring to 140°C, with collected the pyrolysis products in a trap cooled to -78°C. Low-boiling gases were passed through a trap with liquid bromine and then through an alkaline absorber. From the trap, we isolated 4 g (yield ~15%) of a product identified as perfluoro-2-methyloxolan-3-one VIII by comparison of the <sup>19</sup>F NMR and mass spectra with those reported in [6]; bp ~15°C. In the trap with bromine, 1,2-dibromotetrafluoroethane was obtained as a separate phase. The nonvolatile residue contained sodium trifluoroacetate.

#### CONCLUSIONS

(1) Depending on the pyrolysis conditions and structure of perfluorocarboxylic acid salts, the perfluoroalkyl carbanion generated by decarboxylation is stabilized not only by elimination of the fluoride anion to give the alkene, but also with that to give the corresponding ketones through both inter- and intramolecular attack at the acyl fluoride group.

(2) In the pyrolysis of potassium perfluoro-3alkoxypropionates, the perfluorooxaalkyl anion is virtually quantitatively stabilized by elimination of the perfluoroalkoxide anion with the formation of tetrafluoroethylene.

(3) An attack of the bromotetrafluoroethyl anion at the bromine atom of another substrate molecule yields perfluoro-1,1-dibromoethane and tetrafluoroethylene.

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