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REACTIONS OF MESOMERIC FLUOROCARBANIONS WITH ACID ANHYDRIDES.
TRANSFORMATION OF TRIFLUOROMETHYL GROUPS INTO FLUOROCARBONYL
AND PERFLUOROACYL GROUPS[†]

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SUMMARY

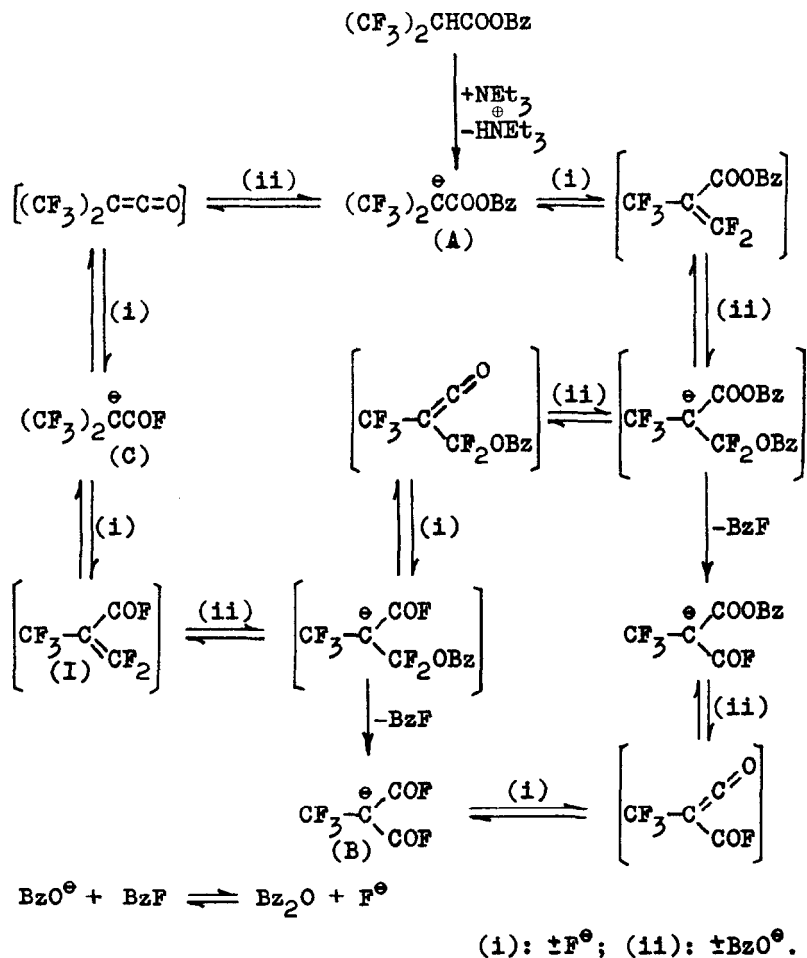
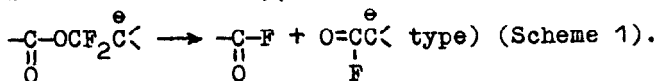
It was found that the reaction of mesomeric fluorocarb-anions of the $\text{CF}_3\overset{\ominus}{\text{C}}\text{XCOY}$ type with benzoic anhydride leads to the loss of benzoyl fluoride and the formation of mesomeric carbanions of the $\text{FCO}\overset{\ominus}{\text{C}}\text{XCOY}$ type. In a similar reaction with perfluorocarboxylic acid anhydrides, besides a $\text{CF}_3 \rightarrow \text{COF}$ transformation, further change of COF into COR_F is observed, leading to the formation of salts containing mesomeric anions of the $\text{R}_F\overset{\ominus}{\text{C}}\text{O}\overset{\ominus}{\text{C}}\text{XCOY}$ type, which, upon acidification, give 1,1-bis(perfluoroacyl)-2,2,2-trifluoroethanes $\text{CF}_3\text{CH}(\text{COR}_F)_2$, tris(perfluoroacyl)methanes $(\text{R}_F\text{CO})_3\text{CH}$ and bis(trifluoroacetyl)-acetic ester $(\text{CF}_3\text{CO})_2\text{CHCOOMe}$. It has been shown that per-fluoroalkyl groups in β -diketones and β, β' -triketones may hinder enolization despite their electron-attracting effect.

INTRODUCTION

As shown earlier [3-5], the unstable anion of the mixed anhydride of α -hydrohexafluoroisobutyric and benzoic acids (A) is easily split into benzoyl fluoride and an anion of trifluoromethylmalonyl difluoride (B). ^{19}F NMR revealed that

[†]Preliminary communications: Ref. [1,2].

the reaction occurs by way of series of parallel transformations which are either reversible (splitting off and readdition of F^\ominus or BzO^\ominus anions), or irreversible (decomposition of the



Scheme 1

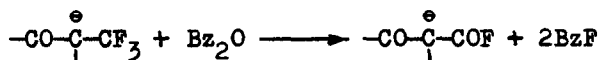
These transformations are characterized by the intermediate formation of considerable amounts of mesomeric perfluoroisobutenolate anion (C) (the anion of α -hydrohexafluoroisobutyryl fluoride), which acts as a 'depot form' for the F^\ominus

anion, and simultaneously as a source of perfluoromethyl acryloyl fluoride (I). The proposed reaction scheme also includes reversible formation of benzoic anhydride from benzoate anion and benzoyl fluoride.

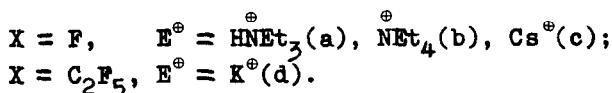
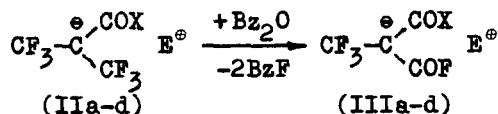
In this light we could expect the reactions leading to the transformation of the CF_3 group into the COF group to occur when carboxylic acid anhydrides react with salts containing perfluoroisobutenolate anion (C) or related mesomeric fluorocarbanions.

REACTIONS WITH BENZOIC ANHYDRIDE

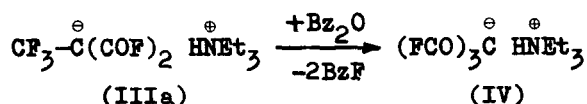
Indeed, it was found that in the process of reaction of benzoic anhydride with mesomeric fluorocarbanions of carbonyl compounds that contain the trifluoromethyl group in the α -position to the carbanion center, benzoyl fluoride splits out, and corresponding acyl fluoride carbanions are formed:



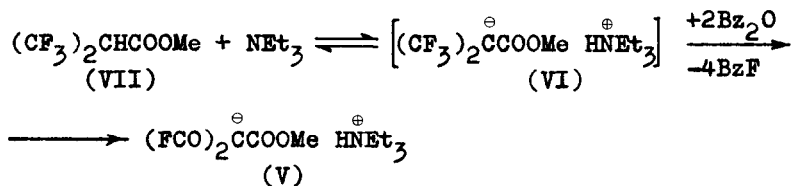
Thus, stable salts of fluorine-containing monocarbonyl-substituted CH-acids (IIa-d) [6-9] are easily transformed into salts (IIIa-d), containing dicarbonyl-substituted anions:



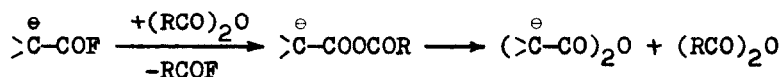
In the case of triethylammonium salt (IIIa), further transformation of the remaining trifluoromethyl group may be caused by adding another mole of benzoic anhydride, yielding a salt of methanetricarboxyl trifluoride (IV):



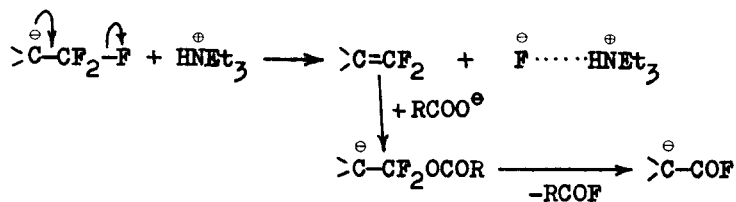
A similar reaction resulting in a salt (V) that contains an anion of a tricarbonyl compound, is observed also for an unstable salt (VI), which is reversibly generated from α -hydrohexafluoroisobutyric acid ester (VII) and triethylamine (cf. [6]):



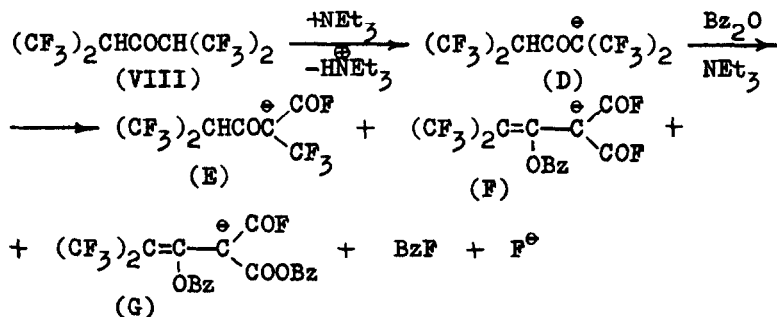
It should be mentioned that choice of the counter-ion has a considerable effect on the reactivity of salts of dicarbonyl-substituted mesomeric fluorocarbanions. Unlike the case of triethylammonium salt (IIIa), the remaining trifluoromethyl group in salts (IIIb-d) containing $\text{Et}_4\text{N}^\oplus$, Cs^\oplus and K^\oplus cations is not capable of a smooth transformation into a fluoro-carbonyl group by means of benzoic anhydride. The reaction ordinarily does not occur under mild conditions, and more drastic conditions lead to side reactions that interfere with the $\text{CF}_3 \rightarrow \text{COF}$ transformation. In the process, a mixture of the initial salt and, evidently, a salt of a mixed or symmetric anhydride is formed; the latter may be formed in the reaction of the COF group with acyloxy-anion and further disproportionation:



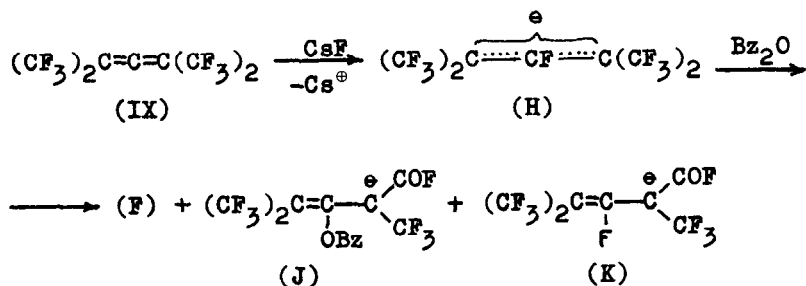
The proton in the triethylammonium cation evidently facilitates the loss of the F^\ominus anion from the mesomeric carbanion, which leads to the reaction $\text{CF}_3 \rightarrow \text{COF}$:



Under the action of triethylamine and benzoic anhydride on bis(α -hydrohexafluoroisopropyl) ketone (VIII), O-benzoylation is observed along with the $\text{CF}_3 \rightarrow \text{COF}$ transformation; as a result, anion (D) [10] yields benzoyl fluoride, fluoride anion, anions (E), (F), and, probably, (G):



Anion (H) of the salt obtained from tetrakis(trifluoromethyl)allene (IX) and cesium fluoride [8], also yields β -benzoyloxy-substituted anions (F) and (J), along with the perfluorinated anion (K):

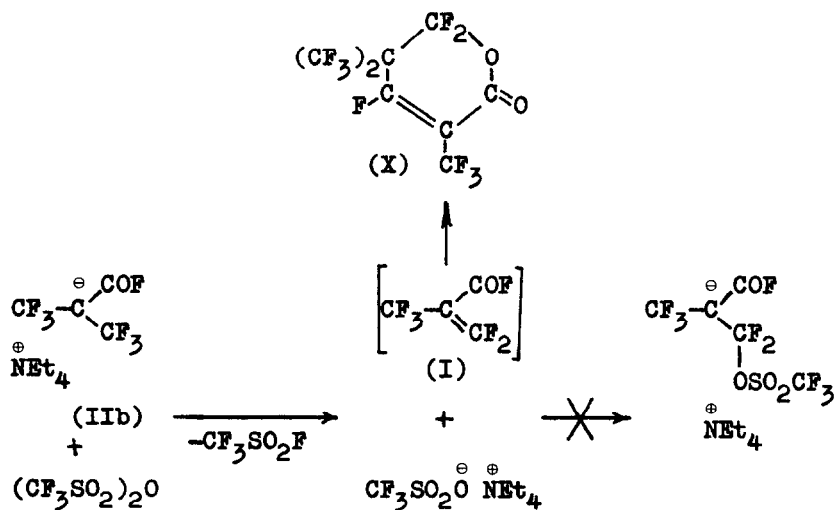


The structure of salts that contain anions of CH-acids is confirmed by NMR spectra. Trifluoromethylmalonyl difluoride $\text{CF}_3\text{CH}(\text{COF})_2$ [3] can be obtained from (IIIa) treated with dry HCl-gas. Attempts to obtain methanetricarboxyl trifluoride $(\text{FCO})_3\text{CH}$ as such or in the form of the α -bromo derivative $(\text{FCO})_3\text{CBr}$ from the salt (IV) failed; however, (IV) was successfully transformed into a triketone salt in a reaction with trifluoroacetic anhydride, and the salt (V) was similarly transformed into a salt of diketo ester (below).

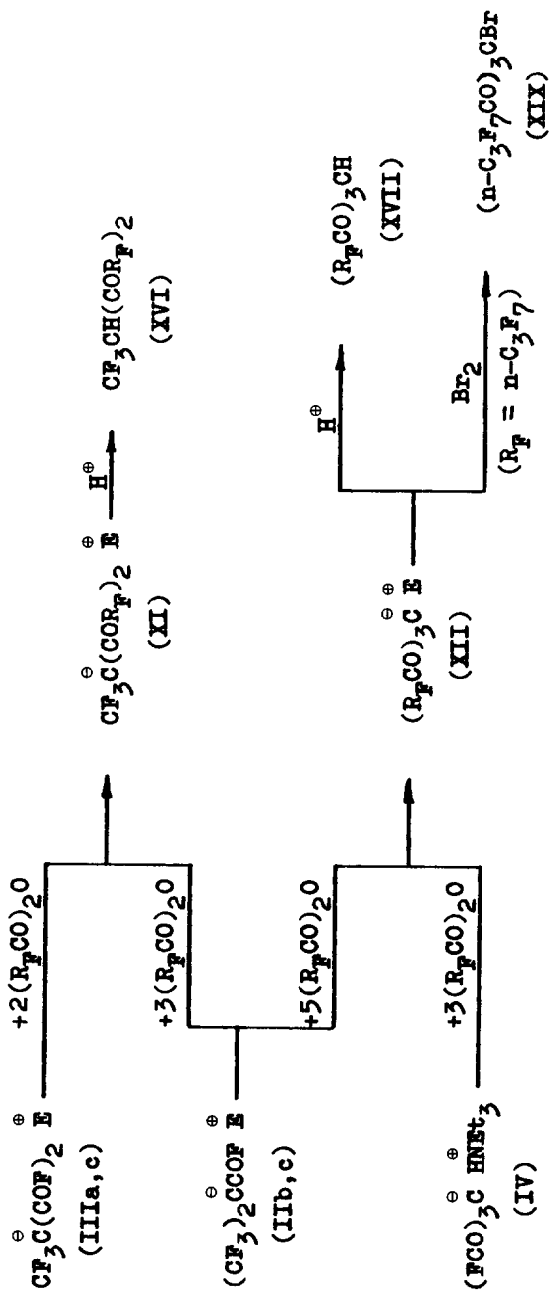
REACTION WITH TRIFLUOROMETHANESULPHONIC ANHYDRIDE

The results described in the previous section show that benzoic anhydride reacts with mesomeric fluorocarbanions in a way that is radically different from that of other typical acylation agents (acyl halides). It is known that when treated with acyl chlorides, mesomeric fluorocarbanions lose the F^{\ominus} anion and turn into unsaturated compounds which are usually isolated as dimers [6].

It turned out that a similar reaction occurs with trifluoromethanesulphonic anhydride. The reaction of this anhydride with tetraethylammonium perfluoroisobutenolate (IIb) yields mainly 'bis(trifluoromethyl)ketene δ -lactonedimer' (X) (cf. [6]), trifluoromethanesulphonyl-fluoride and tetraethylammonium trifluoromethanesulphonate:



It is evident that in contrast to the more nucleophilic benzoate anion, the addition of weakly nucleophilic $\text{CF}_3\text{SO}_2\text{O}^{\ominus}$ anion to the intermediate perfluorometacryloyl fluoride (I) cannot compete with dimerization of the unsaturated compound.



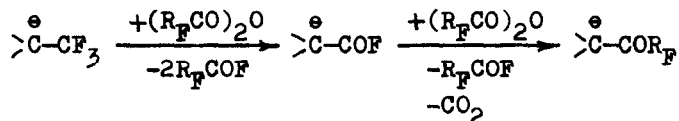
(XI), (XII), (XVI), (XVII): $\text{R}_F = \text{CF}_3$ (a), $\text{n-C}_3\text{F}_7$ (b)

$\text{E}^{\oplus} = \text{HNt}_3^{\oplus}, \text{Nt}_4^{\oplus}, \text{Cs}^{\oplus}$

Scheme 2

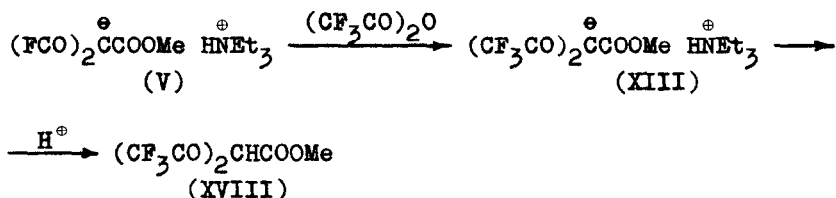
REACTIONS WITH PERFLUOROCARBOXYLIC ACID ANHYDRIDES

An analysis of reactions of mesomeric fluorocarbanions with perfluorocarboxylic acid anhydrides brought unexpected results. It turned out that the reaction as a rule does not stop at the stage of the transformation of the CF_3 group into the COF group: the latter, by the action of perfluorocarboxylic acid anhydride, undergo further change into the COR_F group with perfluoroacyl fluoride and CO_2 being evolved:



In this way, diketone and triketone salts (XI), (XII) have been obtained from salts of α -hydrohexafluoroisobutyryl fluoride (IIB,c), trifluoromethylmalonyl difluoride (IIIa,c) and methanetricarboxyl trifluoride (IV) (Scheme 2).

Similarly, a salt of bis(trifluoroacetyl)acetic ester (XIII) is formed from (V):

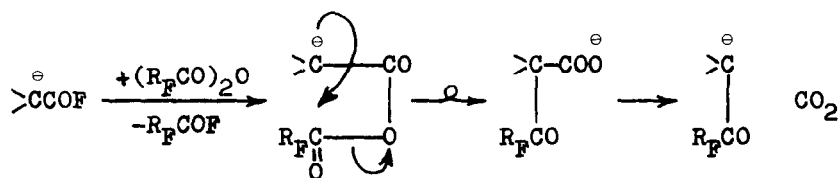


By treating salts of di- and tricarbonyl compounds with an $\text{H}_2\text{SO}_4/\text{P}_2\text{O}_5$ mixture, corresponding CH-acids have been obtained: β -diketones (XVI), β, β' -triketones (XVII), and β, β' -diketoester (XVIII). Bromination of the triketone salt (XIb) produced bromotriketone (XIX).

The mechanism of transformation of the fluorocarbonyl group into the perfluoroacyl group is not clear. Formation of an intermediate mixed anhydride anion can be hypothesized, followed by intramolecular C-acylation[†] and decarboxylation

[†]C-Acylation is usually not characteristic of anions such as the perfluoroisobutenolate ion (C) [6].

leading to the ketone anion[†]:

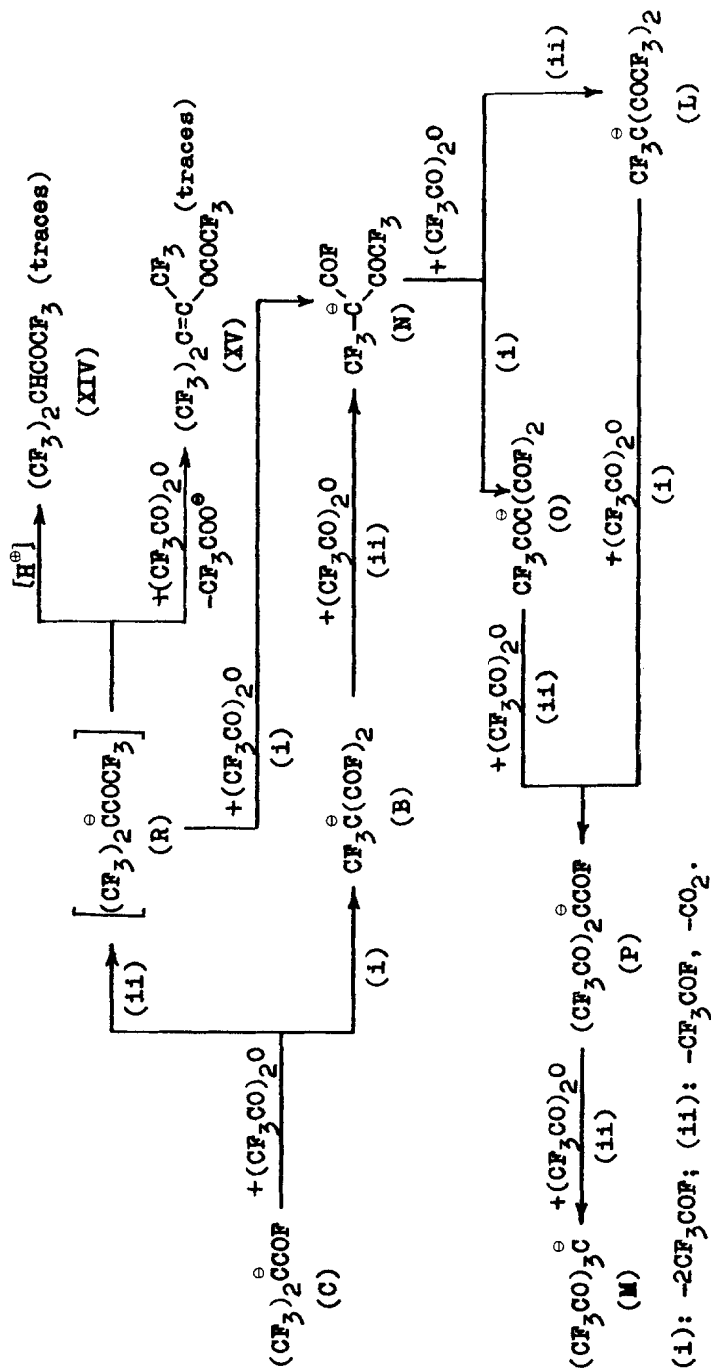


In the case of anions of benzoic acid mixed anhydrides such a reaction does not take place, possibly due to insufficient electrophilicity of the carbon atom of the carbonyl group adjacent to the phenyl group (steric factors may also be important).

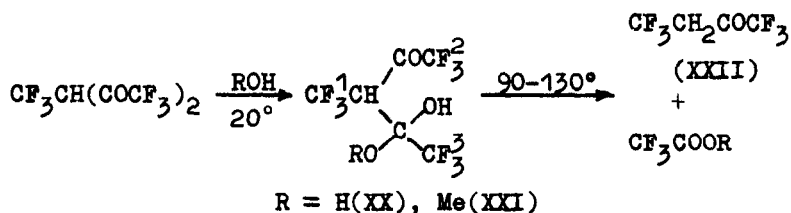
Taking different ratios of reagents (trifluoroacetic anhydride and tetraethylammonium perfluoroisobutenolate) allowed us to detect among the anion (C) transformation products not only diketone and triketone anions (L), (M), but also intermediate anions (N), (O), and (P) that contain both COF and COCF₃ groups together (Scheme 3). The monoketone anion (R), however, has not been detected even with insufficient amounts of trifluoroacetic anhydride (although gaseous reaction products did contain traces of ketone (XIV) and the O-acyl derivative (XV), along with CF₃COF). Presumably, for anions of monocarbonyl compounds, the rate of the CF₃ → COF transformation greatly exceeds the rate of intramolecular C-acylation, whereas these rates are comparable for dicarbonyl derivatives.

Diketones (XVI), and particularly triketones (XVII) are easily cleaved by water and methanole. Diketone (XVIa) first yields products of addition across the carbonyl group - monohydrate (XX) or monosemiketal (XXI), which are wholly cleaved upon heating into trifluoromethyl 2,2,2-trifluoroethyl ketone (XXII) and trifluoroacetic acid or its methyl ester:

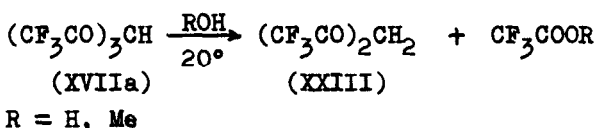
[†]It is possible that a similar mechanism governs the reaction of pentafluoroazapropene CF₃N=CF₂ with acetic acid in the presence of triethylamine, yielding N-acetyltrifluoromethylamine CF₃NHCOCH₃ [11].



Scheme 3



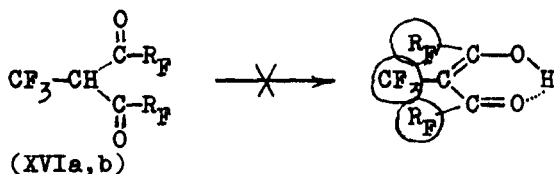
Triketone (XVIIa) yields hexafluoroacetylacetone (XXIII) and CF_3COOR even without heating:



ENOLIZATION OF FLUORO-CONTAINING β -DICARBONYL AND β, β' -TRICARBONYL COMPOUNDS

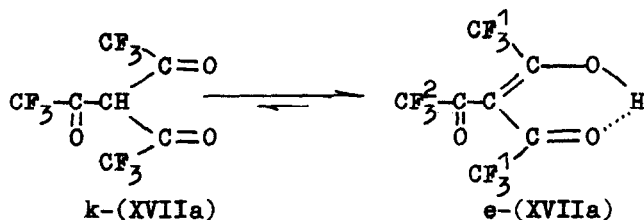
Keto-enol tautomerism of compounds (XVI)-(XVIII) is especially interesting. It is known that the introduction of electron-attracting groups promotes enolization of β -dicarbonyl compounds. Thus, hexafluoroacetylacetone (XXIII) is practically totally enolized [12,13]. Nevertheless, it turned out that diketones (XVIa,b) do not contain enol form neither in an ether solution, nor in the absence of solvent at 20-90°. Thus, the introduction of the trifluoromethyl group into the α -position, despite its electron-attracting effect, suppresses enolization of polyfluorinated β -dicarbonyl compounds (cf. [14]). It seems that the bulkiness of CF_3 groups is sufficient to hinder the formation of the planar chelate ring of the cis-enol form † (cf. [15]):

† Attempts to obtain corresponding copper, zinc, lead and nickel chelates failed.



This is confirmed by Stewart-Briegleb models.

Trifluoroacetyl and methoxycarbonyl groups have lower steric requirements, which is why triketone (XVIIa) and diketoester (XVIII) are largely enolized, although to a lesser degree, than hexafluoroacetylacetone:

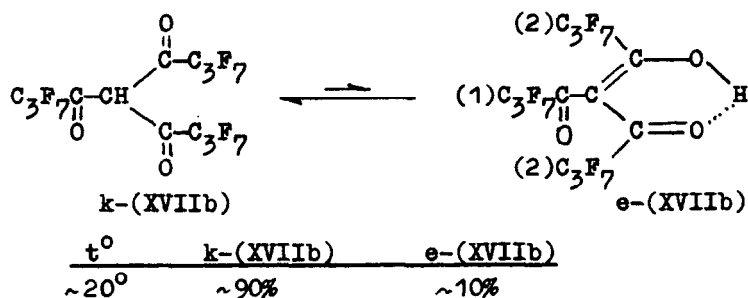
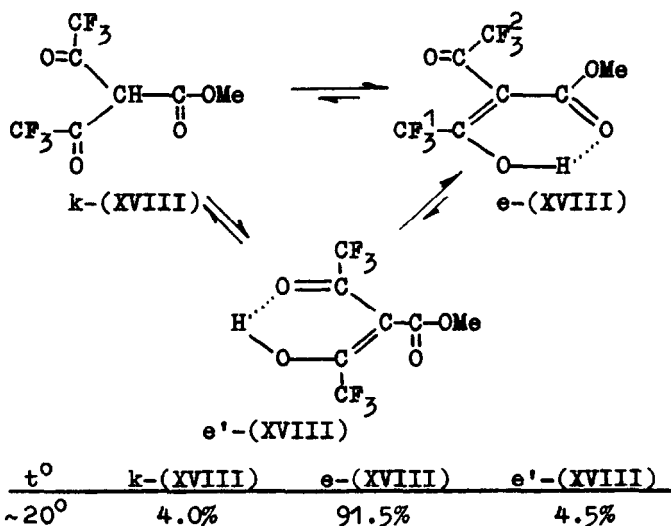


t°	k-(XVIIa)	e-(XVIIa)
$\sim 20^\circ$	$\sim 12\%$	$\sim 88\%$
110°	34.5%	65.5%
150°	45.5%	54.5%

$$\Delta H = -3.7 \text{ kcal mole}^{-1}; \Delta S = -8.4 \text{ cal mole}^{-1} \text{ deg}^{-1}$$

Diketoester (XVIII) mainly exists in the enol form e-(XVIII), wherein the hydrogen bond is fixed to the carbonyl oxygen atom of the methoxycarbonyl group; however, small amounts of the second enol form e'-(XVIII) and ketone form k-(XVIII) are present in the mixture.

Substituting trifluoroacetyl groups in triketone (XVIIa) by bulkier perfluorobutyryl groups leads to a considerable suppression of enolization; that is why triketone (XVIIb) mainly exists in the ketone form k-(XVIIb) (cf. [16]):



EXPERIMENTAL

NMR spectra were obtained with Perkin-Elmer R-32 (^1H , 90 MHz; ^{19}F , 84.6 MHz) and Bruker WP-200 SY (^{19}F , 188.3 MHz) spectrometers; chemical shifts are reported in p.p.m. from external standards $(\text{CH}_3)_4\text{Si}$ (^1H , δ -scale) and CF_3COOH (^{19}F , upfield direction taken as positive). Designations: s - singlet, d - doublet, t - triplet, q - quartet, sp - septet, m - multiplet, br. - broadened. IR spectra were obtained with an UR-20 spectrophotometer in thin layer (ν recorded in cm^{-1}), mass spectra on Varian MAT CH-8 mass spectrometer (ionizing energy of 70 eV); m/z , relative abundance in %, supposed assignment, as well as m^* and supposed transition

are presented. For preparative GLC (PGLC), a QF-1 column on Chromosorb W was used (length 4 m, diameter 25 mm). Starting materials and solvents were purified and dried according to standard procedure. All experiments were performed in a dry argon atmosphere. Molar ratio of main components for obtained mixtures is presented.

Reaction of salts of mesomeric fluorocarbanions with benzoic anhydride

Starting salt and Bz_2O were stirred at $0-110^\circ$ (for triethylammonium salts, triethylamine was sometimes added dropwise to the mixture of Bz_2O and corresponding CH-acid while cooling and stirring). Composition of obtained mixtures was studied with NMR ^{19}F spectrometry.

1 Triethylammonium salt of trifluoromethylmalonyl difluoride (IIIa) (-26.4 t(CF_3), -94.2 q(COF), $J=22.6$ Hz, cf. [3]) and BzF (1.0:2.4) were obtained from $(CF_3)_2CHCOF$ (0.70 g, 3.5 mmole), Bz_2O (0.80 g, 3.5 mmole) and Et_3N (0.41 g, 4.1 mmole) after 1 hour (0°) and 1.5 hrs. (20°). After adding Bz_2O (0.80 g, 3.5 mmole), in six hrs. ($60-65^\circ$) triethylammonium salt of methanetricarboxyl trifluoride (IV) (-104.4 s) and BzF were obtained (1.0:4.2).

2 BzF and tetraethylammonium salt of trifluoromethylmalonyl difluoride (IIIb) (-25.8 t(CF_3), -97.2 q(COF), $J=17.0$ Hz) were obtained from tetraethylammonium perfluoroisobutenolate (IIB) [7] (23.40 g, 71.5 mmole) and Bz_2O (15.64 g, 69.1 mmole) after 14 hrs. (20°). Bz_2O (16.41 g, 72.5 mmole) was added; mixture composition remained unchanged after heating for 4 hrs. at $50-55^\circ$; it was then heated for 3 hrs. at $100-110^\circ$, and BzF (31.86 g, 256.2 mmole) (NMR, GLC) was distilled off in vacuo ($60-10$ mmHg). The residue contained salt (IIIb), probably, salt $[(FCO)_2\overset{\ominus}{C}CO]_2O \overset{\oplus}{N}Et_4$ (-105.6 s in CH_3CN), and a negligible amount of trifluoride salt $(FCO)_3\overset{\ominus}{C} \overset{\oplus}{N}Et_4$ (-102.8 s in CH_3CN).

3 A solution of cesium salt of trifluoromethylmalonyl difluoride (IIIc) (-26.9 t(CF_3), -96.2 q(COF), $J=20.2$ Hz) and BzF (1.0:2.1) was obtained from cesium perfluoroisobutenolate (IIc) [8] (6.53 g, 19.8 mmole), CsF (0.32 g, 2.1 mmole) and Bz_2O (4.95 g, 21.9 mmole) in diglyme (9.7 g) after an hour (20°). Bz_2O (5.09 g, 22.5 mmole) was added; after heating for 0.5 hrs. at $100-110^\circ$, a small amount of precipitate appeared; the solution contained difluoride salt (IIIc), trifluoride salt $(\text{FCO})_3\overset{\ominus}{\text{C}} \text{Cs}^\oplus$ (-104.1 s), probably $[(\text{FCO})_2\overset{\ominus}{\text{C}}\text{CO}_2]_0 2\text{Cs}^\oplus$ (-105.6 s) and BzF (1.0:0.04:0.2:4.0).

4 Potassium salt of α -hydroperfluoro- α -methyl- β -oxopentanoyl fluoride (IIIId) (-24.7 d.t($\text{CF}_3\overset{\ominus}{\text{C}}$), -99.7 br.t.q(COF), $+39.2$ d.q(CF_2), $+2.6$ br.s(CF_3CF_2), $J(\text{CF}_3\overset{\ominus}{\text{C}}-\text{COF})=19.0$ Hz, $J(\text{CF}_3\overset{\ominus}{\text{C}}-\text{CF}_2)=9.1$ Hz, $J(\text{CF}_2-\text{COF})=17.3$ Hz) and BzF (1.0:2.8) were obtained from crude potassium perfluoro-2-methylpenten-2-ol-3-ate (IId) (3.21 g, 9.54 mmole) mixed with $\text{C}_2\text{H}_5\text{I}$ (1.5 g) [9] and Bz_2O (2.16 g, 9.55 mmole) in CH_3CN (7.8 g) after nine days (20°). Further addition of Bz_2O (20°) increases BzF content in the mixture, lowers (IIIId) content, while signals in the ^{19}F NMR (-25.6 t($\text{CF}_3\overset{\ominus}{\text{C}}$), $+38.7$ q(CF_2), $+2.5$ s(CF_3CF_2), $J(\text{CF}_3\overset{\ominus}{\text{C}}-\text{CF}_2)=12.6$ Hz) appear which probably correspond to the $\text{CF}_3\overset{\ominus}{\text{C}}(\text{COOBz})\text{COCF}_2\text{CF}_3 \text{K}^\oplus$.

5 Triethylammonium salt of methyl α, α -di(fluoro-carbonyl)-acetate (V) (-102.6 s; ^1H NMR; 3.4 s(OCH_3)) and BzF (1.0:4.1) were obtained from $(\text{CF}_3)_2\text{CHCOOMe}$ (10.31 g, 49.08 mmole), Bz_2O (22.10 g, 97.69 mmole) and Et_3N (4.99 g, 49.3 mmole) after 18 hrs. (20°).

6 A mixture of triethylammonium salts of anion (F), probably (G) (NMR, Table 1), anion (E) (-14.9 d($(\text{CF}_3)_2\text{CH}$), -25.3 d($\text{CF}_3\overset{\ominus}{\text{C}}$), -95.0 q(COF), $J((\text{CF}_3)_2\text{C}-\text{H})=8.3$ Hz, $J(\text{CF}_3\overset{\ominus}{\text{C}}-\text{COF})=25.0$ Hz), F^\ominus anion (38.7 br.s) and BzF (1.0:0.3:0.2:0.8:5.6) was obtained from bis(α -hydrohexafluoroisopropyl) ketone (VIII) (10.2 g, 30.9 mmole), Bz_2O (21.02 g, 92.9 mmole) and Et_3N (6.39 g, 63.3 mmole) after 20 hrs. (20°).

7 A cesium salt of anion (H) was obtained [8] from tetrakis(trifluoromethyl)allene (IX) (5.4 g, 17.3 mmole) and CsF (3.09 g, 20.3 mmole) in diglyme (9.5 g); the solution of the salt was treated with Bz₂O (4.63 g, 20.5 mmole), after 12 hrs. (20°) a mixture of cesium salts of anions (H) [8], (K), (J) (NMR, Table 1), and BzF (0.3:1.0:1.5:6.2) was obtained. Bz₂O (4.59 g, 20.3 mmole) was added, yielding after 12 hrs. (20°) a mixture of cesium salts of anions (K), (J), (F) and BzF (1.0:0.15:1.5:12.7).

Reaction of tetraethylammonium perfluoroisobutenolate (IIb) with trifluoromethanesulphonic anhydride

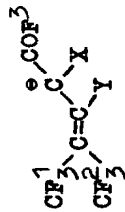
(CF₃SO₂)₂O (2.0 g, 7.1 mmole) was added to a solution of (IIb) [7] (2.28 g, 6.97 mmole) in CF₃COOEt (4.0 g). After an exothermic reaction, the mixture was refluxed for 2.5 hrs., CF₃SO₂F containing small amounts of CF₃COOEt (¹⁹F NMR) was obtained in the cold trap (-78°). Residue contained CF₃COOEt, CF₃SO₃⁻NEt₄⁺ (-4.2 s), CF₃SO₂F, (CF₃)₂CHCOF, perfluoro-3,5,5-trimethyl-5,6-dihydro-2H-pyranon-2 (X) (¹⁹F NMR, cf. [17]), and unidentified trace products. By distilling off volatile products under vacuo (4 mmHg) at 20°, a mixture containing lactone (X) (yield (¹⁹F NMR) ~0.45 g (~35%)) was obtained in the trap (-78°).

Reaction of mesomeric fluorocarbanions with anhydrides of perfluorocarboxylic acids

Perfluorocarboxylic acid anhydride was added dropwise to a mesomeric fluorocarbanion salt at 0-20° (in case of (CF₃CO)₂O, temperature in the reflux condenser was kept at -50°), the mixture was stirred until homogenization and gas evolution was completed, with low-boiling products being collected in the cold trap (-78°). Products were subjected to ¹⁹F NMR analysis (see Table 2 for trifluoroacetyl-substituted anions). Volatile components were distilled off under vacuo (1 mmHg, 40-100° in bath); large excess H₂SO₄/P₂O₅ mixture (from 2:1 to 3:1 by weight) was added to residue while

TABLE 1

^{19}F NMR spectra of hexafluoroisobuteryl-substituted mesomeric anions



Anion	X	Y	Chemical shift, p.p.m.				J(1-2), Hz
			F ¹	F ²	F ³	F ⁴	
(F) ^a	COF ³	OBz	-18.2 t.q	-20.4 q	-96.0 q	-	7.7
(G) ^b	COOBz	OBz	-18.5 d.q	-20.2 q	- ^c	-	7.5
(J)	CF ⁴ ₃	OBz	-19.07 m	-22.3 q	-85.4 m	-25.8 m	7.7
(K) ^d	CF ⁴ ₃	F ⁵	-19.11 m	-22.7 d.q	-86.4 m	-25.5 br.d.d	7.5

^a J(1-3)=1.9 Hz. ^b J(1-3) \approx 2 Hz. ^c The signal of F³ is probably overlapped by signals of other mixture components ((E), (F), BzF). ^d -13.6 m (F⁵); J(2-5) \approx 19 Hz, J(3-4) \approx J(4-5) \approx 17 Hz.

cooling (-30°). Products were distilled off under vacuo (1 mmHg, $0-50^{\circ}$) in the cold trap (-78°), and purified by distillation or PGIC when necessary.

1,1-Bis(trifluoroacetyl)-2,2,2-trifluoroethane (XVIa)

(a) 5.68 g (28.1%) of diketone (XVIa) (b.p. $73-74^{\circ}$) (PGIC, 45°) was obtained from tetraethylammonium perfluoroisobutenolate (IIb) [7] (23.98 g, 73.3 mmole) and $(CF_3CO)_2O$ (46.68 g, 222.3 mmole).

NMR spectra: 1H 5.0 q, $J(H-CF_3)=7.0$ Hz; ^{19}F -13.3 d.sp (CF_3CH), $+2.3$ q(CF_3CO), $J(CF_3-CH)=6.7$ Hz, $J(CF_3-CF_3)=2.3$ Hz.

IR spectrum: 1775 m, 1800 s(C=O), 2977 w(CH).

Mass spectrum (ionizing energy 25 eV): 229, 2.3, $(M-COF)^+$; 207, 100, $(M-CF_3)^+$; 97, 21.6, CF_3CO^+ ; 91, 34.8, $C_3HF_2O^+$; 69, 70.1, CF_3^+ . $\sim 40^{\%}$: $(M-CF_3)^+ - CF_3COF \rightarrow C_3HF_2O^+$; $\sim 36^{\%}$: $(M-COF)^+ - C_2F_6 \rightarrow C_3HF_2O^+$.

Analysis: found C 26.1, H 0.40, F 62.2%; calcd. for $C_6HF_9O_2$ C 26.1, H 0.36, F 61.9%.

(b) ~ 2 g ($\sim 85\%$) of CF_3COF and a diketone triethylammonium salt (XIa) solution in BzF were obtained from crude triethylammonium salt of trifluoromethylmalonyl difluoride (IIIa) (2.91 g, 10.5 mmole) in BzF (2.61 g) and $(CF_3CO)_2O$ (4.42 g, 21.0 mmole). 1.62 g (55.9%) of diketone (XVIa) was obtained; main product content was $\geq 95\%$ (all manipulations were conducted quickly; bath temperature did not exceed 40° during BzF distillation; mixture of salt (XIa) and H_2SO_4/P_2O_5 was heated in vacuo to 0°).

(c) A solution of cesium salt of diketone (XIa) was obtained from crude cesium salt of trifluoromethylmalonyl difluoride (IIIc) (20.6 g, 67.0 mmole), BzF (17.0 g), diglime (28.7 g) and $(CF_3CO)_2O$ (28.07 g, 133.6 mmole) after heating for 30 min. at 50° ; the salt was converted into diketone (XVIa) (2.61 g, 14.1%; PGIC, 45°).

TABLE 2

^{19}F NMR spectra of trifluoroacetyl-substituted salts $\text{E}^{\ominus}\text{C}(\text{COCF}_3)\text{X}$

Salt [anion]	X	Y	E	Solvent	Chemical shift, p.p.m.			J, Hz
					F ¹	F ²	F ³	
(XIa)	COCF_3^1	CF_3^2	HNEt_3	BzF	-5.4q	-25.4sp		7.5
			NEt_4	CF_3COOEt	-4.6q	-23.5sp	-	6.6
			Cs	diglyme	-5.8q	-25.2sp		7.5
(XIIa)	COCF_3^1	COCF_3^1	HNEt_3	BzF	-4.4s			
			NEt_4	CF_3COOEt	-4.1s			
			Cs	diglyme	-4.7s			
(XIII) ^a	COCF_3^1	COOCH_3	HNEt_3	BzF	-5.4s			
[(N)] ^b	CF_3^2	COF^3	NEt_4	CF_3COOEt	-4.8d.q	-23.2d.q	-98.1q.q	2.4 16.9
[(O)]	COF^3	COF^3	NEt_4	CF_3COOEt	-4.2t		-105.9q	7.5
[(P)]	COCF_3^1	COF^3	NEt_4	CF_3COOEt	-4.2d		-108.1sp	7.5

^a ^1H NMR: 3,4 s(OCH₃). ^b J(2-3)=18.8 Hz.

1,1-Bis(perfluorobutyroyl)-2,2,2-trifluoroethane (XVIb)

18.8 g (~100%) of $n\text{-C}_3\text{F}_7\text{COF}$ and 12.29 g (~100%) of diketone salt (XIb) (-25.0 m($\text{CF}_3\overset{\ominus}{\text{C}}$), $+2.6$ m(CF_3CF_2), $+44.8$ m(CF_3CF_2), $+35.0$ m(CF_2CO)) were obtained from tetramethylammonium perfluoroisobutenolate (IIb) [7] (7.00 g, 21.4 mmole) and $(n\text{-C}_3\text{F}_7\text{CO})_2\text{O}$ (25.8 g, 62.9 mmole) at 100° . 7.94 g (77.6%) of practically pure diketone (XVIb), b.p. $128\text{--}129^\circ$, was isolated from the salt.

NMR spectra: ^1H 5.1 q, $J(\text{H}\text{--}\text{CF}_3)=6.7$ Hz; ^{19}F -14.0 m(CF_3CH), $+4.7$ t(CF_3CF_2), $+9.2$ m(CF_3CF_2), $+0.8$ m(CF_2CO), $J(\text{CF}_3\text{--}\text{CF}_2\text{CO})=9.0$ Hz.

IR spectrum: 1765 m, 1790 s(C=O).

Mass spectrum: 429, 1.1, $(\text{M}\text{--}\text{COF})^+$; 307, 15.9, $(\text{M}\text{--}\text{C}_3\text{F}_7)^+$; 197, 12.7, $\text{C}_3\text{F}_7\text{CO}^+$; 169, 100, C_3F_7^+ ; 91, 32.6, $\text{C}_3\text{HF}_2\text{O}^+$; 69, 94.3, CF_3^+ . 145.0^{M} : $\text{C}_3\text{F}_7\text{CO}^+ - \text{CO} \rightarrow \text{C}_3\text{F}_7^+$; 28.2^{M} : $\text{C}_3\text{F}_7^+ - \text{C}_2\text{F}_4 \rightarrow \text{CF}_3^+$.

Analysis: found C 25.5, H 0.22, F 67.2%; calcd. for $\text{C}_{10}\text{HF}_{17}\text{O}_2$ C 25.2, H 0.21, F 67.8%.

Tris(trifluoroacetyl)methane (XVIIa)

(a) ~18 g (~85%) of CF_3COF with trace $(\text{CF}_3\text{CO})_2\text{O}$ and 11 g (~100%) of solid triketone tetraethylammonium salt (XIIa) were obtained from tetraethylammonium perfluoroisobutenolate (IIb) [7] (8.6 g, 26 mmole) and $(\text{CF}_3\text{CO})_2\text{O}$ (30.0 g, 140 mmole) in benzene (15 ml) after heating for 4 hrs. at 80° . 5.50 g of mixture, containing 4.95 g of (XVIIa) was obtained from the salt. Yield 62.6%. Pure triacetylmethane (XVIIa) was isolated by PGIC (70°). B.p. $90\text{--}102^\circ$ (depending on keto-enol composition of initial mixture and distillation speed; thorough distillation allows to enrich distillate with ketone form k-(XVIIa), while residue is almost totally pure enol form e-(XVIIa)).

NMR spectra:

Tautomer	^1H	^{19}F		
		F^1	F^2	$J(1-2)$
k-(XVIIa)	5.7 s		+2.0 s	-
e-(XVIIa) [†]	14.5 s	-4.3 q	+0.2 sp	5.8 Hz

IR spectrum: 1592 s(C=C); 1680 s, 1760 s, 1800 m(C=O); 2200-3400 w(OH).

Mass spectrum: 235, 26.3, $(\text{M}-\text{CF}_3)^+$; 165, 14.7, $\text{C}_5\text{F}_3\text{O}_3^+$; 97, 11.7, CF_3CO^+ ; 69, 100, CF_3^+ ; 182.3^m: $(\text{M}-\text{CF}_3)^+ - \text{CO} \rightarrow (\text{M}-\text{CF}_3\text{CO})^+$; 126.6^m: $(\text{M}-\text{CF}_3-\text{HF})^+ - \text{CF}_2 \rightarrow \text{C}_5\text{F}_3\text{O}_3^+$; 116.0^m: $(\text{M}-\text{CF}_3)^+ - \text{CHF}_3 \rightarrow \text{C}_5\text{F}_3\text{O}_3^+$; 57.0^m: $\text{C}_5\text{F}_3\text{O}_3^+ - \text{C}_3\text{O}_2 \rightarrow \text{CF}_3\text{CO}^+$.

Analysis: found C 27.6, H.0.36, F 56.3%; calcd. for $\text{C}_7\text{HF}_9\text{O}_3$ C 27.6, H 0.33, F 56.2%.

(b) A solution of triketone cesium salt (XIIa) was obtained from cesium perfluoroisobutenolate (IIc) [8] (21.9 g, 66.5 mmole), CsF (0.20 g, 1.3 mmole) in diglime (28.4 g) and $(\text{CF}_3\text{CO})_2\text{O}$ (76.9 g, 366 mmole) after stirring for 6 hrs. at 20° and heating for 2 hrs. at 50°. 14.21 g of mixture containing 9.53 g (yield 47.1%) of triacylmethane (XVIIa) was isolated from the solid salt. PGIC yielded, at 60°, 5.69 g (28.1%) of pure triacylmethane (XVIIa).

(c) ~3 g (~100%) of CF_3COF and a triacylmethane triethylammonium salt (XIIa) solution were obtained from crude triethylammonium salt of methanetricarboxyl trifluoride (IV) (2.02 g, 7.93 mmole) in BzF (3.9 g) and $(\text{CF}_3\text{CO})_2\text{O}$ (6.91 g, 32.9 mmole) after one hour (0°) and 30 min (35°). 1.31 g of mixture containing 1.03 g of triacylmethane was isolated (yield 42.7%). 0.53 g (22.0%) of pure (XVIIa) was obtained by distillation.

[†]The presence of nucleophilic impurities accelerates the interconversion of 'external tautomers' (cf. [18]), leading to broadening, or even coalescence of, F^1 and F^2 signals; however, initial spectrum is fully restored by adding the $\text{H}_2\text{SO}_4/\text{P}_2\text{O}_5$ mixture in catalytic amounts.

Tris(perfluorobutyroyl)methane (XVIIb)

(a) ~18.3 g (~90%) of $n\text{-C}_3\text{F}_7\text{COF}$ and 9.70 g (~95%) of solid tetraethylammonium salt of triacylmethane (XIIb) (+2.8 t(CF_3), +46.3 br.s(CF_3CF_2), +35.3 br.q(CF_2CO), $J(\text{CF}_3\text{-CF}_2\text{CO}) = 9.4$ Hz (in C_6H_6)), were obtained from tetraethylammonium perfluoroisobutenolate (IIb) [7] (4.49 g, 13.7 mmole) and $(n\text{-C}_3\text{F}_7\text{CO})_2\text{O}$ (30.81 g, 75.14 mmole) (2 hrs., $20\text{-}115^\circ$). 7.25 g of mixture containing 6.67 g of triacylmethane (XVIIb) was isolated (yield 80.5%); distillation yielded 4.87 g (58.7%) of pure (XVIIb), b.p. $68\text{-}73^\circ$ (14 mmHg) (depending on initial mixture keto-enol composition and distillation speed).

NMR spectra:

Tautomer	^1H	^{19}F			
		CF_3	CF_2	CF_2CO	$J(\text{CF}_3\text{-CF}_2\text{CO})$
k-(XVIIb)	5.8 s	4.40 t	4.96 br.s	42.3 br.q	9.4 Hz
e-(XVIIb)	15.1 s	(1):4.53 t	50.0 m	39.2 m	9.4 Hz
		(2):4.48 t	48.8 br.s	38.4 m	9.5 Hz

IR spectrum: 1580 w(C=C); 1662 w, 1769 s, 1792 s(C=O); 2970 w(CH).

Mass spectrum: 585, 0.1, $(\text{M-F})^+$; 557, 0.5, $(\text{M-COF})^+$; 435, 9.2, $(\text{M-C}_3\text{F}_7)^+$; 407, 6.9, $(\text{M-C}_3\text{F}_7\text{CO})^+$; 197, 7.6, $\text{C}_3\text{F}_7\text{CO}^+$; 169, 89.1, C_3F_7^+ ; 69, 100, CF_3^+ . 381^{M} : $(\text{M-C}_3\text{F}_7)^+ - \text{CO} \rightarrow (\text{M-C}_3\text{F}_7\text{CO})^+$; 145^{M} : $\text{C}_3\text{F}_7\text{CO}^+ - \text{CO} \rightarrow \text{C}_2\text{F}_7^+$; 89.5^{M} : $(\text{M-C}_3\text{F}_7)^+ - \text{C}_3\text{F}_7\text{COCH}=\text{C}=\text{O} \rightarrow \text{C}_2\text{F}_7\text{CO}^+$; $\sim 70^{\text{M}}$: $(\text{M-C}_3\text{F}_7\text{CO})^+ - \text{C}_3\text{F}_7\text{COCH}=\text{C}=\text{O} \rightarrow \text{C}_3\text{F}_7^+$; 28.1^{M} : $\text{C}_3\text{F}_7^+ - \text{C}_2\text{F}_4 \rightarrow \text{CF}_3^+$.

Analysis: found C 25.8, H 0.35, F 66.4%; calcd. for $\text{C}_{13}\text{HF}_{21}\text{O}_3$ C 25.8, H 0.17, F 66.0%.

(b) 56.2 g (58%) of $n\text{-C}_3\text{F}_7\text{COF}$ and a triacylmethane cesium salt (XIIb) solution were obtained from cesium perfluoroisobutenolate (IIc) [8] (21.1 g, 64.1 mmole) in diglyme (25 ml) and $(n\text{-C}_3\text{F}_7\text{CO})_2\text{O}$ (132.3 g, 322.6 mmole) after heating for 4 hrs. at 80° and 30 min at 110° . The solution was divided into two parts, one of which yielded 11.2 g (~60%) of triacylmethane (XVIIb).

Tris(perfluorobutyryl)methylbromide (XIX)

The second part of the cesium salt (XIIb) solution obtained in the previous experiment was vacuum-evaporated (1 mmHg). CH_3CN (20 ml) was added, followed by excess Br_2 (16 g) (dropwise). Distillation of lower layer yielded 11.87 g (~55%) of bromotriketone (XIX). B.p. $37-40^\circ$ (1 mmHg).

^{19}F NMR spectrum: 4.4 t(CF_3), 47.9 br.s(CF_3CF_2), 29.8 br.q (CF_2CO), $J(\text{CF}_3-\text{CF}_2\text{CO})=9.5$ Hz.

IR spectrum: 1769 s, 1777 sh($\text{C}=\text{O}$).

Mass spectrum (for bromo-containing ions, data is given only for the ^{79}Br isotope): 603, 0.5, ($\text{M}-\text{Br}$) $^+$; 513, 2.0, ($\text{M}-\text{C}_3\text{F}_7$) $^+$; 485, 3.2, ($\text{M}-\text{C}_3\text{F}_7\text{CO}$) $^+$; 197, 14.8, $\text{C}_3\text{F}_7\text{CO}^+$; 169, 100, C_3F_7^+ ; 69, 51.5, CF_3^+ ; 145.0 $^{\text{M}}$: $\text{C}_3\text{F}_7\text{CO}^+ - \text{CO} \rightarrow \text{C}_3\text{F}_7^+$; 28.2 $^{\text{M}}$: $\text{C}_3\text{F}_7 - \text{C}_2\text{F}_4 \rightarrow \text{CF}_3^+$.

Analysis: found C 22.7, Br 12.2, F 58.4%; calcd. for $\text{C}_{13}\text{BrF}_{21}\text{O}_3$ C 22.9, Br 11.7, F 58.4%.

Methyl α,α -bis(trifluoroacetyl)acetate (XVIII)

A solution of crude methyl α,α -di(flurocarbonyl)-acetate triethylammonium salt (V) (13.12 g, 49.08 mmole) in BzF (~25 g) was added dropwise while stirring (0°) to $(\text{CF}_3\text{CO})_2\text{O}$ (21.08 g, 100.4 mmole). Obtained were ~7 g (~60%) of CF_3COF and a triethylammonium salt (XVIII) solution in BzF . 8.38 g (64.5%) of diketoester (XVIII) was isolated from the salt. B.p.= $60-61^\circ$ (23 mmHg).

IR spectrum: 1642 m($\text{C}=\text{C}$); 1694 s, 1758 s, 1795 sh($\text{C}=\text{O}$); 2980 w(CH); 2250-3500 w(OH).

Mass spectrum: 266, 0.3, M^+ ; 235, 4.6, ($\text{M}-\text{OCH}_3$) $^+$; 215, 6.0, ($\text{M}-\text{OCH}_3-\text{HF}$) $^+$; 197, 39.4, ($\text{M}-\text{CF}_3$) $^+$; 165, 45.9, $\text{C}_5\text{F}_3\text{O}_3^+$; 97, 24.0, CF_3CO^+ ; 69, 100, CF_3^+ ; 59, 32.3, COOCH_3^+ ; 15, 35.1, CH_3^+ . 138 $^{\text{M}}$: ($\text{M}-\text{CF}_3$) $^+ - \text{CH}_3\text{OH} \rightarrow \text{C}_5\text{F}_3\text{O}_3^+$; 113.7 $^{\text{M}}$: $\text{C}_5\text{F}_3\text{O}_3^+ - \text{CO} \rightarrow \text{C}_4\text{F}_3\text{O}_2^+$; 57.0 $^{\text{M}}$: $\text{C}_5\text{F}_3\text{O}_3^+ - \text{C}_3\text{O}_2 \rightarrow \text{CF}_3\text{CO}^+$.

NMR spectra:

Tautomer	^1H			^{19}F		
	CH	OH	CH_3	F^1	F^2	J(1-2)
k-(XVIII)	5.2 s	-	3.46 s	+1.5 s	-	-
e-(XVIII)	-	12.6 s	3.52s	-6.5 q	+0.1 q	2.6 Hz
e'-(XVIII)	-	14.1 s	3.43 s	-3.9 s	-	-

Analysis: found C 31.1, H 1.25, F 42.1%; calcd. for $\text{C}_7\text{H}_4\text{F}_6\text{O}_4$ C 31.6, H 1.52, F 42.8%.

Reaction of tetraethylammonium perfluoroisobutenolate (IIb) with trifluoroacetic anhydride

An equimolar amount of $(\text{CF}_3\text{CO})_2\text{O}$ was added in portions to a 36% solution of (IIb) [7] in CF_3COOEt . After violent gas emission, mixture was refluxed (-50° in condenser) and its composition was determined by ^{19}F NMR. This was repeated five times, until a ratio of 5:1 was attained for $(\text{CF}_3\text{CO})_2\text{O}$ and (IIb). ^{19}F NMR spectra of anions (N), (O), and (P) are in Table 2. Composition of obtained mixtures:

Amount of $(\text{CF}_3\text{CO})_2\text{O}$ in moles per 1 mole of (IIb)	Relative anion content, %						
	(C)	(B)	(N)	(O)	(L)	(P)	(M)
1	20	40	40	-	-	-	-
2	-	7	53	10	27	3	-
3	-	-	-	-	60	25	15
4	-	-	-	-	10	10	80
5	-	-	-	-	-	-	100 ^a

^a Along with anion (M), the solution contains a quantity of ion $\text{CF}_3\text{COO}^\ominus$.

Reaction of 1,1-bis(trifluoroacetyl)-2,2,2-trifluoroethane (XVIa) with water and methanol

An equimolar mixture of diketone (XVIa) and H_2O (1.5% excess) was shaken in a sealed ampoule until exothermic

reaction was over and the mixture turned homogeneous. In 7 days (20°) the mixture contained 1,1-bis(trifluoroacetyl)-2,2,2-trifluoroethane monohydrate (XX), starting diketone (XVIa), probably $\text{CF}_3\text{C}(\text{OH})_2$ (NMR: ^1H -4.5 br.s[†]; ^{19}F -0.5 s) and trifluoromethyl 2,2,2-trifluoroethyl ketone (XXII) (1.0:0.4:0.06:0.06).

NMR spectra:

Hydrate (XX): ^1H 4.1 q(CH), ~4.5 br.s(OH)[†], $J(\text{CH}-\text{F}^1)=7.1$ Hz; ^{19}F -15.6 d.q.q(F^1), +2.9 m(F^2), +7.8 q.q(F^3), $J(1-\text{H}) \approx 7$ Hz, $J(1-2)=2.1$ Hz, $J(1-3)=5.5$ Hz, $J(2-3) \approx 1$ Hz.

Monoketone (XXII): ^1H 3.2 q, $J=9.3$ Hz (cf. [19]); ^{19}F -13.0 t.q(CF_3CH_2), +4.0 q(CF_3CO), $J(\text{CF}_3-\text{CH}_2)=9.4$ Hz, $J(\text{CF}_3-\text{CF}_3) \approx 1$ Hz.

After heating for 80 hrs. at 100-110° and 70 hrs. at 130°, the solution did not contain starting diketone (XVIa), and was composed of monoketone (XXII), CF_3COOH and hexafluoroacetylacetone (XXIII) (1.0:1.0:0.1) (NMR, GLC).

In a similar fashion, a mixture of monosemiketal of 1,1-bis(trifluoroacetyl)-2,2,2-trifluoroethane (XXI) (two diastereomers - (XXIa) and (XXIb), 2.6:1), starting diketone (XVIa), monoketone (XXII), $\text{CF}_3\text{COOCH}_3$ and, probably, semiketal $\text{CF}_3\text{CH}_2\text{C}(\text{OH})(\text{OCH}_3)\text{CF}_3$ (1.0:0.1:0.1:0.15:0.05) was obtained from diketone (XVIa) and CH_3OH (6.5% excess) in 7 days (20°).

NMR spectra of monosemiketal (XXI):

	^1H		^{19}F		
	(XXIa)	(XXIb)	(XXIa)	(XXIb)	
CH	4.4 q	4.3 q	F^1	-15.3 d.q.q	-16.4 m
OH	~4.5 br.s [†]		F^2	+2.7 q	+2.5 m
CH_3	3.2 s	3.3 q	F^3	+3.6 q	+5.2 m
$J(\text{CH}-\text{F}^1)$	7.6 Hz	7.6 Hz	$J(\text{F}^1-\text{CH})$	7.9 Hz	-
$J(\text{CH}_3-\text{F}^3)$	-	~3 Hz	$J(\text{F}^2-\text{F}^1)$	1.9 Hz	-
			$J(\text{F}^1-\text{F}^3)$	7.9 Hz	-

[†]Exchange signal of all OH groups in the mixture.

NMR spectra of semiketal $\text{CF}_3\text{CH}_2\text{C}(\text{OH})(\text{OCH}_3)\text{CF}_3$: ^1H 2.3 q(CH_2), ~ 4.5 br.s(OH)[†], 3.1 m(CH_3), $J(\text{CH}_2-\text{F}^1)=10.4$ Hz; ^{19}F -15.6 t.q(F^1), +6.2 m(F^2), $J(1-\text{H})=10.2$ Hz, $J(1-2)=3.4$ Hz.

After heating for 6 hrs. at 90° , the solution did not contain starting diketone (XVIa), and was composed of monoketone (XXII), $\text{CF}_3\text{COOCH}_3$ and semiketal $\text{CF}_3\text{CH}_2\text{C}(\text{OH})(\text{OCH}_3)\text{CF}_3$ (1.0:1.0:0.07) (NMR, GLC).

Reaction of tris(trifluoroacetyl)methane (XVIIa) with water and methanol

An equimolar mixture of triacetylmethane (XVIIa) with H_2O or CH_3OH ($\sim 15\%$ excess) was shaken in a sealed ampoule until exothermic reaction was over and the mixture turned homogeneous. Mixtures of hexafluoroacetylacetone (XXIII) and CF_3COOH or $\text{CF}_3\text{COOCH}_3$ (1:1) were obtained (NMR, GLC).

Influence of temperature on keto-enol equilibrium of tris-(trifluoroacetyl)methane

A drop of conc. H_2SO_4 with P_2O_5 mixture was added to triacetylmethane (XVIIa) containing 94.2% of main product, 2.1% CF_3COOH and 3.7% of hexafluoroacetylacetone (XXIII). The mixture was heated at a constant temperature until equilibrium was attained, while periodically taking ^1H and ^{19}F NMR spectra (after quenching by quick cooling to 20°). See p. for relative content of ketone k-(XVIIa) and enol e-(XVIIa) forms, and also for ΔH and ΔS values calculated as in Ref. [13]. After heating for 20 hrs. at 150° , 31 hrs. at 110° and standing 2 years ($\sim 20^\circ$), mixture composition remained almost unchanged (90.5% (XVIIa), 2.5% CF_3COOH and 7.0% hexafluoroacetylacetone (XXIII)).

[†]Exchange signal for all OH groups in the mixture.

CONCLUSION

A method has been developed for the transformation of CF_3 groups located in the α -position to the carbanion center of mesomeric fluorocarbanions, into COF and COR_F groups, which allowed us to synthesize novel fluoro-containing di- and tri-carbonyl compounds.

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