DECARBOXYLATION OF SALTS OF PERFLUORO- α , β -UNSATURATED ACIDS

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Saturated perfluoroorganic acids and their salts have been successfully used in the preparation of perfluoroalkanes, perfluoroalkyl halides, and perfluoromercury compounds [1-3]. Analogous reactions of unsaturated perfluorinated acids have not been investigated.

In the present work it has been shown that salts of perfluoro- α , β -unsaturated acids (Ia-c) can be employed for the preparation of various types of unsaturated compounds having atoms of H, I, and Hg at the double bond. Thus, by heating the salt (Ia) in ethyleneglycol, one obtains l-hydro-3-trifluoromethylhexafluorobut-l-ene (II), reaction of the salts (Ia-b) with iodine yields the iodoolefins (IIIa-b)* and thermal decomposition of the mercury carboxylates (IVa-c) gives the perfluoroalkenyl derivatives of Hg(Va-c).**



$$\begin{split} R_{F} &= (CF_{3})_{2}CF(Ia), \ (II), \ (IIIa); \ (CF_{3})_{3}C(Ib), \ (IIIb); \ n-C_{5}H_{10}(Ib). \\ & (R_{F}CF = CFCOO)_{2}Hg \xrightarrow{[K_{2}CO_{3}]}_{110-140^{\circ}} \ (R_{F}CF = CF)_{2}Hg \\ & (IV) & (V) \\ R_{F} &= n-C_{3}F_{7}(IVa), \ (Va); \ (CF_{3})_{2}CF(IVb), \ (Vb); \ (CF_{3})_{3}C(IVc), \ (Vc). \end{split}$$

Thermal decomposition of the salts (Ia-c) is accompanied by β -elimination of a fluorine atom and leads to the formation of perfluoroacetylenes (VIa-c). + It should be noted that thermolysis of the salts (Ia) and (Ic) forms allenes (VIIa-b) (3-10%) in addition to acetylenes (VIa) and (VIc), evidently via isomerization of the corresponding acetylenes under the influence of NaF.[‡]

**For a preliminary communication on this synthesis, see [5].

[†]Tetrafluoropropyne has been obtained by the thermal decomposition of the Na salt of perfluorocrotonic acid [6].

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^{*}Reaction of the Ag salt of α , β -difluorocinnamic acid with I_2 gives β -iodo- α , β -difluorostyrene [4].

[‡]Tetrafluoropropyne isomerizes to tetrafluoroallene under the action of CsF [6]; preparation and constants of the allene (VIIa) are given in [7].

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Compound	bp, °C (p, mm Hg)	Found/calc., %		IR spectrum, cm ⁻¹
		С	F	(C=Č)
(II) *	38-38,5	$\frac{25,91}{25,86}$	$\frac{73,64}{73,73}$	1722
(IIIa)	92-93	$\frac{16,70}{16,76}$	$\frac{47,65}{47,76}$	1685
(IIIb)	45-46 (60)	$\frac{17,70}{17,65}$	$\frac{51,40}{51,25}$	1670
(Va)	88-92(3)	<u>18,75</u> 18,13	51,97 51,66	1635 1645 1660
(Vb)	8587 (2)	<u>18,39</u> 18,13	$\frac{51,87}{51,66}$	1630 сл 1670
(Vc)	T.m p. 113–116	<u>18,89</u> 18,89	$\frac{55,51}{54.86}$	1653
(VIa) + (VIIa)	19-21			2045 (C=C=C) 2360 (C=C)
(VIb)	41-42	$\frac{27,55}{27,48}$	$\frac{72,38}{72,52}$	2365 (C=C)
(VIc) + (VIIb)	72-73	$\frac{26,66}{26,92}$	$\frac{73,16}{73,08}$	2043 (C=C=C) 2360 (C≡C)

TABLE 1. Characteristics of Compounds Prepared

*Found, %: H 0.41; calculated, %: H 0.43.

TABLE 2. ¹⁹F NMR Spectra

Compound	δ, ppm; J, Hz		
$\begin{array}{c} \begin{pmatrix} 1 & 2 \\ (CF_3)_2 CF \\ 3 \\ F \\ & 3 \\ F \\ & H \end{array} = C \begin{array}{c} 4 \\ F \\ H \\ & H \end{array} $ (II)	0.4 d,d,d, (F^1), 112.7 d,d,d, sept (F^2), 97.8 d,d,d, sept (F^3), 90.7 d,d,d, sept (F^4), 6.94 d,d,d (H); $J_{1-2}=8,5, J_{2-4}=33,9, J_{3-4}=136,5, J_{1-3}=8,5, J_{2-3}=8,5, J_{1-4}=56, J_{2-H}=2,5, J_{3-H}=7, J_{4-H}=71,5$		
$\begin{array}{c} (\overset{1}{CF_{3}})_{2}\overset{2}{CF} \\ \overset{3}{F} & C = C & I \\ & I \\ & I \end{array} $ (IIIa)	-1.1 d,d d (F ¹), 109.5 d,d, sept (F ²), 65.0 d,d, sept (F ³), 32.0 d,d, sept (F ⁴); $J_{1-2} = 8.9$, $J_{1-3}=8.9$, $J_{1-4}=4.7$, $J_{2-3}=13.2$, $J_{2-4}=41.4$, $J_{3-4}=148.8$		
$(CF_{3})_{2}C = C \int_{I}^{3} (IIIb)$	-10.2 d.d, (F ¹), 24.9 d, dec (F ²), 58.5 d, dec (F ³); $J_{1-2} = 12.5$ $J_{2-3}=155$, $J_{1-3}=16,65$		
$(CF_3CF_2CF_2CF_2CF=CF)_2 Hg (Va)$ (mixture of isomers)	4.0 m (F ¹), 51.6 m (F ²), 40.8 m (F ³), 92.3 m (F ⁴), 62.8 (F ⁵); $J_{4-5} = 122.4$		
$(CF_{3})_{2}CF \xrightarrow{4} F (Vb)$	-0.5 d,d,d (F ¹), 111.0 d,d, sept (F ²), 90.6 d,d, sept (F ³), 66.4 d,d, sept (F ⁴); $J_{1-2}=8,33, J_{1-3}=9,1, J_{1-4}=5,3, J_{2-3}=3,63, J_{2-4}=37,55, J_{3-4}=117,1; J_{3-Hg}=276,0, J_{4-Hg}=276,0$		
$(CF_{3})_{3}C$ (Vc) $(Solution in DMF)$ (Vc)	12.0 d,d, (F^1), 83.4 d dec (F^2), 55.6 d dec (F^3); $J_{2-3}=113.2$, $J_{2-Hg}=315.4$. $J_{3-Hg}=933.6$, $J_{3-3}'=4.4$		
$(CF_3)_2 CFC \equiv CF$ (VIa)	5.78 d,d, (F^1), 96.8 d sept (F^2), 123.5 d sept (F^3); $J_{1-3}=0.8$, $J_{2-3}=8$		
$\begin{array}{c} 1\\ CF_3\\ CF_3 \end{array} C = C = CF_2 \qquad (VIIa)*$	-8 t (F ¹), 19.5 sept (F ²); $J_{1-2} \approx 3.13$		
1 2 (CF₂)3 CC≡CF (VI b)*	$-5.67 (F^1)$, 121.0 dec (F ²); J ₁₋₂ = 0.73		
$\left. \begin{array}{c} {}^{1}_{C} {}^{2}_{3} {}^{3}_{2} {}^{4}_{C} {}^{5}_{2} C = {}^{6}_{2} C F (VIc) * \\ \end{array} \right)$	8.7 m (F^1), 53.2 m (F^2), 50.6 m (F^3), 49.2 m (F^4), 24.8 m (F^5), 123.4 m (F^6); $J_{5-6}=1,2$		

*Internal standard 10^{-3} M CF₃COOH in D₂O.

(Ib)
$$\xrightarrow{\Delta} (CF_3)_3CC \equiv CF$$

(VIb)
(Ia, c) $\xrightarrow{\Delta} R_FC \equiv CF + R_F'R_F''C = C = CF_2$
(VI a, c) (VII a, b)
 $R_F = (CF_3)_2CF(VIa); n-C_5F_{11}(VIc); R_F' = R_F'' = CF_3(VIIa);$
 $R_{F'} = n-C_4F_9, R_F'' = F$ (VIIb).

EXPERIMENTAL

Fluorine-19 NMR spectra were run on Perkin-Elmer R-32 (84.6 MHz) and Bruker WP-200SY (188.154 MHz) instruments using trifluoroacetic acid as internal standard. A UR-20 instrument was used for the infrared spectra. The salts (Ia-c), (IVa-c), and the fluoroalkenyl derivatives (II), (IIIa-b), and (Va-c) contain 93-95% of the trans-isomer. The salts (Ia-c) and (IVa-c) were prepared from acids whose synthesis is described in [8]. Elemental analyses, constants, and IR spectra of the products are set out in Table 1 and the ¹⁹F NMR spectra in Table 2.

<u>1-Hydro-3-trifluoromethylhexafluorobut-1-ene (II)</u>. A mixture of 12 g of salt (Ia) and 40 ml ethylene glycol was heated for 40 min at 170-195°C, collecting the products in a receiver and a trap cooled to -78°C. The contents of trap and receiver were combined and the lower layer separated and dried over MgSO₄. Distillation yielded 6.4 g (69%) of the olefin (II).

<u>Perfluoroalkenyl Iodides (IIIa-b)</u>. A mixture of 12 g (40 mmole) of salt (Ia), 14 g (55 mmole) iodine, and 50 ml anhydrous sulfolane was heated at 105-150°C (60-80 mm), distilling the volatile products into a trap cooled to -78°C. Distillation yielded 8.2 g (57%) of the iodide (IIIa). (IIIb) was prepared in 56% yield from (Ib) and iodine in a similar way.

<u>Perfluoroalkenyl Mercury Derivatives (Va-c)</u>. Mercury perfluoroalkenyl carboxylates (IVa-c) were prepared from HgO and the corresponding acid, prepared as in [8].

A mixture of 22 g (26 mmole) (IVc) and 7.5 g (53 mmole) anhydrous K_2CO_3 was heated at 220-260°C (5-7 mm) in a retort with a curved outlet. At the end of the reaction, the sublimate in the curved outlet was dissolved in CHCl₃, the solution filtered, the solvent evaporated, and the residue recrystallized from benzene. Yield 9.5 g (48.2%) (Vc). (Va) was prepared from (IVa) in 35.4% yield, and (Vb) from (IVb) in 37.5% yield, by a similar procedure.

<u>Perfluoroacetylenes (Va-c)</u>. Salt (Ic) (12 g) was heated over a Bunsen burner at 15-20 mm pressure and the products collected in a trap cooled to -78°C. Distillation yielded 1.5 g (16%) of acetylene (VIc) which contained around 10% allene (VIIb) as impurity. Pyrolyis of (Ia) likewise yielded (VIa) (26%) containing around 3% allene (VIIb) and pyrolysis of (Ib) gave (VIb) in 37% yield.

CONCLUSIONS

A series of poly- and perfluorinated olefins and acetylenes have been prepared from sodium and mercury salts of α , β -unsaturated perfluorinated acids by reactions which are accompanied by decarboxylation.

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POLYFLUORINATED a, &-UNSATURATED KETONES

substantially [9].

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The α,β -unsaturated ketones (α,β -UK), particularly those groups containing fluoroalkyl groups, are of interest as highly reactive compounds having two nonequivalent electrophilic centers and also as promising monomers and intermediate products in the synthesis of biologically active compounds. In the literature there is information principally on the synthesis and properties of trifluoromethyl-containing α,β -UK [1-8], although in many cases the introduction of long fluoroalkyl substituents alters the reactivity and properties of the compounds

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In the present investigation, by boiling polyfluorinated aldehydes with methylketones in glacial acetic acid, we have obtained for the first time the polyfluorinated β -hydroxyketones (I)-(IX), the dehydration of which has been used to synthesize the corresponding polyfluorinated α,β -UK (X)-(XVI) (Table 2), and their structure and reactions with the nucleophiles NH₃, PhNH₂, MeOH have been studied

 $R_{F}-C \xrightarrow[H]{O} + Me-C-R \xrightarrow[H]{HOAC} R_{F}-CH-CH_{2}-C-R \xrightarrow[H_{3}SO_{4}; P_{4}O_{1_{3}}]{H_{3}SO_{4}; P_{4}O_{1_{3}}} R_{F}-CH=CH-C-R \xrightarrow[H]{H_{3}SO_{4}; P_{4}O_{1_{3}}} R_{F}-CH=CH-C-R \xrightarrow[H]{H_{3}SO_{4}; P_{4}O_{1_{3}}} R_{F}-CH=CH-C-R$

The structure of (I)-(XVI) has been confirmed by elemental analysis, and also by IR and PMR spectra. In the IR spectra of (I)-(IX) OH and C=O bands are observed in the regions of 3600 and 1670-1690 cm⁻¹. The presence of an asymmetrical C atom in the β -hydroxyketones (I)-(IX) determines the characteristic AB system in the PMR spectra of the CH₂ protons at 3.9-3.8 ppm [10].

In the IR spectra of (X)-(XVI) the OH absorption appears and the C=C band appears in the region 1630-1650 cm⁻¹. In the PMR spectra of the α,β -UK (X)-(XVI) two doublets of trip-



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