α-FLUOROALKYLAMINES – A NEW SOURCE OF THE UNHYDRATED FLUORIDE ION. 4. ACYLATION OF PERFLUOROALKYL CARBANIONS WITH THE FLUOROANHYDRIDES OF CARBOXYLIC ACIDS

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It has previously been shown that perfluoroalkyl carbanions are formed when N,N,N',N'-tetramethylformamidinium bifluoride (I) reacts with perfluoroalfins



The acylation of the carbanions generated in this manner is a practicable method for the preparation of perfluoroalkyl alkyl ketones and their enol derivatives. Thus, perfluoropropylene (II) readily reacts, in the presence of catalytic quantities of (I), with benzoyl fluoride to form the previously known perfluoroisopropyl phenyl ketone [2].

$$CF_{3}CF = CF_{2} + PhCOF \xrightarrow{(I)} (CF_{3})_{2}CFCOPh$$
(II)
(III)

When (II) reacts with acetyl fluoride in the presence of (I), in addition to perfluoroisopropyl methyl ketone (IV), the acetate of its enol form (V) is also formed.

(II) + MeCOF
$$\xrightarrow{(1)}$$
 (CF₃)₂CFCOMe + (CF₃)₂CF-C=CH₂
(IV) (V) OCOMe

When (II) reacts with isobutyroyl fluoride, only the isobutyrate of the enol form of perfluoroisopropyl isopropyl ketone (VI) is obtained



The acylates of enols are formed apparently as the result of the acylation of the enolates which are obtained from the ketones under the action of the perfluoroisopropyl anion

$$(CF_{3})_{2}CFCOCHRR' \xrightarrow{\bigcirc CF(GF_{3})_{2}} \left[\begin{array}{c} 0 \\ (CF_{3})_{2}CFC \xrightarrow{\frown} CRR' \end{array} \right] \xrightarrow{RR'CHCOF} (CF_{3})_{2}CFC \xrightarrow{\frown} CRR' \\ 0 \\ OCOCHRR' \xrightarrow{\frown} OCOCHRR'$$

R = R' = H; R = R' = Me.

Perfluoroisobutylene also readily enters into the reaction described above, but when this occurs, the acylates and perfluoroisobutenylenolates of the corresponding ketones are formed.

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| TABLE 1 | | | |
|----------|------------------------------------|---|--|
| | | NMR Spectra | (6, ppm, J, Hz) |
| Compound | IK spectrum (v, cm ⁻¹) | J.er | Hı |
| (111) | 1720 (G=0) | -3,3d (CF ₃), +101 h (F), $J_{CF_3-CF} = 7$ | 7,0m, 7,5m (Ph) |
| (IV) | 1770 (C=0) | $-2 \text{ d} (CF_3), +105, 5 \text{ m} (F), J_{CF_3-CF} = 7, 3$ | $2,1$ d (Me), $J_{\mathrm{Me-CF}}=7,2$ |
| . (A) | 1800(C=0), 1670 (C=C) | -1,3 d (CF ₈), $+103,3$ m (F), $J_{CF_8-CF} = 7,5$ | 1,9 s (Me), 5,4 d (CH), 5,3 d, (CH), $J_{CH-H} = 4$ (CH), $J_{CH-H} = 4$ |
| (IV) | | -2,2 s (CF ₃), $+98,0$ m (UF) | 1,0 d (1-Me), $1_{f}4_{s}$ (3-Me), $1,8d$ (2-Me), 2,5 h (CH), $J_{Me-CH}=8, J_{Me-CF}=5$ |
| (III) | | -13,1 s (CF ₃) | 1,8s (Me), 5,2 d (CH), 5,6 d (CH), $J_{CH-H}^{2} = 4,5,6$ d (CH), |
| (1111) | 1720, 1670 2 (C=C) | $-18,2 \text{ m} (1-\text{CF}_9), -15,5 \text{ m} (1-\text{CF}_9), 13,0 \text{ s} (2-\text{CF}_9), -7,5 \text{ m} (\text{CF})$ | 5,1 d.d. (CH), 5,7 d (CH), $J_{\rm CH-H} = 6$, $J_{\rm CH-F} = 3$ |
| (XI) | 1720, 1680 2 (C=C) | $-15,0 \text{ m} (1-\text{CF}_8), -13,0 \text{ s} (2-\text{CF}_8) -8,5 \text{ m} (\text{CF})$ | $\begin{array}{llllllllllllllllllllllllllllllllllll$ |
| (IIIX) | 1860 (C=O), 1680 (C=C) | $-17, 8$ d.q. (CF ₃), $-18, 9$ d.q. (CF ₃), $+7, 1$ m (CF), $-105, 0$ d (COF), $J_{CF_{3}-CF} = 22, 3$ & $9, 5$ | 1,55 d. (Me), $J_{Me \rightarrow F} \rightarrow 4$ |
| (XIV) | 1770 (C=U) | -2.2 d (GF ₃), +109,0 d.h. (F), $J_{\text{CF}_3-\text{CF}} = 7,5$ | 0.6d (Me), 2.8 d.h. (CH), $J_{Mc-UH} = 8$, $J_{CH-CF} = 4$ |
| (X V) | 1770 (C=0) | 14,5 s (CF ₃) | 2,3s (Me) |

TABLE 2

| Com. | bp, [°] C (p, mm Hg) | Yield, % | | Empirical | | |
|---------------|----------------------------------|--------------|---------------------------------------|----------------------------|-------------------------|---|
| pound | | | С | H | F | formula |
| (III) (IV) | 162 | 93,0 25,0 | 28,36 | - | <u>63.20</u> | $ \left \begin{array}{c} C_{10}H_5F_7O\\ C_5H_3F_7O \end{array} \right $ |
| (V) | 107-108 | 25,0 | 28,30 <u>32,64</u> <u>33,07</u> | $\frac{1.76}{1.97}$ | 62,73 52,26 52,36 | $C_7H_5F_7O_2$ |
| (VI) | 73-75(23) | 24,4 * | - | _ | - | C11H13F7O2 |
| (VII) | 134-136 | 12,8 | <u>31,64</u> 31,58 | 1.78 | - | $C_8H_5F_9O_2$ |
| (VIII) | 124-126 | 19,2 | $\frac{27,46}{27,20}$ | 0,43 | — | C ₁₀ H ₂ F ₁₆ O |
| (IX) | 32-34(1) | 49,0 | 30,99 | 1.49 | <u>63,70</u> 64.68 | $C_{12}H_{6}F_{16}O$ |
| (XII) | 48-51(10) | 40,0 | 35.93 | 2,26 | 57,01 56 30 | C ₈ H ₆ F ₈ O |
| (XIV) | 62-63 | 95,0 | 35,28 | 2,92 | 54,84 | C7H7F7O |
| (XV) | 58 | 92,0 | $\frac{27.31}{27,48}$ | <u>1.13</u> <u>1,14</u> | 65.39 65,27 | C ₆ H ₃ F ₉ O |

| *The | unpurified | (VI) was | characterized | by i | ts ¹⁹ F | NMR | and | PMR | spectra |
|-------|-------------|------------|---------------|------|--------------------|-----|-----|-----|---------|
| and h | ydrolyzed i | into the l | cetone (XIV). | | | | | | |

$$({}^{2}CF_{3})_{5}C-C={}^{3}CH-{}^{2}CH_{2}-{}^{1}CH_{3}$$

 $0-CF=C({}^{2}CF_{3})_{2}$
(IX)

These products are probably obtained according to the same scheme as in the reaction of (II). Perfluoroisobutylene with isobutyroyl fluoride in the presence of (I) forms the fluoroanhydride of 2,2-dimethyl-3,5,5,5-tetrafluoro-4-trifluoromethyl-3-pentenoic acid (XII). In this case, perfluoro-t-butyl isopropyl ketone is not formed apparently on account of the steric hindrance between the initial fluoroanhydride and the perfluoro-t-butyl anion, but a proton is split off from position 2 in (X) to form the anion (XI), which reacts with perfluoroisobutylene to give the final product (XII).

$$(CF_3)_3C + Me_2CHCOF \xrightarrow{(CF_3)_3CH} Me_2CCOF \xrightarrow{(CF_3)_2C=CF_2} (CF_3)_2C = CFC(Me_2)COF$$
(XI)
(XII)

A similar condensation has previously been observed in the reaction of perfluoroisobutylene with acetyl bromide in the presence of CsF [3]. In the reactions of perfluoroisobutylene with the fluoroanhydrides of carboxylic acids, we were unable to prepare perfluoro-t-butyl ketones. This is apparently associated with their facile decomposition under the action of the F⁻ ion (cf. [4]). Upon boiling with H_2SO_4 , the acylates of the enols were quantitatively transformed into the perfluoroalkyl alkyl ketones.

 $\begin{array}{ccc} R_FC=CRR' & \xrightarrow{H_3SO_4} & R_FCOCHRR' \\ & & \downarrow \\ & OCOCHRR' \\ R_F=(CF_3)_2CF, & R=R'=H~(IV); & R_F=(CF_3)_2CF, & R=R'=Me~(XIV); \\ & R_F=(CF_3)_3C, & R=R'=H~(XV). \end{array}$

EXPERIMENTAL

The ¹⁹F NMR and PMR spectra were recorded on a Perkin–Elmer R-32 instrument (84.6 and 90 MHz). The chemical shifts are shown in ppm relative to CF_3 COOH and HMDS, respectively (PMR on the δ scale). The IR spectra were recorded on a UR-20 spectrometer.

Typical Experiment. a) Perfluoropropylene (0.3 mole) was gradually introduced with intense mixing into 0.1 mole of the fluoroanhydride and 0.01mole of (I) in 10 ml of absolute DMF. The reaction mixture was then poured onto ice and acidified with HCl. The lower layer was separated off, washed three times with cold and dried with MgSO₄.

Compounds (III), (IV), (V), and (VI) were obtained by distillation.

b) Perfluoroisobutylene (0.15 mole) was gradually added to 0.2 mole of the fluoroanhydride and 0.01 mole of (I) in 20 ml of absolute diglyme and mixed for 5 h. The reaction mixture was subsequently poured onto ice and acidified with HCl. The lower layer was separated, washed three times with cold water, and dried over $MgSO_4$. Compounds (VII), (VIII), (IX), and (XII) were obtained by distillation.

c) Compounds (V), (VI), and (VII) (0.01 mole) were mixed with an equal volume of H_2SO_4 and boiled for 1.5 h. Compounds (IV), (XIV), and (XV) were obtained. The yields, physical constants, results of analyses, and IR, NMR, and PMR spectra of the compounds prepared are shown in Tables 1 and 2.

CONCLUSIONS

1. The perfluoroalkyl carbanions generated by the reaction between N,N,N',N'-tetramethylformamidinium bifluoride and perfluoroalefins are readily acylated with the fluoroanhydrides of carboxylic acids with the formation of perfluoroalkyl alkyl ketones and their enol derivatives.

2. Hydrolysis of the acylates of the enols of perfluoroalkyl alkyl ketones leads to perfluoroalkyl alkyl ketones.

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SYNTHESIS OF FIVE-MEMBERED HETEROCYCLIC COMPOUNDS FROM PERFLUORO-α-LACTAM

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We determined previously in [1] that the extension of the three-membered ring of 1-(perfluoro-tert-butyl)-3,3-bis-(trifluoromethyl)aziridin-2-one (I) to a four-membered ring takes place by rupture of a C-C bond. This paper reports a study of the direction of the cyclic addition of α -lactam (I) with respect to the multiple bonds containing the heteroatom, to the carbonyl compounds, and to the nitriles.*

Aromatic aldehydes react slowly with perfluoro- α -lactams (I) even at $\sim 20^{\circ}$ C, forming oxazolid-5-ones (II), and anisic aldehyde is much more active than benzaldehyde. A similar result is obtained with acetone. Unlike the aldehydes, nitriles react with the α -lactam of (I) only on heating, with the formation of imidazol-5-ones (III), and acetonitrile is more active than benzonitrile. Such a substituent effect on the cyclic addition reaction rate indicates that these reactions belong to a polar type of cyclic addition:



*These reactions are unknown for α -lactams (see [2]). See [3] for the interaction of α -lactams with phenyl isocyanates.

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