Totally Fluorinated Esters, $R^1_FCO_2R^2_F$

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Summary Fluoride ion catalyses the dimerisation of trifluoroacetyl fluoride to perfluoroethyl trifluoroacetate and reactions between perfluoroacyl fluorides and perfluoroacetone to give perfluoroisopropyl esters.

DURING a study of the reactions of the $HNF_2 \cdot KF$ adduct with perfluoroacyl fluorides, we observed not only the formation of the totally fluorinated amides, $R_FC(O)NF_2$, at −23° and at −78° but also, in the case of $CF_3C(O)F$, that more than 40% of the HNF_2 consumed is found as the ester $CF_3CO_2C(NF_2)_2CF_3$. However, when the reaction temperature is lowered to −105°, the amide, $CF_3C(O)NF_2$, and a totally fluorinated ester, $CF_3CO_2C_2F_5$, are prepared in a 1:3 ratio and no $CF_3CO_2C(NF_2)_2CF_3$ is formed. Since FCO_2CF_3 and $(CF_3O)_2CO$ are the only reported totally fluorinated esters,[1] alkali metal catalysed dimerisations of other perfluoroacyl fluorides and reactions of perfluoroketones with perfluoroacyl fluorides were examined.

Attempts to dimerise higher perfluoroacyl fluorides in the presence of alkali metal fluorides were unsuccessful, and, in the absence of HNF_2, perfluoroethyl trifluoroacetate was formed from $CF_3C(O)F$ in only trace amounts, if at all. Although the role of the HNF_2 in this dimerisation reaction is not understood and no other initiator was found, the overall reaction is described by reactions (1) and (2).

$$CF_3C(O)F + MF \rightarrow CF_3CF_2O^- + M^+ \qquad (1)$$

$$CF_3CF_2O^- + CF_3C(O)F \rightarrow CF_3CF_2O_2CCF_3 + F^- \qquad (2)$$

$$M = (K \text{ and } Cs)$$

However, the reaction between perfluoroacyl fluorides and perfluoroacetone in the presence of alkali metal fluoride proceeds without HNF_2 and without product decomposition at −105° and, in the case of the higher acid fluorides, at −78° [reactions (3) and (4)].

$$(CF_3)_2CO + MF \rightarrow (CF_3)_2CFO^- + M^+ \qquad (3)$$

$$(CF_3)_2CFO^- + R_FC(O)F \rightarrow R_FCO_2CF(CF_3)_2 + F^- \qquad (4)$$

$$(R_F = F,\ CF_3,\ C_2F_5, \text{ and } C_3F_7)$$

These new esters are stable to fluoride ion attack at low temperature (< −78°) but are decomposed by fluoride ion when warmed. These compounds, which may be removed from the reaction vessel under vacuum at −78° and purified using fractional condensation, are stable at room temperature and above.

The carbonyl frequency of the ester is shifted to lower energy from the acyl fluoride and occurs characteristically in the 1840—1850 cm^{-1} region with the exception of the frequency of perfluoroisopropyl fluoroformate which occurs at 1906 cm^{-1}. In the mass spectra of all the compounds, $(M - F)^+$ is found except for $FCO_2CF(CF_3)_2$ where $(M - CF_3)^+$ is the highest *m/e* observed. Invariably for $R^1CO_2R^2$ *m/e* fragments corresponding to R^1, R^1CO, R^2, R^2O, and R^2CO_2, but not R^1CO_2, are found. Elemental analysis, n.m.r. spectra and molecular weights were used to characterise the compounds.

This work is supported by the Office of Naval Research and the National Science Foundation.

(*Received, October* 19*th*, 1970; *Com.* 1784.)

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† Alfred P. Sloan Foundation Research Fellow.

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