

## THE PREPARATION OF PERFLUORINATED CARBOXYLIC ESTERS AND PERFLUORO CARBONATES

P. G. JOHNSON AND B. TITTLE\*

*Imperial Chemical Industries, Mond Division, The Heath, Runcorn, Cheshire (Gt. Britain)*

(Received July 28, 1972)

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### SUMMARY

Aliphatic perfluorinated carboxylic esters have been prepared by two methods; (i) the reaction of the potassium salt of perfluoro 3-ethyl pent-3-ol,  $\text{KOC}(\text{C}_2\text{F}_5)_3$ , with perfluoro acid chlorides  $\text{R}_f\text{-CO-Cl}$ , to yield perfluorinated esters of composition  $\text{R}_f\text{-CO-O-C}(\text{C}_2\text{F}_5)_3$ , and (ii) the reaction of carbonyl chloride or thionyl chloride with a mixture of the potassium salt  $\text{KOC}(\text{C}_2\text{F}_5)_3$  and perfluoro acid salts of the general formula  $\text{KO-CO-R}_f$  in a polar solvent. The product ester has the composition  $\text{R}_f\text{-CO-O-C}(\text{C}_2\text{F}_5)_3$ , and in this instance carbon dioxide or sulphur dioxide is liberated during the reaction. A qualitative study of the thermal decomposition of a perfluoro ester has been made.

A tertiary perfluoro carbonate of composition  $[(\text{C}_2\text{F}_5)_2\text{CF}_3\text{C-O}]_2\text{-CO}$  has been prepared by the reaction of phosgene with the potassium salt  $\text{KOC}(\text{C}_2\text{F}_5)_2\text{CF}_3$  in a polar solvent. The intermediate acid chloride  $(\text{C}_2\text{F}_5)_2\text{CF}_3\text{C-O-CO-Cl}$  can be isolated.

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### INTRODUCTION

The preparation of perfluorinated esters by the reaction of lithium pentafluorophenyl with perfluoro acid chlorides has been reported<sup>1</sup>. The availability of perfluorinated tertiary alcohols<sup>1-6</sup> makes other routes to perfluorinated esters possible.

### RESULTS AND DISCUSSION

Two reactions have been employed for the preparation of perfluorinated esters. In the first instance, the elimination of potassium chloride from a perfluoro

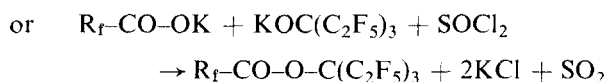
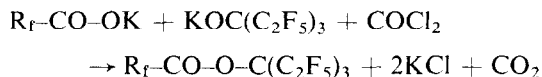
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\* Present address: Department of Chemistry, University of the Witwatersrand, Jan Smuts Avenue, Johannesburg (South Africa).

acid chloride  $R_f\text{-CO-Cl}$  and a tertiary perfluoro alcohol salt,  $(C_2F_5)_3C\text{-OK}$ , in a polar solvent such as acetonitrile was used. This was found to yield tertiary perfluoro esters according to the equation



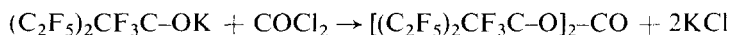
A second method involves the reaction of phosgene or thionyl chloride with a mixture of a perfluoro acid salt and the tertiary perfluoro alcohol salt in a polar solvent. Reaction appears to be according to the following equations with the formation of carbon dioxide or sulphur dioxide.



Reactions were carried out under strictly anhydrous conditions at low temperatures, *ca.*  $-20^\circ$ , in some instances.

The product ester separated as a more dense phase and was usually isolated together with some precipitated potassium chloride. This was removed by washing with water or vacuum transfer. The products were dried and then purified by distillation. Structures have been confirmed by elemental analysis,  $^{19}\text{F}$  NMR and IR spectroscopy. Boiling points have been determined and are quoted in the experimental section. The perfluoro esters have been shown to be reasonably thermally stable in a qualitative study. Thus heating the ester perfluoro 3-ethyl-3-pentyl propionate,  $(C_2F_5)_3C\text{-O-CO-C}_2F_5$ , in a Pyrex tube for 12 h at  $250^\circ$  resulted in no decomposition. However, in the presence of caesium fluoride in catalytic amounts considerable decomposition occurred after 12 h at  $200^\circ$ . The products of decomposition were identified as the ketone  $C_2F_5\text{-CO-C}_2F_5$ , the acid fluoride  $C_2F_5\text{-CO-F}$ , pentafluoroethane and the perfluoro olefins  $C_4F_8$  and  $C_5F_{10}$ . Mass spectroscopic and IR examination of these olefins suggested they were unbranched.

The perfluoro carbonate  $[(C_2F_5)_2CF_3C\text{-O}]_2\text{-CO}$  has been prepared by the reaction of phosgene with the potassium salt of the corresponding tertiary perfluoro alcohol according to the equation



The reaction was carried out in acetonitrile. An excess of the salt was used. Formation of perfluoro 3-methyl-3-pentyl chloroformate  $(C_2F_5)_3CF_3C\text{-O-CO-Cl}$  resulted when an excess of phosgene was employed.

## EXPERIMENTAL

*Preparation of the potassium salt of perfluoro 3-ethyl-pent-3-ol*

Potassium hydroxide (6.6 g), dissolved in the minimum volume of water, was stirred vigorously with benzene (200 ml). The tertiary perfluoro alcohol (40 g) was added from a dropping funnel and the mixture distilled up a Dean and Stark condenser. When all the water and excess alcohol had been removed as the azeotrope, the mixture was cooled and the salt filtered off. The yield was 39.3 g of the dry potassium salt.

*Preparation of perfluoro 3-ethyl-3-pentyl acetate (nc)**Method A*

A 250 ml three-necked flask was fitted with a stirrer, gas inlet tube, thermometer and condenser. The condenser was cooled with methanol at  $-30^{\circ}$  and was fitted with a drying tube to protect the apparatus from atmospheric moisture. Potassium perfluoro 3-ethyl-pent-3-oxide (10 g) and potassium trifluoroacetate (7 g) were dissolved in 170 g of acetonitrile and cooled to  $-20^{\circ}$ . Phosgene (20 g) was bubbled into the mixture over a period of 1 h. After this time the reaction was stopped and the mixture allowed to settle. A more dense fluorocarbon layer was separated and purified by distillation to give the pure ester. (Found: C, 22.3; F, 71.0%.  $C_9F_{18}O_2$  requires C, 22.4; F, 70.95%.)

The  $^{19}F$  NMR spectrum showed absorptions at 74.2, 76.2 and 105.2 ppm with respect to  $CFCl_3$  with the relative intensity ratio 1:3:2. The IR spectrum showed a  $C=O$  stretching frequency at  $1849\text{ cm}^{-1}$ . The mass spectrum of the ester showed a weak parent ion current of  $m/e$  482 with a much greater ion current at  $m/e$  463 representing the parent ion less one fluorine atom.

*Method B*

Trifluoroacetyl chloride (14 g) was bubbled through a solution of potassium perfluoro 3-ethyl-pent-3-oxide (40 g) in acetonitrile. A precipitate of KCl and a more dense fluorocarbon phase were produced in the cooled reaction mixture. The fluorocarbon phase was separated and distilled from residual potassium chloride followed by careful fractionation to give a pure material boiling at  $122\text{--}124^{\circ}$ .

This product was shown to have  $^{19}F$  NMR, IR and mass spectra identical to the material prepared in Method A.

*Preparation of perfluoro 3-ethyl-3-pentyl propionate (nc)*

A mixture of potassium perfluoro 3-ethyl-pent-3-oxide and potassium perfluoropropionate (30 g) was dissolved in 50 ml of dry acetonitrile. This solution was then introduced slowly into a solution of phosgene (3.5 g) in acetonitrile (150 ml) cooled to  $-20^{\circ}$ . Reaction took place immediately with the formation of

a white precipitate of potassium chloride. The mixture was stirred at  $-20^{\circ}$  for 2 h. After this time the heavy fluorocarbon phase was separated and distilled to give 11 g of VPC pure material boiling at  $137^{\circ}$ . This was characterised as perfluoro 3-ethyl-3-pentyl propionate. (Found: C, 22.8; F, 70.2%.  $C_{10}F_{20}O_2$  requires C, 22.5; F, 71.4%.)

$^{19}F$  NMR spectrum:  $(CF_3CF_2)_3C-O-$  group;  $CF_3$ , 76.8;  $CF_2$ , 106.0.  $-CO-CF_2CF_3$  group:  $CF_3$ , 82.8;  $CF_2$ , 119.6 ppm relative to  $CFCl_3$ . The integrated intensities agreed with the proposed structure.

#### *Thermal decomposition study of perfluoro 3-ethyl-3-pentyl propionate*

##### *Method A*

A sample of the ester was sealed in a Pyrex tube and heated to  $250^{\circ}$  for 12 h. After this time the ester was recovered unchanged.

##### *Method B*

A sample of the ester (7 g) was sealed in a Pyrex tube together with very dry calcium fluoride (0.5 g). The tube was heated at  $200^{\circ}$  for 12 h. The volatile products were then expanded into a 500 ml bulb and examined, after micro VPC separation, by mass spectrometry and IR spectroscopy.

Four products were obtained in addition to pentafluoroethane. These were identified as perfluoropropionyl fluoride and bis(pentafluoroethyl)ketone, and the fluoro olefins  $C_5F_{10}$  and  $C_4F_8$ , probably unbranched.

#### *Preparation of perfluoro 3-ethyl-3-pentyl butyrate (nc)*

The potassium salt of perfluoro 3-ethyl-pent-3-ol (36 g) was dissolved in acetonitrile. An equivalent amount of perfluorobutyryl chloride was added from a dropping funnel under the protection of a drying tube. A heavy fluorocarbon layer separated out and was isolated. The yield was 26 g. This material was fractionally distilled. The product, boiling at  $150-152^{\circ}$ , was shown by VPC to be 99% pure and was characterised as the ester perfluoro 3-ethyl-3-pentyl butyrate. (Found: C, 23.9; F, 72.9%.  $C_{11}F_{22}O_2$  requires C, 22.7; F, 72.0%.)

$^{19}F$  NMR spectrum:  $(CF_3CF_2)_3C-$  group;  $CF_3$ , 71.9;  $CF_2$ , 98.8.  $CF_3CF_2^A-$   $CF_2^B-CO-$  group;  $CF_3$ , 75.6;  $CF_2(A)$ , 116.6;  $CF_2(B)$  108.4 ppm relative to  $CFCl_3$ . The IR spectrum of this compound showed a strong  $C=O$  absorption at  $1847\text{ cm}^{-1}$ . The mass spectrum indicated an intense ion current at  $m/e$  563 representing the parent less one fluorine atom.

#### *Preparation of perfluoro 3-ethyl-3-pentyl octanoate (nc)*

This compound was prepared only in small quantity and characterised by analysis and mass spectrometry. The tertiary alcohol salt (10 g) and potassium perfluoro-octanoate (6 g) were added to 150 ml of dry acetonitrile. In this instance, the perfluoro-octanoic acid salt remained as a fine suspension. Phosgene (18 g)

was bubbled through the cooled solution over a period of 1 h. After this time the product was poured into water and the most dense phase isolated. This material was dried over calcium sulphate and purified by vacuum transfer, the quantity of material being insufficient for distillation. This material was characterised as the ester perfluoro 3-ethyl-3-pentyl octanoate by analysis and mass spectrometry only. (Found: C, 23.3; F, 74.7%.  $C_{15}F_{30}O_2$  requires C, 23.0; F, 75.4%.)

The mass spectrum showed a parent ion of  $m/e$  782 of low current intensity and an ion of  $m/e$  763 of very high intensity representing the parent less one fluorine atom.

*Preparation of perfluoro 3-methyl-3-pentyl propionate (nc)*

The potassium salt  $(C_2F_5)_2CF_3C-OK$  (15 g) and potassium perfluoropropionate (7 g) were dissolved in dry acetonitrile (150 ml) in a 250 ml flask fitted with a dropping funnel and condenser. The flask was cooled to  $0^\circ$  in an ice bath. Thionyl chloride (5 g) mixed with an equal volume of acetonitrile was slowly added from a dropping funnel. A white precipitate immediately formed. The mixture was stirred at  $0^\circ$  for 4 h. After this time the more dense fluorocarbon phase was separated and distilled. A VPC pure material was obtained of boiling point  $120^\circ$ . This was characterised as the ester perfluoro 3-methyl-3-pentyl propionate. (Found: C, 22.5; F, 71.6%.  $C_9F_{18}O_2$  requires C, 22.4; F, 70.9%.)

$^{19}F$  NMR spectrum:  $(CF_3CF_2)_2C-$  group;  $CF_3$ , 73.5;  $CF_2$ , 103.0.  $F_3C-C-$  group;  $CF_3$ , 58.2.  $CF_3CF_2-CO-$  group;  $CF_3$ , 76.5;  $CF_2$ , 108 ppm relative to  $CFCl_3$ . The integrated intensities were those expected for the structure. The IR spectrum showed a  $C=O$  vibration at  $1845\text{ cm}^{-1}$ .

*Preparation of perfluoro 3-ethyl-3-pentyl chloroformate (nc)*

Phosgene (5 g) was bubbled into dry acetonitrile (120 ml) at  $-20^\circ$ . A solution of the potassium salt (23 g) in acetonitrile (50 ml) was then added slowly, the temperature of the reaction mixture being maintained at  $-20^\circ$ . An exothermic reaction took place. Additional phosgene (16 g) was bubbled into the reaction mixture. The products were then allowed to stand and a more dense fluorocarbon layer separated. Vacuum transfer from residual KCl followed by distillation gave a VPC pure material characterised as perfluoro 3-ethyl-3-pentyl chloroformate, b.p.  $132^\circ$ . (Found: C, 21.8; F, 64.2%.  $C_8F_{15}O_2Cl$  requires C, 21.5; F, 63.5%.)

The mass spectrum of the product indicated a very intense ion current corresponding to  $m/e$  429, representing the parent ion less one fluorine atom. Ion currents at  $m/e$  413, parent less one chlorine atom, and  $m/e$  379, parent less one  $CF_3$  group, were observed in addition to an ion current attributable to  $-CO-Cl$ .

*Preparation of bis(perfluoro 3-methyl-3-pentyl) carbonate (nc)*

An excess of the potassium salt over phosgene was used in this experiment to avoid formation of the chloroformate. A 250 ml reaction flask was evacuated

and connected to a gas burette filled with phosgene to just below atmospheric pressure. A solution of the potassium salt (17.6 g) in acetonitrile (60 ml) was then run in with shaking. An additional 5 g of the potassium salt dissolved in acetonitrile (20 ml) was then added to react with any chloroformate. The more dense fluorocarbon layer was isolated. The fluorocarbon was then separated from potassium chloride by vacuum transfer. This was followed by distillation which gave 9 g of VPC pure liquid, b.p. 176°, characterised as bis(perfluoro 3-methyl-3-pentyl) carbonate. (Found: C, 22.6; F, 71.0%.  $C_{13}F_{26}O_3$  requires C, 22.3; F, 70.8%.)

$^{19}F$  NMR spectrum:  $(CF_3CF_2)_2C-O-$  group;  $CF_3$ , 79.7;  $CF_2$ , 113.8.  $F_3C-C-O-$  group;  $CF_3$ , 62.3 ppm relative to  $CFCl_3$ . Integrated intensities were in very good agreement with the proposed structure. The mass spectrum indicated an abundant ion at  $m/e$  363 corresponding to the fragment  $(C_2F_5)_2CF_3C-O-CO-$ . A weak ion current corresponding to the parent ion at  $m/e$  698 was observed.

Yields for all these experiments were about 25%.

#### ACKNOWLEDGEMENTS

The authors acknowledge the collaboration of many members of the laboratory, and in particular those of the analytical and spectroscopic group, without whose assistance this work could not have been completed.

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