Tetrahedron. Vol. 30, pp. 3539 to 3544. Pergamon Press 1974. Printed in Great Britain

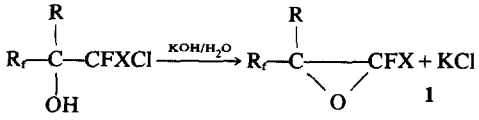
POLYHALOGENATED α-OXIDES—V
ROLE OF STERIC FACTORS IN REACTIVITY OF POLYFLUORINATED α-OXIDES

R. A. BEKKER,* G. V. ASRATYAN, B. L. DYATKIN and I. L. KNUNYANTS
Institute of Organoelement Compounds, USSR Academy of Sciences, Moscow, USSR

(*Received in the UK 4 January* 1974; *Accepted for publication* 17 *April* 1974)

Abstract—Steric shielding of the α-oxide 2-C-atom, as well as increase in the volume of the attacking nucleophilic agent, is shown to hinder the usual opening of polyfluorinated α-oxides at the 2-C-atom and to direct the nucleophilic attack to an other reaction centre. A mechanism of isomerisation of polyfluorinated α-oxides under the action of nucleophilic agents is suggested.

The methods of producing fluorine-containing α-oxides are based, mainly, on oxidation of corresponding fluoroolefines by oxygen (photochemically) or by hydrogen peroxide (in an alkaline medium). Until recently, only rare cases were known when these compounds could be synthesized by dehydrohalogenation of vicinal halogenoalcohols, i.e. by the method conventional for non-fluorinated α-oxides (see[1] and references cited there). Not long ago we showed[2-4] that heating of solutions of tertiary polyfluorochlorocarbinols in aqueous alkali gives polyfluorinated α-oxides in good yields.



1

a $R_f = CF_2Cl$, R = C_6H_5, X = F;
b $R_f = CF_2Cl$, R = C_6H_5, X = Cl;
c $R_f = CF_2Cl$, R = CH_3, X = Cl;
d $R_f = CF_2Cl$, R = $CH_2{=}CH{-}CH_2$, X = Cl;
e $R_f = CF_2Cl$, R = $CH_2{=}CH$, X = Cl;
f R = CF_2Cl, R = $CF_2{=}CF$, X = Cl;
g $R_f = CF_2Cl$, R = C_6F_5, X = Cl;
h $R_f = CF_2Cl$, R = C_6F_5, X = F;
i $R_f = CF_3$, R = C_6F_5, X = F;
j $R_f = CF_2Cl$, R = o-CF_3–C_6H_4, X = F;
k $R_f = CF_2Cl$, R = m-CF_3–C_6H_4, X = F;
l $R_f = CF_2Cl$, R = p-CF_3–C_6H_4, X = F

This reaction seemed somewhat unexpected, since, as is well known, the chlorine atom in the perfluoroalkyl group is not liable to nucleophilic substitution reactions (it may even be to some extent positively polarized[5]); moreover, polyfluorochlorocarbinols are highly acidic,[6,7] so that the nucleophilicity of the corresponding anions must be lowered. Heating with an alkali may cause haloformic decomposition. Nevertheless, this reaction proceeds rather smoothly. Evidently, the favourable statistical factor determined by the intramolecular character of the reaction is decisive here. Insolubility of the resulting α-oxides in water facilitates their isolation.

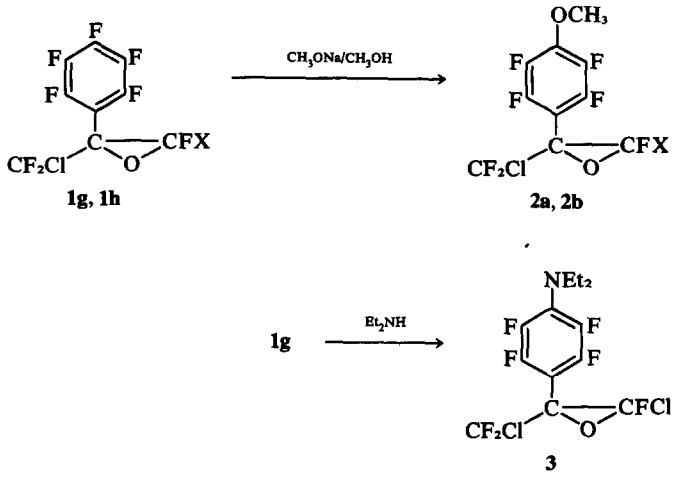
The reaction opens the way to a large group of previously unavailable (in view of the unavailability of corresponding fluoroolefines) fluorine-containing α-oxides. The starting alcohols are easily produced by reacting polyfluorochloroacetones with organomagnesium or organolithium compounds,[8] or by Friedel-Crafts condensation of these ketones with aromatic hydrocarbons.[9]

Our investigations[2-4,10] showed that these new α-oxides are easily opened by nucleophilic reagents at the central carbon atom, being, as a whole, analogues of the perfluoropropene and perfluoroisobutene oxides studied earlier.[1] However, the presence of various substituents at the central carbon atom, as well as variations of the CF_2 and CFCl groups in the oxirane ring revealed a number of specific features of the reactions of these compounds with nucleophiles, indicating that the reactivity of polyfluorinated α-oxides as a whole should be somewhat re-estimated.

In α-oxides with the C_6F_5-group at the 2-C-atom, the oxirane ring is rather stable to nucleophilic attack. These compounds either do not react with nucleophilic agents (AgF, KF, ROH), or there takes place a substitution of the fluorine atom in the para-position of the perfluorophenyl ring.

Evidently, this stability is conditioned by steric shielding of the central carbon atom by two ortho-atoms of fluorine. This supposition is confirmed by the consideration of models, and also by the non-equivalence of all the five fluorine atoms of the C_6F_5-group in ^{19}F NMR spectra, which indicates that the rotation of this group is hindered. It is interesting to note that a similar non-equivalence of fluorine atoms in the C_6F_5-group was observed by Sheppard and Foster for $C_6F_5SF_3$.[11]

To verify the supposition about the steric effect



1g, 1h

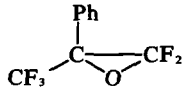
2a, 2b

1g

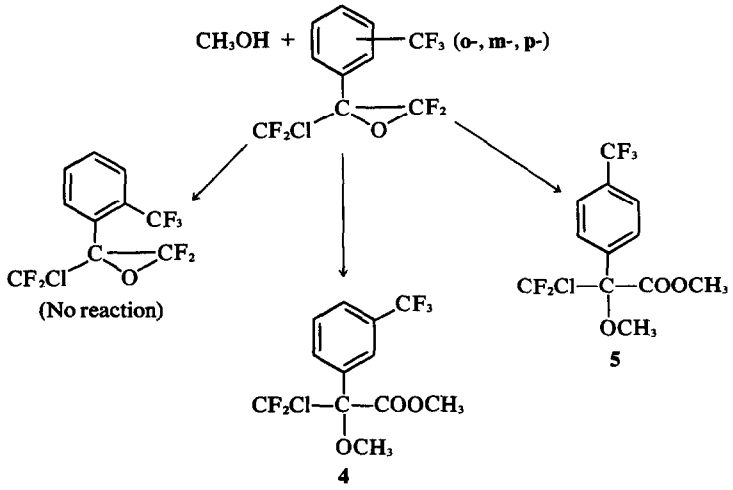
3

of ortho-substituents, we investigated the reaction of methanol with α-oxides containing the trifluoromethyl group in the ortho-, meta- and para positions of the phenyl ring at the 2-C-atom of the oxirane cycle. α-Oxides with the CF_3-group in meta- and para- positions proved to be easily opened by methanol, whereas the compound with the CF_3-group in the ortho-position exibited stability.

excess aqueous alkali, and therefore it can be isolated by the interaction of KOH in water with 1,3 - dichloro - 2 - phenyltetrafluoro - 2 - propanol,[2]

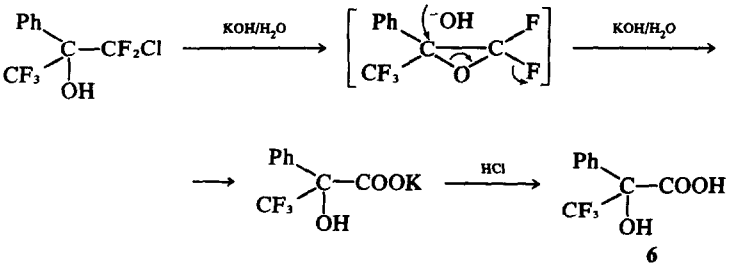


A



It is of interest that the ^{19}F NMR spectrum of the oxirane **1j** with the ortho-CF_3–C_6H_4 group at the 2-C-atom contains a double set of signals. Evidently, it may be concluded that there exists atropoisomerism in oxiranes with aromatic substituents at the central carbon atom.[4] Also worthy of attention is the fact that structurally analogous oxiranes **1a** and **A**, which differ only in that one of them includes the CF_3-group and the other the CF_2Cl, display different reactivity to nucleophiles. Oxirane **1a** does not isomerize when heated for a short period with whereas oxirane **A** under the same conditions is unstable and cannot be isolated, since it is opened by the hydroxyl ion with the formation of the corresponding oxyacid **6**.

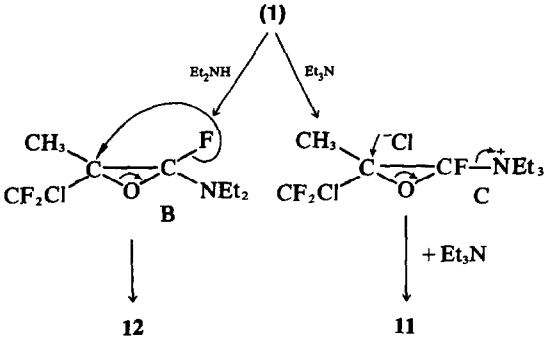
We attribute this to the fact that a more bulky CF_2Cl-group inhibits the attack of HO^- on the central carbon atom. In the case of oxiranes with the C_6F_5-group, in which the central carbon atom is shielded by the ortho-atoms of fluorine of the pentafluorophenyl ring, the replacement of the CF_2Cl-group by the CF_3-group does alter the



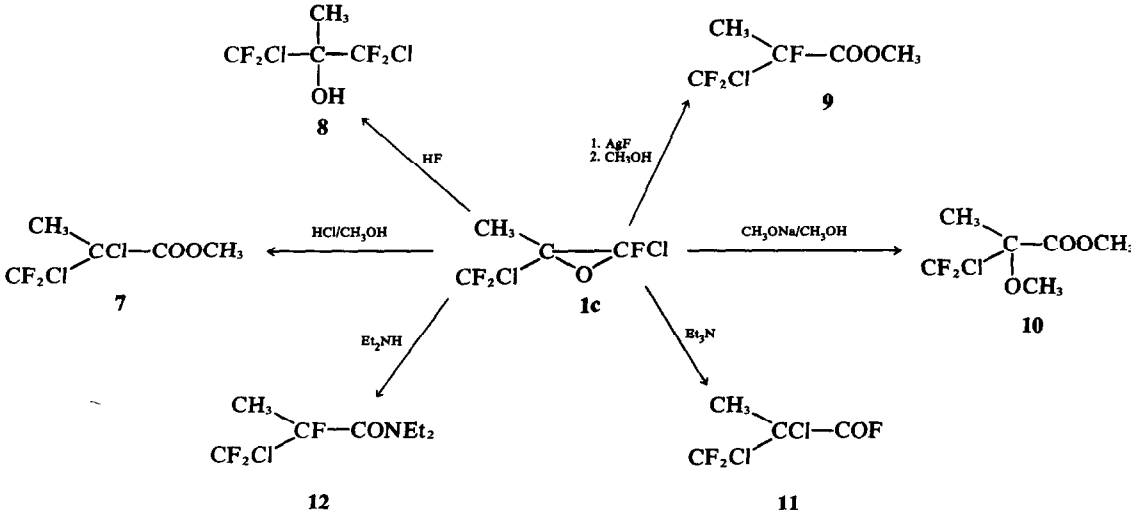
reactivity of these compounds and the both α-oxides **1a** and **1h** are stable to short heating with excess aqueous alkali.[3]

Another factor of steric character which influences the direction of reactions of polyfluorinated oxiranes is the bulk of the attacking nucleophilic reagent. Perfluoropropene oxide and perfluoroisobutene oxide undergo not only opening of oxirane ring by nucleophiles, but also isomerization to perfluoropropionic and perfluoroisobutyric acid fluorides respectively, with triethylamine, and formation of corresponding amides in reactions with secondary amines.[1, 12, 13] There is no satisfactory explanation of this rearrangement in the literature. The results obtained allow certain conclusions to be drawn in this respect.

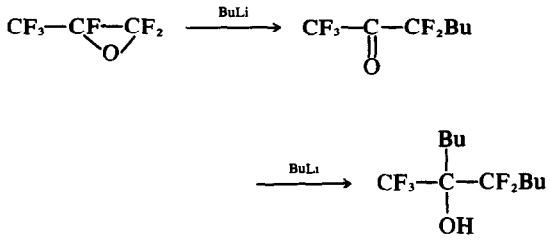
The behaviour of **1c** in reactions with the majority of nucleophilic agents is similar to that of perfluoroisobutene oxide, but differences are observed for reactions with amines. While the reaction with diethylamine gives a derivative of α-fluoro-acid **12**, the reaction with triethylamine leads to the formation of α-chloro-acid fluoride **11**. If we assume that isomerization precedes reaction with Et_2NH and that the reasons causing it are the same for Et_2NH and Et_3N, it remains unclear why in the case of Et_2NH the migrating atom is that of F, and in the case of Et_3N the migrating atom is that of Cl. This difference, however, can be well explained by the following scheme.

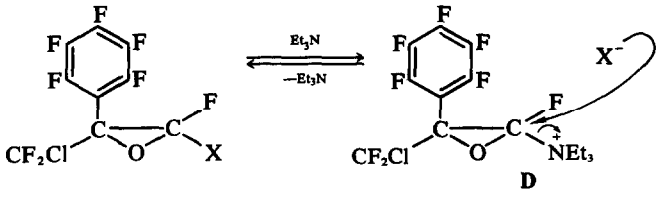


This scheme is constructed on the assumption that under the action of such bulky agents as tertiary amines the attack takes place not on the central carbon atom, as being sterically hindered, but on the more accessible terminal carbon atom. In both cases substitution of the Cl atom takes place. But in the case of Et_2NH oxirane (**B**) is formed which has a labile F atom in the α-position to the strong electron donor Et_2N-group and must therefore easily isomerize to diethylamide of α-fluoro-acid **12**. In the case of Et_3N quaternary ammonium



salt C is formed, where the F atom is in the α-position to the electron acceptor ammonium group and is not labile, as a result of which the oxirane ring is opened in the usual manner by the Cl^-, found on the outer sphere of the ammonium complex. The fact that, unlike oxirane **1c**, compounds **1g** and **1h** are not isomerized under the effect of catalytic amount of Et_3N can also be easily explained.



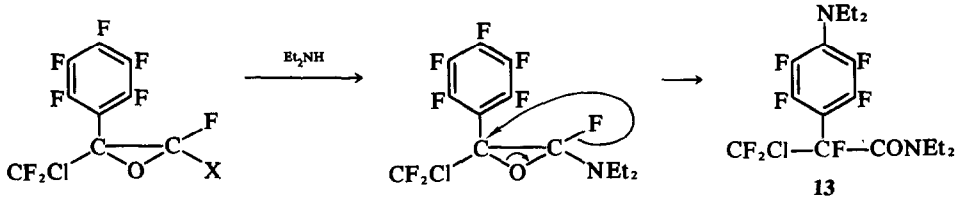


D

These oxiranes are not attacked by nucleophilic agents on the central C atom in view of the steric influence of the ortho-atoms of F. For this reason X^- from the outer sphere of the intermediate oxirane **D** does not attack the 2-C-atom and, if these oxiranes do react with Et_3N, the reaction is reversible and no transformation takes place. In the reaction with Et_2NH, however, there are no obstacles for the intramolecular rearrangement.

of butyllithium on perfluoropropene oxide.[14] Isomerization, however, is not observed here, while opening of the oxirane cycle takes place from the side of the 3-C-atom. Rare cases of nucleophilic substitution of F in monofluorinated oxiranes are also known.[15,16]

Thus, if nucleophilic attack on the central carbon atom of a polyfluorooxirane is hindered because of the shielding effect of substituents or in view of a



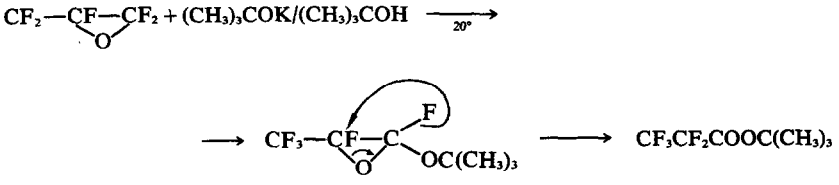
13

We have demonstrated the general character of this phenomenon. As is known, the reaction of perfluoropropene oxide with alcoholates of aliphatic alcohols gives esters of alkoxyperfluoropropionic acids.[1] By reacting perfluoropropene oxide with solution of $(CH_3)_3COK$ in $(CH_3)_3COH$ we obtained $CF_3CF_2COOC(CH_3)_3$, as should be expected according to the scheme given above. Perfluoropropene oxide does not change under the action of alkali metal fluorides in $(CH_3)_3COH$. Evidently, oxirane **E** substituted at the terminal carbon atom is actually an intermediate in this reaction.

There is one indication[14] concerning the attack on the terminal carbon atom; this relates to the action large bulk of the attacking agent, the attack is directed to other reaction centres, particularly the terminal carbon atom, this being ultimately equivalent to rearrangement of oxirane into an α-halogeno-acid halide. This rearrangment probably proceeds through the oxirane substituted at the terminal carbon atom by the residue of the nucleophile.

EXPERIMENTAL

^{19}F NMR spectra were obtained on a Hitachi H-60 spectrometer at 56·4 MHz, with CF_3COOH as external standard; IR spectra were obtained on a UR-10 instrument. GLC analysis: heat conductivity detector, adsorbent-Chromosorb-W, the liquid phase SE-30, 13%.



1,3 - *Dichloro* - 1,2 - *epoxy* - 2 - (*p-methoxytetrafluorophenyl*) *perfluoropropane* **2a**. To a solution of 5 g of α-oxide **1g** in 10 ml of methanol a solution of 3·2 g of KOH in 50 ml of methanol was added, the mixture allowed to stand for 20 h, then poured into water, extracted with ether, the extract was dried with magnesium sulphate, the ether distilled off, and the residue vacuum-distilled. 4·1 g (80%) of α-oxide **2a** were obtained with b.p. 68°/1·0 mm. Found: C, 33·60; H, 0·91; F, 37·00. Calculated $C_{10}H_3F_7Cl_2O_2$: C, 33·45; H, 0·84; F, 37·04%. The ^{19}F NMR spectrum is given in the Table.

3 - *Chloro* - 1,2 - *epoxy* - 2 - (*p-methoxytetrafluorophenyl*) *perfluoropropane* **2b**. Into a 150 ml flask provided with a stirrer, a reflux condenser and a dropping funnel a solution of 5 g of α-oxide **1h** in 5 ml of methanol is placed and a solution of sodium methylate in methanol was added dropwise until the reaction to phenolphthalein becomes alkaline; then the mixture is stirred for 2 h and poured into water. The separated oil is dried over magnesium sulphate and distilled. 3·8 g (83%) of α-oxide **2b** are obtained, b.p. 102°/20 mm. Found: C, 35·29; H, 0·96; F, 44·28. Calculated $C_{10}H_3F_8ClO_2$: C, 35·06; H, 0·87; F, 44·37%. The ^{19}F NMR spectrum is given in the Table.

1,3 - *Dichloro* - 1,2 - *epoxy* - 2 - (*p* - *diethylaminotetrafluorophenyl*) - *perfluoropropane* **3**. A solution of 4·8 g of α-oxide **1g** and of 4·5 g of diethylamine in 15 ml of ether is allowed to stand for 8 days. The precipitate was filtered off and the filtrate was distilled. 3·9 g (71%) of α-oxide **3** were obtained with b.p. 80°/0·1 mm. Found: N, 3·68. Calculated $C_{13}H_{10}F_7Cl_2O$: N, 3·99%. The ^{19}F NMR spectrum is given in the Table.

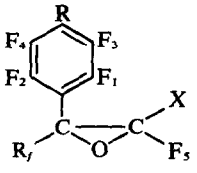
2 - *Oxy* - 2 - *phenyltrifluoropropionic acid* **6**. Into a 150 ml flask there were placed 5·2 g (0·02 mole) of 1 - chloro - 2 -phenylpentafluoropropanol - 2[17] and 4·48 g (0·08 mole) of KOH dissolved in 70 ml of water. The reaction mixture was boiled and stirred for 3 h, after which it was acidified with hydrochloric acid and extracted with ether. The combined ethereal extracts were dried over magnesium sulphate, the ether was evaporated and the product was recrystallized from hexane. 3·3 g (75%) of **6** are obtained, m.p. 110°. Lit[18]: m.p. 110·5–111°. The IR-spectrum coincides with reported.[18] ^{19}F NMR spectrum: singlet, $\delta = -2{\cdot}8$ ppm (CF_3).

Methyl 3,3 - *difluoro* - 2,3 - *dichloro* - 2 - *methylpropionate* **7**. To 10 ml of saturated methanol solution of hydrogen chloride 2·5 g of α-oxide **1c** are added under stirring, the mixture is stirred for 20 min at 40–45°, then poured into water, the organic layer was separated, dried with magnesium sulphate and distilled. 2·2 g (84%) of the ester **7** were obtained, b.p. 85°/80 mm. IR-spectrum: 1760 cm^{-1} (C=O). ^{19}F NMR spectrum: AB system with centre at $\delta = -20{\cdot}6$ ppm, $J_{F_AF_B} = 162{\cdot}5$ Hz. Found: C, 28·27; H, 2·97; F, 18·43. Calculated $C_5H_6F_2Cl_2O_2$: C, 28·99; H, 2·92; F, 18·35%.

1,3 - *Dichloro* - 2 - *methyltetrafluoro* - 2 - *propanol* **8**. A 50 ml steel autoclave was charged with 5·0 g of α-oxide **1c** and 10 ml of anhydrous hydrogen fluoride, was heated for 1 h at 90°, and then the reaction mixture was poured onto ice, the organic layer was separated, dried over magnesium sulphate and distilled. 5·2 g of the alcohol **8** were obtained, b.p. 118°. Lit[8]: b.p. 116·5–118°. The substance was compared by GLC with the authentic sample obtained by the described method.[8] ^{19}F NMR spectrum: AB system with centre at $\delta = -16{\cdot}1$ ppm, $J_{F_AF_B} = 169$ Hz.

Methyl 2,3,3 - *trifluoro* - 3 - *chloro* - 2 - *methylpropionate* **9**. To a solution of 4·8 g of silver fluoride in 40 ml of anhydrous acetonitrile 5·0 g of α-oxide **1c** were added dropwise, the mixture was stirred at 40–50° for 2 h, 5 ml of absolute methanol were added, and the reaction mixture was decomposed by water, the organic layer was separated, dried with magnesium sulphate and distilled. 3·0 g (61%) of the ester **9** were obtained with b.p. 130–132°. Found: C, 31·89; H, 3·23; F, 30·20. Calculated $C_5H_6F_3ClO_2$: C, 31·53; H, 3·15; F, 29·91%. IR-spectrum: 1770 cm^{-1} (C=O). ^{19}F NMR spectrum: of ABX type with

Table 1. Chemical shifts (ppm) of ^{19}F atoms in polyfluorinated α-oxides containing pentafluorophenyl group



A R = OCH_3, $R_f = CF_2Cl$, X = Cl
B R = OCH_3, $R_f = CF_2Cl$, X = F_6
C R = NEt_2, $R_f = CF_2Cl$, X = Cl

	R	F_1	F_2	F_3	F_4	F_5	F_6
A	−18·4	+59·3	+62·2	+79·0	+79·8	+16·2	—
B	−16·1	+62·9	+63·5	+80·6	+81·3	+37·1	+27·5
C	−18·7	+61·5	+64·0	+72·5	+73·1	+15·6	—

Methyl 3 - *chloro* - 2 - (*m* - *trifluoromethylphenyl*) - 2 - *methoxy* - 3,3 - *difluoropropionate* **4**. A solution of 4·56 g of α-oxide **1k** in 15 ml of methanol was allowed to stand at room temperature for 3 days, after which it was decomposed by water, the oil was separated, washed with water, dried with magnesium sulphate and distilled; 4·13 g (84·1%) of the ester **4** are obtained with b.p. 100°/3 mm. Found: C, 43·45; H, 3·00; F, 28·45. Calculated $C_{12}H_{10}F_5ClO_3$: C, 43·35; H, 3·03; F, 28·55%. IR-spectrum: 1759 cm^{-1} (C=O). ^{19}F NMR spectrum: $\delta = -15{\cdot}0$ ppm (CF_3), $\delta = -20{\cdot}9$ ppm (CF_2Cl).

Methyl 3 - *chloro* - 2 - (*p* - *trifluoromethylphenyl*) - 2 - *methoxy* - 3,2 - *difluoropropionate* **5**. By the same procedure, from 5·0 g of α-oxide **1l** 4·4 g (80·9%) of the ester **5** were obtained, bp 102°/2 mm. Found: C, 43·90; H, 3·03; F, 29·18. Calculated $C_{12}H_{10}F_5ClO_3$: C, 43·35; H, 3·03; F, 28·55%. IR-spectrum: 1760 cm^{-1} (C=O). ^{19}F NMR spectrum: $\delta = -14{\cdot}8$ ppm (CF_3), $\delta = -21{\cdot}2$ ppm (CF_2Cl). (CF_2Cl).

additional splitting of X-part on CH_3-group; $\delta = -13{\cdot}5$ ppm (CF_2Cl–AB-part), $\delta = +31{\cdot}9$ ppm $J_{F_AF_X} = 8{\cdot}9$ Hz, $J_{f_AF_X} = 8{\cdot}9$ Hz, $J_{F_BF_X} = 9{\cdot}7$ Hz, $J_{F_XCH_3} = 21{\cdot}4$ Hz, $J_{F_AF_B} = 172$ Hz.

Methyl 3,3 - *difluoro* - 3 - *chloro* - 2 - *methyl* - 2 - *methoxypropionate* **10**. To a sodium methylate solution (prepared from 1·5 g of metallic sodium and 50 ml of absolute methanol) 5·8 g of α-oxide **1c** are added at 10°, the mixture is stirred for 1 h, then poured into water, the organic layer is dried with magnesium sulphate and distilled. 4·8 g of the ester **10** are obtained, b.p. 85°/27 mm. Found: C, 35·37; H, 4·39; F, 18·06. Calculated $C_6H_9F_2ClO_3$: C, 35·59; H, 4·44; F, 18·75%. IR-spectrum: 1760 cm^{-1} (C=O). ^{19}F NMR spectrum: singlet, $\delta = -16{\cdot}7$ ppm.

3,3 - *Difluoro* - 2,3 - *dichloro* - 2 - *methylpropionic acid fluoride* **11**. To 5·6 g of α-oxide **1c** one drop of triethylamine was added and the compound is boiled for 10–15 min. Acid fluoride **11** was obtained. ^{19}F NMR spectrum of ABX type: AB centre at $\delta = -16{\cdot}4$ ppm (CF_2Cl), F_X signal at $\delta = -106$ ppm (COF); $J_{F_AF_B} = 166{\cdot}0$ Hz, $J_{F_AF_X} = 15{\cdot}3$ Hz $= J_{F_BF_X} = 15{\cdot}3$ Hz. The unpurified acid fluoride **11** was treated with methanol, washed with water, the organic layer was dried with magnesium sulphate and distilled. 4·5 g (89%) of ester were obtained, the substance having been compared by GLC and ^{19}F NMR techniques with authentic sample of **7**.

Diethylamide of 2,3,3 - *trifluoro* - 3 - *chloro* - 2 - *methylpropionic acid* **12**. To a solution of 12 ml of diethylamine in 30 ml of absolute ether 10·0 g of α-oxide **1c** were added dropwise and the mixture was allowed to stay for one day at room temperature; the precipitate was then filtered off, the solvent was distilled off together with excess diethylamine, and the residue was vacuum distilled. 8·4 g (70%) of the diethylamide **12** were obtained with b.p. 84–85°/11 mm. Found: C, 41·19; H, 5·65. Calculated $C_8H_{13}F_3ClNO$: C, 41·07; H, 5·57%. IR-spectrum: 1655 cm^{-1} (C=O). ^{19}F NMR spectrum: $\delta = -15{\cdot}3$ ppm (CF_2Cl), $\delta = +78{\cdot}6$ ppm (CF); $J_{F_AF_B} = 169$ Hz, $J_{F_AF_X} = 9{\cdot}6$ Hz, $J_{F_BF_X} = 9{\cdot}6$ Hz, $J_{F_XCH_3} = 22{\cdot}5$ Hz.

Diethylamide of 3 - *chloro* - 2 - (*p* - *diethylaminotetrafluorophenyl*) - *perfluoropropionic acid* **13**. (A) A mixture of 5 g of α-oxide **1h** and 7 ml of dry diethylamine was boiled for 20 h, then washed with water and extracted with ether. The ethereal extract was dried over magnesium sulphate, the ether was distilled off, and the residue was vacuum distilled. 5 g (77·2%) of the amide **13** were obtained with b.p. 152/1·0 mm. Found: C, 47·21; H, 4·84; F, 6·33. Calculated $C_{17}H_{20}F_7Cl_2O$: C, 46·74; H, 4·61; F, 6·41%. IR-spectrum: 1680 cm^{-1} (C=O). ^{19}F NMR spectrum: $\delta = -13{\cdot}6$ ppm (CF_2Cl), $\delta = +62{\cdot}7$ ppm (F_{ortho}) $\delta = +73{\cdot}4$ ppm (F_{meta}), $\delta = +85{\cdot}0$ ppm (CF). (B) In a similar fashion from 5 g of α-oxide **1g** and 7 ml of diethylamine 4·0 g of the amide **13** were obtained.

Tert-butyl perfluoropropionate **14**. A 150 ml flask equipped with a thermometer, a stirrer, a gas inlet pipe and a reflux condenser (dry ice-acetone) was charged with 1 g (0·025 g.at.) of metallic potassium dissolved in 70 ml of absolute tert-butyl alcohol, and then 4·3 g (0·025 m) of perfluoropropylene oxide were passed in at 15–20°. The reaction was washed with water, the organic layer was separated, dried over magnesium sulphate and distilled. 5·2 g (91%) of the ester **14** was obtained, b.p. 45°/100 mm. Found: C, 38·02; H, 4·17; F, 42·75. Calculated $C_7H_9F_5O_2$: C, 38·21; H, 4·09; F, 43·15%. IR-spectrum: 1783 cm^{-1} (C=O). ^{19}F NMR spectrum: singlet, $\delta = +6{\cdot}2$ ppm (CF_3); singlet, $\delta = +45{\cdot}0$ ppm (CF_2).

REFERENCES

[1] P. Tarrant, C. O. Allison and K. P. Barthold, *Fluorine Chem. Reviews* **5**, 71 (1971)
[2] R. A. Bekker, G. V. Asratyan, B. L. Dyatkin and I. L. Knunyants, *Doklady Akad. Nauk SSSR*, **204**, 606 (1972)
[3] R. A. Bekker, G. V. Asratyan and B. L. Dyatkin, *Zhr. Org. Khim.* **9**, 1635 (1973)
[4] R. A. Bekker, G. V. Asratyan and B. L. Dyatkin, *Ibid.* **9**, 1640 (1973)
[5] R. N. Haszeldine, *Nature* **167**, 139 (1951)
[6] B. L. Dyatkin, E. P. Mochalina and I. L. Knunyants, *Tetrahedron* **21**, 2991 (1965)
[7] J. S. Chang, J. T. Price, A. J. Tomlinson and C. J. Willis, *Can. J. Chem.* **50**, 512 (1972)
[8] M. H. Kaufman and J. D. Braun, *J. Org. Chem.* **31**, 990 (1966)
[9] B. S. Farah, E. E. Gilbert and J. P. Sibilia, *J. Org. Chem.* **30**, 998 (1965)
[10] R. A. Bekker, G. V. Asratyan and B. L. Dyatkin, *Zhr. Org. Khim.* **9**, 1644 (1973)
[11] W. A. Sheppard and S. S. Foster, *J. Fluor. Chem.* **2**, 53 (1972)
[12] D. Sianesi, A. Pasetti and E. Tarli, *J. Org. Chem.* **31**, 2312 (1966)
[13] I. L. Knunyants, V. V. Shokina, V. V. Tyuleneva, Yu. A. Cheburkov and Yu. E. Aronov, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1966, 1831
[14] P. Tarrant and E. Stump, *Zhr. V. Khim. Ob. im. Mendeleeva* **15**, 34 (1970)
[15] J. Cantacuzene and J. M. Normant, *C.R. Acad. Sci.* **C271**, 748 (1970)
[16] A. Kirrman and R. Nouri-Bimorghi, *Bull. Soc. Chim. France* 1972, 2338
[17] P. M. Barna, *Austr. J. Chem.* **21**, 1089 (1968)
[18] J. M. Dale, D. L. Dull and M. S. Mosher, *J. Org. Chem.* **34**, 2543 (1969)