Translated from *Uspekhi Khimii*, **45**, 1177 - 1204 (1976) U.D.C. 547.464.6

Derivatives of Perfluoromethacrylic Acid

E.M.Rokhlin, Ë.G.Abduganiev, and U.Utebaev

Methods for the synthesis and the chemical properties of perfluoromethacrylic acid derivatives are examined. The most characteristic reactions of these compounds are those with nucleophiles, including very weak nucleophiles; cycloaddition reactions are very common, and some perfluoromethacrylic acid derivatives polymerise and copolymerise with various unsaturated compounds.
The bibliography includes 83 references.

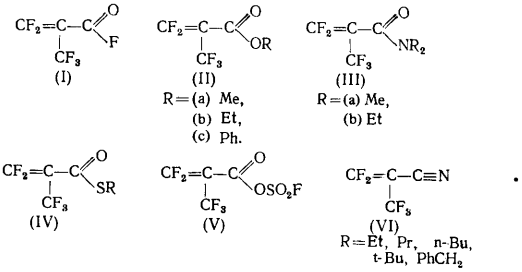
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I. INTRODUCTION

The comparatively ready availability and high reactivity of derivatives of $\alpha\beta$-unsaturated fluorine-containing carboxylic acids are responsible for the understandable interest shown in these compounds by investigators working in the fields of both pure and applied chemistry of organofluorine compounds. Derivatives of perfluoromethacrylic acid (**PFMA**) proved to be particularly reactive. Vigorous studies on compounds belonging to this class did not begin until very recent years, but during this short period it has proved possible to demonstrate the wide variety of their reactions and their synthetic possibilities. One cannot rule out the possibility that some **PFMA** derivatives may be used as monomers.

PFMA itself and its salts have not so far been obtained. It is quite likely that these compounds (particularly the salts) are altogether incapable of existence, since their molecules would contain simultaneously a nucleophilic centre (the COOH or COO^- group) and the highly electrophilic group $CF_2=C(CF_3)$. However, PFMA derivatives have been described in the literature: the acid fluoride (I), esters (II), dialkylamides (III), esters of the corresponding thiolo-acid (IV), the mixed anhydride of PFMA and fluorosulphonic acid (V), and perfluoromethacrylonitrile (VI).



This review describes methods for the synthesis of these derivatives and their chemical reactions.

II. METHODS OF SYNTHESIS

The high reactivity of PFMA derivatives as a rule precludes the use for their synthesis of the usual synthetic methods for perfluoro-olefins or perfluorocarboxylic acid derivatives. In most cases it has been necessary to develop special methods (or special procedures) in order to obtain these compounds.

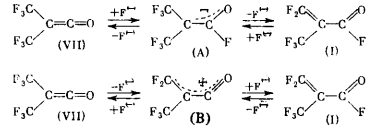
1. The Isomerisation of Bis(trifluoromethyl)keten

The first **PFMA** derivative, the acid fluoride (I), was obtained by the isomerisation of the comparatively readily available bis(trifluoromethyl)keten (**VII**):[1]

$$(CF_3)_2C{=}CF_2 \xrightarrow{H_2O} (CF_3)_2CHCOOH \xrightarrow{P_2O_5} (CF_3)_2C{=}C{=}O \xrightarrow[\text{catalyst}]{t^\circ} \underset{\text{(VII)}}{} \rightarrow CF_2{=}C(CF_3){-}COF \quad \text{(I)}$$

This reaction takes place when gaseous bis(trifluoromethyl)keten is passed over NaF at 200–300°C[2-5] or through a hollow glass tube at 400°C[6] and also on heating under pressure with glass wool[1], with a catalytic amount of $Et_2O.BF_3$,[7] or with butylether (preferably in the presence of $ZnCl_2$).[1]

The reaction is reversible; resulting in the formation of equilibrium mixtures containing about 60% of bis(trifluoromethyl)keten (b.p. 5–6°C) and about 40% of perfluoromethacryloyl fluoride (b.p. 51.5°C). The catalytic effect of NaF indicates the intermediate formation of a mesomeric fluorine-containing carbanion (A); in the absence of NaF, small amounts of F^- ions are obtained, probably as a result of the etching of the glass[6]. On the other hand, in the isomerisation under the influence of Lewis acids ($ZnCl_2$ and BF_3), the elimination of the F^- anion with intermediate formation of a mesomeric carbonium ion (B) is postulated[7]:

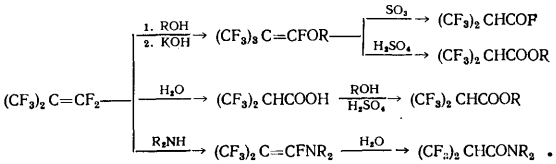


The isomerisation of bis(trifluoromethyl)keten is the most convenient method for the preparation of perfluoromethacryloyl fluoride. However, unfortunately other **PFMA** derivatives cannot usually be obtained directly from the acid fluoride, since attack by nucleophiles is directed primarily to the β-carbon atom of the "acrylic" system and not to the carbonyl group (see Section III). The formation of PFMA derivatives from the fluoride (I) therefore requires protection of the reactive $CF_2=C<$ group (for

example by halogenation) followed by reaction with a nucleophile (e.g. an alcohol), and the removal of the protecting group[8]†. Incidentally, in most cases it is more convenient to use other methods for the synthesis of PFMA derivatives—dehydrofluorination of derivatives of α-hydrohexafluoroisobutyric acid and electrophilic elimination of alkyl fluorides from alkoxypolyfluoroisobutenes.

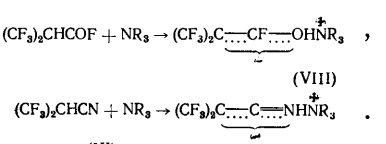
2. Dehydrofluorination of α-Hydrohexafluoroisobutyric Acid Derivatives

Derivatives of α-hydrohexafluoroisobutyric acid (HFIBA) are fairly readily available; they are obtained from perfluoroisobutene (see, for example, Refs. 9–11):

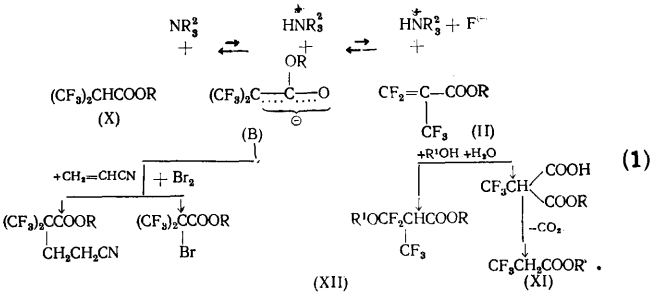


These derivatives contain in the α-position a labile hydrogen atom and in principle should be readily dehydrofluorinated in the presence of bases. However, the usual methods for the preparation of perfluoro-olefins—dehydrofluorination of fluoroalkanes by alkalis[12–14]—is inapplicable in this instance, since PFMA derivatives very readily undergo further attack by the nucleophiles[7] (see Section III).

When the acid fluoride of HFIBA is acted upon by triethylamine, only the first dehydrofluorination stage is achieved—the elimination of the proton—and the stable salt (VIII), containing the mesomeric perfluoroisobutenoxide anion, is formed[1]. The nitrile of HFIBA (IX) reacts similarly[15]:

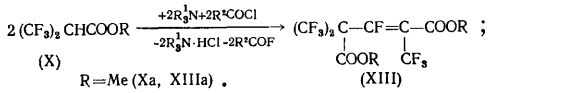


HFIBA esters (X) in which the hydrogen atom is less mobile, form on treatment with a tertiary amine equilibrium mixtures containing mainly the initial ester together with small amounts of the mesomeric carbanion (C) and PFMA esters (II). The addition of a third component, which reacts either with the carbanion or with the PFMA ester, displaces the equilibrium towards the formation of the final products[6,14]. Indeed, in the presence of triethylamine or pyridine, HFIBA esters are readily brominated[16,17] and cyanoethylated[18] and, on treatment with water and alcohols, give respectively the esters of ββ-trifluoropropionic acid (XI)[19] and those of α-hydro-β-alkoxypentafluoroisobutyric acids (XII)[20]:

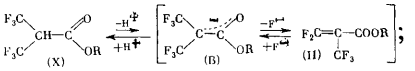


(1)

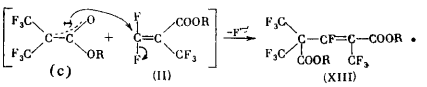
The removal of the F^- anion from the equilibrium (for example on treatment with an acyl chloride) should lead to the formation of the PFMA ester. It is known that, when nonafluoroisobutane $(CF_3)_3CH$ reacts with triethylamine and benzoyl chloride it is dehydrofluorinated, yielding perfluoroisobutene $(CF_3)_2C{=}CF_2$.[20] However, the analogous reaction with the HFIBA ester leads only to the "dimer" (XIIIa):[21,22]



Evidently this involves the intermediate formation of the PFMA ester (II), but the exceptional reactivity of this compound precludes its isolation, since it reacts immediately with the fluoro-carbanion (C); substitution of the vinyl fluorine atom yields the "dimer" (XIII):



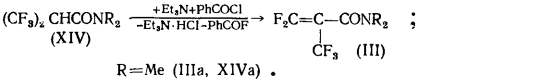
(2)



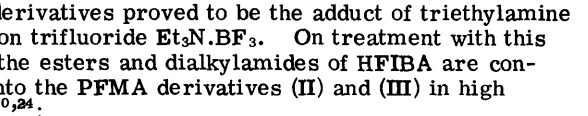
(3)

The analogous interaction of triethylammonium perfluoroisobutenoxide (VIII) with an acyl chloride leads to "δ-lactone-dimers"[6,23] [cf. Eqn. (10)].

The dimethylamide of PFMA, which is less reactive than its fluoride and esters, can be obtained from the saturated amide (XIVa) on treatment with triethylamine and benzoyl chloride[7]:



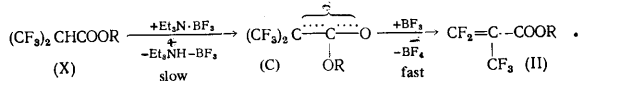
A very convenient dehydrofluorinating agent for the synthesis of PFMA derivatives from the corresponding HFIBA derivatives proved to be the adduct of triethylamine with boron trifluoride $Et_3N.BF_3$. On treatment with this adduct, the esters and dialkylamides of HFIBA are converted into the PFMA derivatives (II) and (III) in high yields[7,10,24]:



† The method for the preparation of methyl perfluoromethacrylate from the acid fluoride via perfluoromethacryloyl fluorosulphonate (V) is described at the end of Section II.

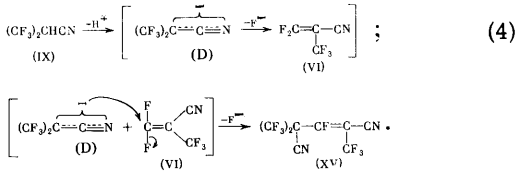
‡ The ester of difluoromethylenemalonic acid $F_2C{=}C(COOMe)_2$ has been obtained similarly from the ester of trifluoromethylmalonic acid[25].

There are no "dimers" in the reaction products even when HFIBA esters are dehydrofluorinated. Evidently the nucleophilic properties of the adduct $Et_3N.BF_3$ are reduced so much that the carbanion (C) is formed slowly compared with the next stage—the elimination of the F^- anion from the carbanion:



The carbanion (C) does not accumulate in the mixture and there is not sufficient time for its reaction with the PFMA ester, which would lead to the "dimer" (XIII). The dehydrofluorination of the dimethylamide of PFMA is accelerated in the presence of triethylamine and retarded in the presence of $Et_2O.BF_3$. This apparently confirms that the slowest stage determining the rate of the entire dehydrofluorination process is heterolysis of the C–H bond[10].

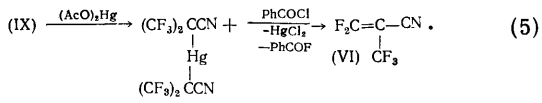
When an attempt was made to synthesise perfluoromethacrylonitrile by this procedure from the nitrile of HFIBA, only the "dimer" (XV) was obtained. The equilibrium in the heterolysis of the C–H bond of a strong CH acid such as the nitrile (IX) is displaced to the right[15], so that sufficient carbanion (D) is obtained for it to be able to react with perfluoromethacrylonitrile, forming the dinitrile (XV)[10]:



(4)

When the less basic adduct of pyridine and boron trifluoride was used, only the "dimer" was again obtained[10].

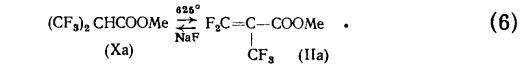
Perfluoromethacrylonitrile can be synthesised from the saturated nitrile (IX) by an indirect procedure—via an organomercury derivative[26]:



(5)

Yet another method for the synthesis of PFMA derivatives from the corresponding HFIBA derivatives involves thermal dehydrofluorination in the vapour phase over a catalyst. In the dehydrofluorination of the fluoride of HFIBA, the reaction is complicated by isomerisation and dimerisation. Thus, when the vapour of the HFIBA fluoride was passed over NaF, a mixture of perfluoromethacryloyl fluoride and bis(trifluoromethyl)keten was obtained[9]. Under other conditions, treatment with KF leads to the formation of "δ-lactone-dimers" [cf. Eqn. (10)] and at 400°C over glass wool one obtains a mixture containing 1,1,3,3,3-pentafluoropropene and other products in addition to perfluoromethacryloyl fluoride and bis(trifluoromethyl)keten[8].

Methyl perfluoromethacrylate is obtained by the dehydrofluorination of the methyl ester of HFIBA over sodium chloride[9,27]:

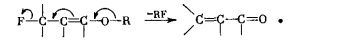


(6)

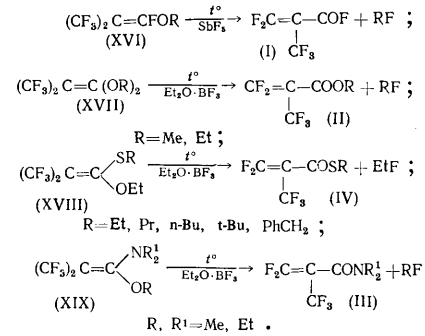
This results in the formation of an equilibrium mixture containing almost equal amounts of the dehydrofluorination products and of the initial saturated ester; the separation of the mixture by distillation is difficult owing to the similar boiling points of these two compounds. It has been stated (without experimental evidence) that it is useful to employ NaF together with quartz in this reaction[27] §.

3. Electrophilic Elimination of Alkyl Fluorides from Alkoxypolyfluoroisobutenes

One of the possible ways of forming a fluorine-containing conjugated $\alpha\beta$-unsaturated carbonyl system involves the elimination of an alkyl fluoride from an alkoxyfluoroolefin[29-31]:



This method, which has not been widely used in other instances, has been successfully employed to synthesise PFMA derivatives from the relatively readily available alkoxypolyfluoroisobutenes[7,32-34]. Thus, when alkyl perfluoroisobutenyl ethers (XVI) are heated in the presence of catalytic amounts of SbF_5 or $Et_2O.BF_3$ with simultaneous distillation of the product, perfluoromethacryloyl fluoride is formed[33]. On heating dialkylacetals of bis(trifluoromethyl)keten (XVII), dialkylthioacetals (XVIII), or *ONN*-trialkylaminoacetals (XIX) with a catalytic amount of $Et_2O.BF_3$, the corresponding esters[33], thiolo-esters[34], or dialkylamides of PFMA are formed[33] ¶.



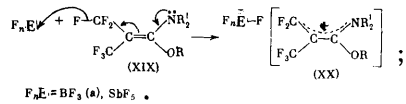
These reactions are carried out at approximately 100–140°C. Ethyl fluoride is usually split off under somewhat milder conditions than methyl fluoride[7,33]. On heating to 200°C, the aminoacetal (XIX, R = R^1 = Me) is cleaved even in the absence of a catalyst. The role of the Lewis acid evidently involves the elimination of the allyl fluorine atom from the alkoxyolefin, which leads to the formation of a mesomeric carbonium ion. Stable salts (XX) containing

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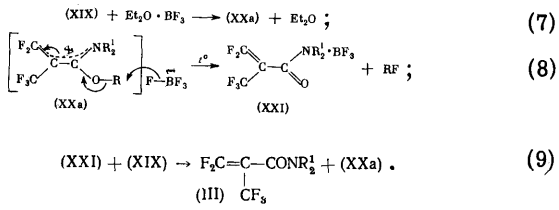
§ In the dehydrofluorination of 2,3,3,3-tetrafluoropropionyl fluoride, the use of NaF and quartz makes it possible to obtain perfluoroacryloyl fluoride in a high yield. The tube is packed alternately with these two catalysts, which are arranged in layers[28].

¶ Perfluoroacryloyl fluoride has been obtained similarly from the esters $CF_3CF{=}CFOR$[7,33], and the esters of difluoromethylenemalonic acid $CF_2{=}C(COOR)COOR^1$ have been synthesised from the acetals of alkoxycarbonyltrifluoromethylketens[35].

such cations have been obtained from the aminoacetals (XIX)[7,33]:



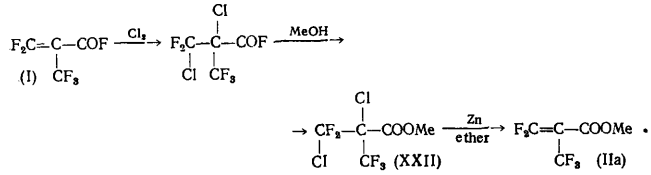
The cleavage of aminoacetals on heating with catalytic amounts of a Lewis acid is carried out in accordance with the following scheme (each stage has been confirmed experimentally): the formation of a salt (XXa) [Eqn. (7)]; the cleavage of this salt on heating owing to the alkylation of the complex anion BF_4^- by the mesomeric carbonium ion [Eqn. (8)]; the exchange reaction between the adduct of the dialkylamide of PFMA with boron trifluoride (XXI), on the one hand, and the next aminoacetal molecule, on the other, which results in the formation of the final product—the dialkylamide of PFMA (III)—and the regeneration of the salt (XXa) [Eqn. (9)]; the salt is again cleaved and this is continued until almost the entire aminoacetal is converted into the alkyl fluoride and the dialkylamide of PFMA[7,33]:



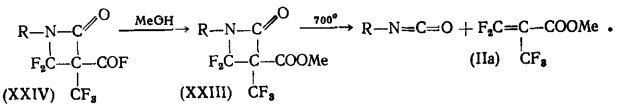
The mechanism of the cleavage of the esters (XVI), the acetals (XVII), and the thioacetals (XVIII) probably differs in detail from the above scheme, but the role of the Lewis acid as an agent for the elimination of the F^- ion remains[7].

4. Other Methods for the Synthesis of PFMA Derivatives

A PFMA ester was obtained for the first time by the dechlorination of an ester of $\alpha\beta$-dichloropentafluoroisobutyric acid (XXII)[8]:

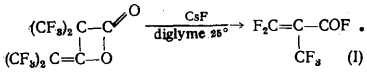


The same ester is formed in a low yield on thermal cleavage of 2-oxoacetidine-3-carboxylic acid ester (XXIII) obtained from the 1,2-cycloadduct of perfluoromethacryloyl fluoride with alkyl isocyanate (XXIV)[5,36] (see subsection 7 in this Section):



A new method for synthesising a PFMA ester, involving the interaction of perfluoromethacryloyl fluorosulphonate (V) with methyl ether[37] [see Eqn. (15)], has been proposed recently. A disadvantage of this method is the difficulty of separating the mixture containing the PFMA ester and FSO_3Me. The mixed anhydride (V) was obtained by treating perfluoromethacryloyl fluoride with SO_3 [see Eqn. (22)].

Perfluoromethacryloyl fluoride is formed in a low yield together with other products when the "β-lactone-dimer of bis(trifluoromethyl)keten" is treated with CsF[3]:

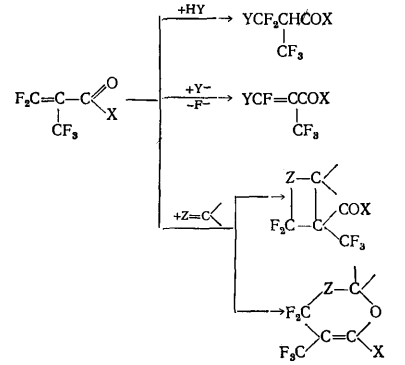


The mechanism of this reaction is obscure. Possibly the dimer decomposes at least partially with formation of bis(trifluoromethyl)keten, which isomerises to perfluoromethacryloyl fluoride.

The formation of perfluoromethacrylonitrile from bis-(α-cyanohexafluoroisopropyl)mercury was described above [Eqn. (5)].

III. CHEMICAL PROPERTIES

The chemical properties of PFMA derivatives are as a rule determined by the reactivity of the highly electrophilic terminal difluoromethylene group. For this reason, reactions with nucleophiles resulting in addition to the C=C bond, "vinyl" substitution, and 1,2- or 1,4-cycloaddition, depending on the initial compound and reagents (and sometimes also the conditions), are most characteristic of these compounds:

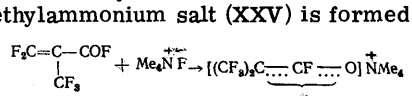


Thus PFMA derivatives behave mainly like fluoro-olefins[38,39], but they usually manifest a higher reactivity with respect to nucleophiles. Compared with non-fluorinated $\alpha\beta$-unsaturated carbonyl compounds[40,41], PFMA derivatives also exhibit appreciably more marked electrophilic properties.

The reactions of PFMA derivatives with electrophiles are almost unknown and their homolytic reactions have been little studied.

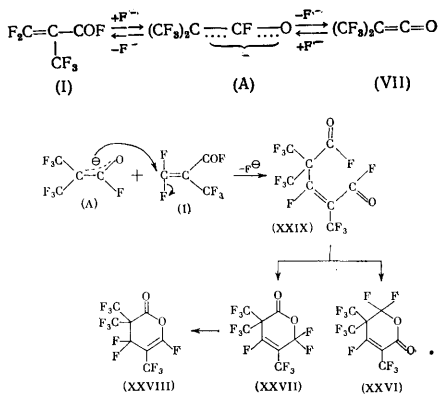
1. Reactions with Halide Anions

Perfluoromethacryloyl fluoride reacts readily with the F^- anion, forming a mesomeric fluoro-carbanion—the perfluoroisobutenoxide anion (A).[6] Depending on the reaction conditions, the subsequent fate of this carbanion may be various. Thus, when perfluoromethacryloyl fluoride reacts with tetramethylammonium fluoride in acetonitrile, the tetramethylammonium salt (XXV) is formed[42]:



On heating at 300°C over NaF, perfluoromethacryloyl fluoride reversibly isomerises to bis(trifluoromethyl)-keten[2-5] (see subsection 1 of Section II).

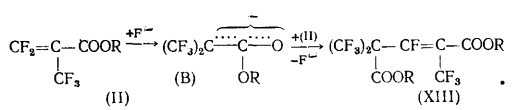
When perfluoromethacryloyl fluoride or the isomeric bis(trifluoromethyl)keten are acted upon by alkali metal fluorides or triethylamine, the "δ-lactone-dimers" (XXVI), (XXVII), and (XXVIII) are formed[3,21,43]. Evidently, the initial product is the mesomeric carbanion (A), which reacts with perfluoromethacryloyl fluoride, substituting the vinyl fluorine atoms, and the resulting dicarboxylic acid fluoride (XXIX) cyclises to the "δ-lactone-dimers" (XXVI) and (XXVII); the isomerisation of compound (XXVII) leads to compound (XXVIII):[6]



(10)

The dimerisation to "δ-lactone-dimers" also occurs in the presence of tetraethylammonium chloride[3,44] or zinc chloride[45].

PFMA esters dimerise very readily in the presence of the F^- ion, forming the dicarboxylic acid esters (XIII)[10,46,47]† [see also Eqns. (3), (14), and (21)]:

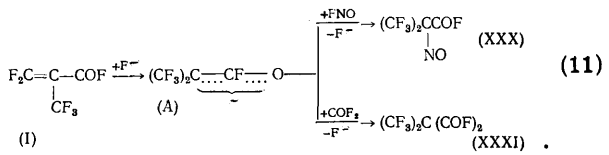


Perfluoromethacrylonitrile dimerises even more readily and cannot be obtained even in the presence of the adduct $R_3N.BF_3$ [10] [see Eqn. (4)]. The less reactive dialkyl amides of PFMA show no tendency towards dimerisation[7,46].

The perfluoro-t-butyl anion $(CF_3)_3C^-$, formed when the F^- ion adds to perfluoroisobutene, reacts with a wide variety of electrophiles, yielding the compounds $(CF_3)_3CR$.[49-52] The mesomeric carbanions obtained from PFMA derivatives and the F^- anion are also capable of combining with electrophiles, although such reactions have been studied much less than in the case of perfluoroisobutene.

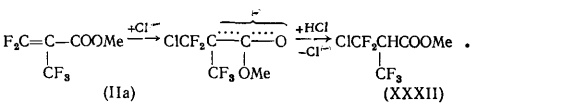
The addition of a proton results in the formation of HFIBA derivatives. Thus methyl perfluoromethacrylate combines with hydrogen fluoride in the presence of NaF, the reaction being reversible[9,27]‡ [Eqn. (6)]. Like perfluoroisobutene[53,54], PFMA esters can play the role of dehydrofluorinating agents in the presence of tertiary amines [Eqn. (19)]. The dimethylamide of PFMA reacts with hydrogen fluoride evolved when the vinyl fluorine atom is substituted on treatment with phenols or mercaptans [Eqns. (13) and (18)].

The interaction of nitrosyl fluoride with perfluoromethacryloyl fluoride, leading to the fluoride of the α-nitrosocarboxylic acid (XXX), probably also begins with the addition of the F^- anion to the C=C bond[55] (cf. Ref. 38). On treatment with carbonyl difluoride in the presence of KF, perfluoromethacryloyl fluoride is converted into the difluoride of bis(trifluoromethyl)malonic acid (XXXI):[56]§



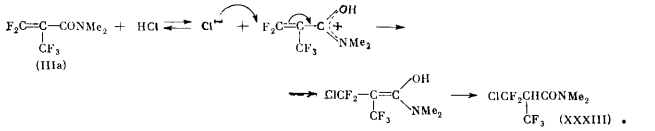
(11)

Methyl perfluoromethacrylate does not react with hydrogen chloride at room temperature in the absence of a catalyst, but, in the presence of a catalytic amount of pyridinium chloride, it readily gives rise to the chloropentafluoroisobutyrate ester (XXXII)[57]¶:

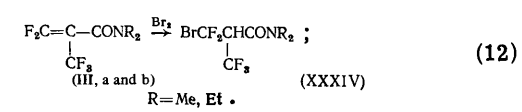


In the absence of a catalyst, perfluoromethacrylonitrile does not react with hydrogen chloride and bromide even at 150°C.[26]

In contrast to the ester and the nitrile, the dimethylamide of PFMA readily combines with hydrogen chloride in a non-polar solvent in the absence of a catalyst, forming the amide of the chloro-substituted acid (XXXIII).[57] Evidently we are dealing here with "intramolecular base catalysis". The protonation of the amide group leads, on the one hand, to the activation of the PFMA dialkylamide molecule, and, on the other, to the appearance in the mixture of the fairly nucleophilic anion Cl^-, which is capable of attacking the β-carbon atom[46,57]:



The hydrogen bromide addition products (XXXIV) have been obtained in low yields in attempts to brominate PFMA dialkylamides[7]:



(12)

---

† The esters of difluoromethylenemalonic acid dimerise just as readily[21,35]. The analogous dimerisation of perfluoroisobutene[48] and the perfluoroacrylate ester[9] has also been described.

‡ Perfluoroacryloyl fluoride also combines with HF in the presence of NaF.[9]

§ Perfluoroacryloyl fluoride gives rise similarly to the difluoride of α-fluoro-α-trifluoromethylmalonic acid[56]. The analogous reaction with a perfluoromethacrylate ester is described in subsection 7 of the present Section.

¶ Perfluoroisobutene also combines with hydrogen halides in the presence of bases[58].

2. Reactions with *O*-Nucleophiles

Perfluoromethacryloyl fluoride reacts readily with water, being converted into trifluoromethylmalonic acid $CF_3CH(COOH)_2$.[7] When HFIBA esters react with water in the presence of triethylamine, the intermediate PFMA esters are converted into esters of ββγ-trifluoropropionic acid as a result of decarboxylation[10] [Eqn. (1)]. On treatment with water, perfluoromethacrylonitrile yields ββγ-trifluoropropionitrile[26]:

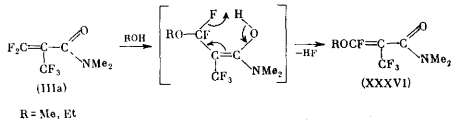
$$\underset{\text{(VI)}}{F_2C{=}C(CF_3){-}CN} \xrightarrow[-HF,\ -CO_2]{H_2O} CF_3CH_2CN .$$

The C=C double bond in perfluoromethacryloyl fluoride is so electrophilic that it reacts with hydroxy-compounds faster than the acid fluoride group. On treatment with equimolar amounts of alcohols (MeOH, $CH_2{=}CHCH_2OH$, $HOCH_2COOMe$) under mild conditions, perfluoromethacryloyl fluoride is converted into the corresponding addition products (XXXV)[9,27] [see also Eqn. (17)]†. The COF group also reacts with an excess of the alcohol, forming esters of α-hydro-β-alkoxypentafluoroisobutyric acids (XII)[4,8,21,59]. PFMA esters likewise combine readily with alcohols, forming the adducts (XII)[8,59]‡:

$$\underset{\text{(I)}}{F_2C{=}C(CF_3){-}COF} \xrightarrow{R^1OH} \underset{\text{(XXXV)}}{R^1OCF_2CH(CF_3)COF} \xrightarrow{ROH}$$

$$\xrightarrow{ROH} \underset{\text{(II)}}{F_2C{=}C(CF_3){-}COOR} \xrightarrow{R^1OH} \underset{\text{(XII)}}{R^1OCF_2CH(CF_3)COOR} .$$

In contrast to the acid fluoride and esters, the dimethylamide of PFMA reacts with alcohols to form only products arising from the substitution of the vinyl fluorine atom—the dimethylamides of β-alkoxy-β-fluoro-α-trifluoromethylacrylic acids (XXXVI) (in the form of a mixture of *cis*- and *trans*-isomers)[59]§. This difference can probably be accounted for by the appreciable basicity of the $CONMe_2$ group, which can bind the proton and can prevent its addition to the carbanionic centre[7,46,59]:



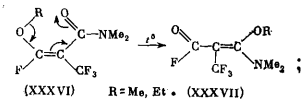
Perfluoroisobutene is known to react readily with alcohol, forming mainly addition products together with small amounts of substitution products[61,62]. It has been shown by the method of competition kinetics that methyl perfluoromethacrylate reacts with alcohol much faster than perfluoroisobutene or PFMA dimethylamide[46].

†The analogous reaction of perfluoroacryloyl fluoride with methanol takes place in the presence of NaF and leads to a mixture containing $MeOCF_2CHFCOOMe$ and $MeOCF_2CHFCOF$ as well as traces of $F_2C{=}CFCOOMe$ and $CF_3CHFCOOMe$.[9]

‡It has been stated[26] that perfluoromethacrylonitrile reacts very readily with alcohols, but the structure of the resulting products has not been given. Ethyl perfluoroacrylate reacts with alcohols under somewhat more severe conditions[60].

§Hexafluoroisopropyl alcohol $(CF_3)_2CHOH$ does not react with PFMA dimethylamide at room temperature[57].

The β-alkoxyamides (XXXVI) have proved to be relatively unstable. They rearrange on heating to the acid fluorides (XXXVII) as a result of the 1,5-migration of the alkyl group from the "enolic" oxygen atom to the carbonyl oxygen atom of the alkoxyvinylcarbonyl system[59]:



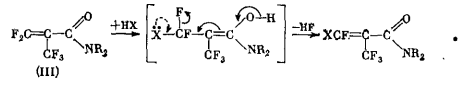
In contrast to the reaction with alcohols, in the reaction with phenols the PFMA ester is less reactive than PFMA dimethylamide. Methyl perfluoromethacrylate does not react with phenol and pentafluorophenol at room temperature¶, while PFMA dimethylamide does react under these conditions, although more slowly than in the analogous reaction with alcohols[57]. The reaction with unsubstituted phenol yields the "vinyl" substitution product (XXXVIII) (the *cis*- and *trans*-isomers); the hydrogen fluoride evolved adds to the initial amide (IIIa), forming the dimethylamide of HFIBA (XIV):

$$\underset{\text{(IIIa)}}{F_2C{=}C(CF_3){-}CONMe_2} \xrightarrow{PhOH} \underset{\text{(XXXVIII)}}{PhOCF{=}C(CF_3){-}CONMe_2} + \underset{\text{(XIV)}}{(CF_3)_2CHCONMe_2} . \qquad (13)$$

Pentafluorophenol forms mainly the addition product (XXXIX) and only small amounts of the substitution product (XL) (the *cis*- and *trans*-isomers):

$$\text{(IIIa)} \xrightarrow{C_6F_5OH} \underset{\text{(XXXIX)}}{C_6F_5OCF_2CH(CF_3)CONMe_2} + \underset{\text{(XL)}}{C_6F_5OCF{=}C(CF_3)CONMe_2} + \text{(XIV)} .$$

Comparison of the reactivities of various *O*- and *S*-nucleophiles in reactions with PFMA dimethylamide showed that the rate of reaction decreases in a sequence which is quite different from the sequence of the corresponding acidities: AlkOH ($pK_a \simeq 18$) > RCOOH† ($pK_a = 0.23$–4.75) > PhSH‡ ($pK_a = 8.0$) > C_6F_5OH ($pK_a = 5.5$) > $PhCH_2SH$‡ ($pK_a \simeq 12$) > PhOH ($pK_a = 9.9$) ≫ $(CF_3)_2CHOH$ ($pK_a = 9.3$). Evidently, when the nature of the nucleophile (acidity, nucleophilic properties of the reaction centre) changes appreciably, there is also a change in reaction mechanism, the influence of the basic properties of the amide group having an effect to different extents[46,57]. The +*M* effect of the substituent X, which promotes the dissociation of the C–F bond, probably plays a significant role in the formation of the "vinyl" substitution products:



If this effect is insignificant, the addition product is formed in a larger amount as a result of the attack by the proton on the central carbon atom.

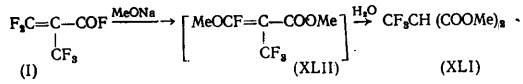
Little information is available about the interaction of PFMA derivatives with alkoxides and phenoxides. The reaction of perfluoromethacryloyl fluoride with sodium methoxide followed by hydrolysis yields the ester of trifluoromethylmalonic acid (XLI).[9] This probably involves

¶Perfluoromethacryloyl fluoride reacts with phenol at 100°C to form the adduct $PhOCF_2CH(CF_3)COF$.[9]

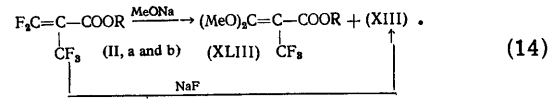
†See Eqn. (16).

‡See Eqn. (18).

the initial formation of the "vinyl" substitution product (XLII):



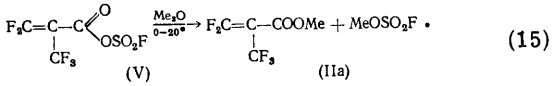
Treatment of PFMA esters with sodium methoxide leads to the formation of acetals of the substituted ketens (XLIII) together with the "dimers" (XIII):[47]



(14)

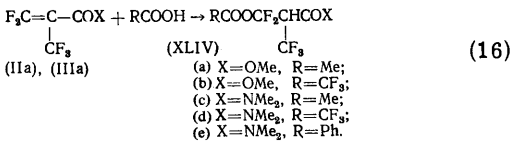
The "vinyl" substitution product (XXXVIII) has been obtained from PFMA dimethylamide and sodium phenoxide[57].

The mixed anhydride of PFMA and fluorosulphonic acid (V) readily reacts with methyl ether. In contrast to other reactions of PFMA derivatives with nucleophiles, the β-carbon atom is not involved in this process and one PFMA derivative is thus converted into another; this results in the formation of a PFMA ester and methyl fluorosulphonate[37]:



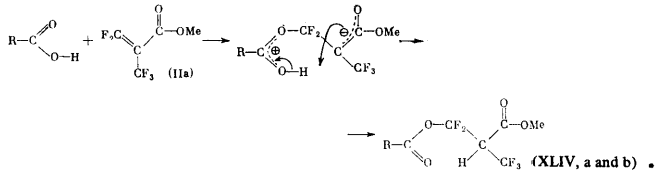
(15)

PFMA derivatives are able to combine even with very slightly nucleophilic carboxylic acids in the absence of basic catalysts. Methyl perfluoromethacrylate reacts readily with acetic or trifluoroacetic acid, forming the addition products (XLIV, a and b). The analogous reactions of PFMA dimethylamide led to the β-acyloxyamides (XLIV, c, d, and e):[57]

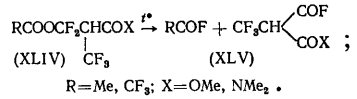


(16)

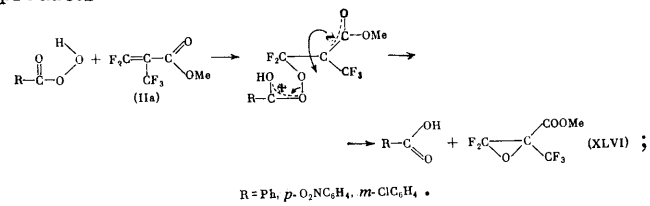
Whereas "intramolecular base catalysis" can be suggested for the reactions with PFMA dimethylamide, this is much less likely for the PFMA ester (see subsection 1 in this Section); possibly the carboxylic acid, even trifluoroacetic acid, behaves as a nucleophile in the reaction with the PFMA ester[57]. The addition probably takes place via a six-membered cyclic transition state, which facilitates the reaction[46]:



The addition of carboxylic acids is not characteristic of the usual αβ-unsaturated carbonyl compounds[41]. This can also be said of electrophilic perfluoro-olefins. Only in the presence of a base (triethylamine) does perfluoroisobutene react with acetic acid, but the resulting adduct immediately decomposes into acetyl fluoride and the fluoride of HFIBA.[43] The analogous cleavage of the adduct (XLIV) takes place on heating and leads to derivatives of trifluoromethylmalonic acid (XLV) containing one acyl fluoride group[57]:



Peracids are probably more powerful nucleophiles than carboxylic acids[63]. It is therefore not surprising that peracids react still faster with the PFMA ester. However, they give rise to an epoxide [the fluorine-containing glycidyl ether (XLVI)] in this reaction and not to addition products[46,64]:

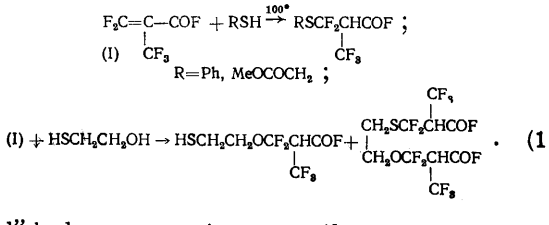


R = Ph, *p*-$O_2NC_6H_4$, *m*-ClC_6H_4.

In the usual epoxidation of ethylenic compounds by peracids (the Prilezhaev reaction), the latter are known to behave as electrophiles and the introduction of electron-withdrawing substituents into the molecule of the unsaturated compound hinders its epoxidation[63]. However, it has been found that the PFMA ester is epoxidised more readily than perfluoroisobutene or methyl acrylate[64]. Evidently the epoxidation of the highly electrophilic PFMA ester involves an unusual inversion of the mechanism of the Prilezhaev reaction, the peracid behaving as a nucleophile. O-Nucleophiles capable of reacting with PFMA derivatives include also certain carbonyl compounds. Reactions with these compounds, leading to cycloadducts or their conversion products, are examined in a separate subsection (subsection 7).

3. Reactions with *S*-Nucleophiles

The reactions of PFMA derivatives with mercapto-compounds have been little investigated. Perfluoromethacryloyl fluoride gives rise to products formed by addition to the C=C bond on interaction with thiophenol and the mercaptoacetate ester[9]; in contrast to the reaction with alcohols, this process takes place only on heating. 2-Mercaptoethyl alcohol adds to perfluoromethacryloyl fluoride, forming 1 : 1 and 1 : 2 adducts[9]:

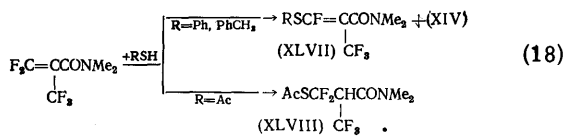


(17)

The "hard" hydroxy-group is apparently somewhat more reactive with respect to the carbon atom of the CF_2= group than the "soft" mercapto-group.

The reaction of PFMA dimethylamide with thiophenol or phenylmethanethiol gives the "vinyl" substitution product (XLVII) (the *cis*- and *trans*-isomers) together with the HFIBA dimethylamide (XIV) (the rate of this reaction is discussed in subsection 2 of this Section). Thioacetic acid reacts readily with PFMA dimethylamide, but it gives rise

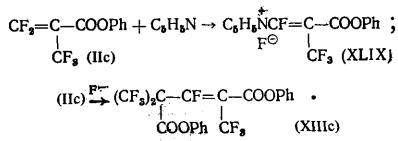
to a mixture of products from which only the thioloacetyl derivative (**XLVIII**) could be isolated in a low yield[57]:



(18)

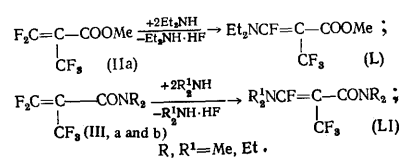
4. Reactions with *N*-Nucleophiles

When **PFMA** derivatives are acted upon by tertiary amines, they usually dimerise readily (subsection 1 of this Section). For example, phenyl perfluoromethacrylate (**IIc**) is converted into the dicarboxylate ester (**XIIIc**) in the presence of a catalytic amount of pyridine at room temperature[10]. Possibly the reaction begins with the substitution of the vinyl fluorine atom by the pyridinium residue and the F^- anion split off then catalyses the dimerisation reaction:

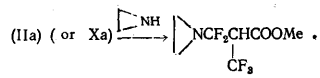


However, this mechanism remains purely speculative, since there is no direct evidence for the formation of compounds of type (**XLIX**). Like tertiary amines, certain carboxylic acid dialkylamides also catalyse the dimerisation of **PFMA** esters (see subsection 7 of this Section).

The reactions with secondary amines usually lead to the formation of the "vinyl" substitution products (**L**) and (**LI**)[59,65§]:

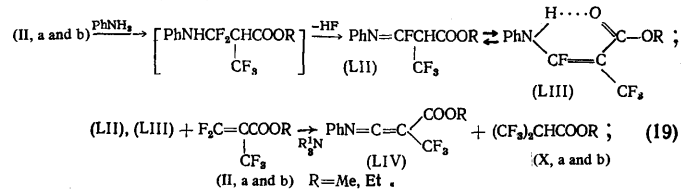


In contrast to dimethyl- and diethyl-amines, aziridine forms an addition product on reaction with the perfluoromethacrylate ester. The same product has been obtained from the **HFIBA** ester[67]:



Here the **PFMA** ester behaves like perfluoroisobutene, which reacts with dialkylamines to form substitution products and with aziridine to form addition products[67].

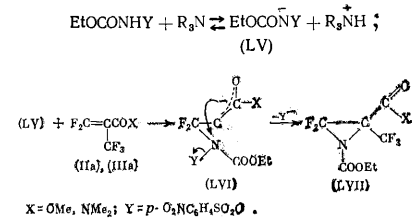
The reaction of perfluoroisobutene with arylamines in the presence of tertiary amines leads to imidoyl fluorides and ketenimines[53]. **PFMA** esters react with aniline via a similar mechanism, forming imidoyl fluorides (**LII**) [in the form of tautomeric mixtures with enamines (**LIII**)] and ketenimines (**LIV**)[68]:



(19)

An excess of the **PFMA** ester acts in this reaction like a dehydrofluorinating agent. The enamines (**LIII**) are comparatively stable owing to the hydrogen bond between the NH and COOR groups.

The anion (**LV**), formed from *p*-nitrobenzenesulphonyloxyurethane on treatment with triethylamine, is an active *N*-nucleophile. Like perfluoroisobutene, methyl perfluoromethacrylate and **PFMA** dimethylamide readily react with this anion; the resulting carbanions (**LVI**) are stabilised by cyclisation with elimination of the *p*-nitrobenzenesulphonyloxy-group, readily removed in the form of the anion, and not by the elimination of an F^- anion (as in "vinyl" substitution) or by the capture of a proton (as in an addition reaction). Nucleophilic elimination of **PFMA** derivatives is thus achieved with formation of substituted aziridines (**LVII**)[64]:

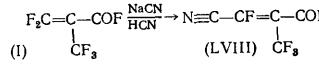


X = OMe, NMe_2; Y = *p*-$O_2NC_6H_4SO_2O$.

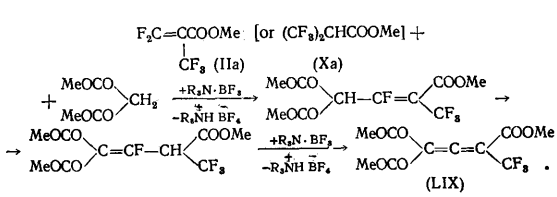
The reactions involving the cycloaddition of *N*-nucleophiles such as nitriles and isocyanates to perfluoromethacryloyl fluoride are discussed below in subsection 7.

5. Reactions with *C*-Nucleophiles

The "vinyl" substitution product (**LVIII**) has been obtained in a low yield by the reaction of perfluoromethacryloyl fluoride with the cyanide anion[36]:



When the malonic ester reacts with the **PFMA** ester in the presence of the adduct $Et_3N.BF_3$, a "vinyl" substitution product is also formed; isomerisation and subsequent dehydrofluorination lead to 1-trifluoromethyl-1,3,3-tri(methoxycarbonyl)allene (**LIX**). The same product was obtained also from the **HFIBA** ester, which is converted into a **PFMA** ester under the reaction conditions[25]:



As in many other reactions, the **PFMA** ester behaves here like perfluoroisobutene[69].

Another type of reactions of **PFMA** derivatives with *C*-nucleophiles involves dimerisation, the vinylfluorine

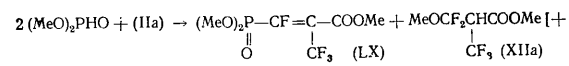
§The reaction of perfluoromethacrylonitrile with diethylamine followed by hydrolysis yields the amidonitrile $Et_2NCOCH(CF_3)CN$.[26] On treatment with secondary amines, methyl perfluoroacrylate forms unstable addition products, which undergo further transformations[66].

atom being substituted on treatment with a mesomeric carbanion of type (A), (C), or (D) [Eqns. (2), (4), and (10)].

Certain *C*-nucleophiles are involved in cycloaddition reactions with perfluoromethacryloyl fluoride (see subsection 7 below).

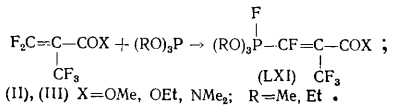
6. Reactions with *P*-Nucleophiles

Methyl perfluoromethacrylate reacts with dimethyl phosphite at room temperature, forming the "vinyl" substitution product (LX) together with the methanol addition product (XIIa)[47]:



The mechanism of this reaction is obscure.

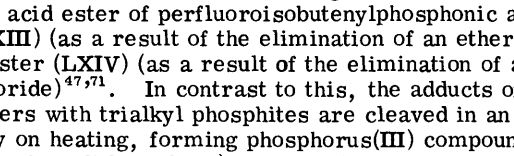
PFMA esters and dialkylamides react very readily with trialkyl phosphites, forming substituted perfluoroalkenyltrialkoxyfluorophosphoranes (LXI)[47,70]¶:



An analogous reaction is known for perfluoroisobutene, which interacts with triethyl phosphite to form a stable intermediate of the Arbuzov rearrangement, namely $(EtO)_3PFCF{=}C(CF_3)_2$ (LXII).[71] As in the reactions with other nucleophiles, methyl perfluoromethacrylate proved to be more reactive than perfluoroisobutene in the reaction with trimethyl phosphite[46].

The structures of the adducts of trialkyl phosphites with PFMA derivatives [compounds (LXI)] and with perfluoroisobutene [compounds (LXII)] have been confirmed by NMR. The covalent character of the P–F bond leads to spin–spin coupling between the ^{31}P and ^{19}F nuclei ($J = 820$ Hz).[47,70] The formation of these adducts constitutes a rare instance of the isolation of pentacovalent (and not tetracovalent quasiphosphonium) intermediates of the Arbuzov rearrangement[72].

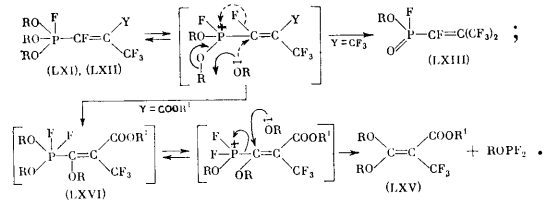
The adducts of perfluoroisobutene with trialkyl phosphite decompose in two ways on heating, forming the products of the Arbuzov rearrangement—the fluoride of the acid ester of perfluoroisobutenylphosphonic acid (LXIII) (as a result of the elimination of an ether)—and the diester (LXIV) (as a result of the elimination of an alkyl fluoride)[47,71]. In contrast to this, the adducts of PFMA esters with trialkyl phosphites are cleaved in an unusual way on heating, forming phosphorus(III) compounds (alkyl phosphorodifluoridites) and acetals of substituted ketens (LXV)[47,70]†:



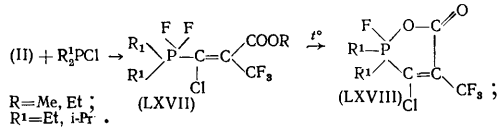
¶The esters of difluoromethylenemalonic acid react similarly[35].

†The adduct of the difluoromethylenemalonic ester with $(MeO)_3P$ is cleaved similarly to $MeOPF_2$ and $(MeO)_2C{=}C(COOMe)_2$.[35]

This sharp difference in behaviour can probably be accounted for by the much more marked electrophilic properties of the carbon atom in the CF= group in the phosphoranes obtained from PFMA esters, compared with the phosphoranes derived from perfluoroisobutene. It is suggested that the first stage in the cleavage of the phosphoranes (LXI) and (LXII) is their reversible dissociation into an anion (RO^- or F^-) and a quasiphosphonium cation. Further reactions depend on which electrophilic centre is attacked by the anion. In the adducts formed from perfluoroisobutene, the carbon atom of the alkyl group R functions as the electrophilic centre, while in adducts obtained from PFMA esters the electrophilic centre is the β-carbon atom of the "acrylic" system. The new phosphorane (LXVI) formed in the latter case dissociates into an anion RO^- and a quasiphosphonium cation; the repeated attack by the alkoxide anion on the β-carbon atom cleaves the molecule into an acetal (LXV) and an alkyl phosphorodifluoridite[46,47]‡:



Thus, owing to the enhanced electrophilic properties of the β-carbon atom, in the decomposition of the adducts of PFMA esters with trialkyl phosphites the substituents at the phosphorus and carbon atoms change places. A similar exchange occurs also in the interaction of PFMA esters with dialkylchlorophosphines, which leads to the phosphoranes (LXVII), containing the PF_2 and CCl= groups [when these phosphoranes are heated, an alkyl fluoride is split off and cyclisation products are obtained—substituted oxaphospholens (LXVIII)][47]:



In contrast to this, the products obtained from chlorodiethylphosphine and perfluoroisobutene retain the CF= group and only bis(dialkylamino)chlorophosphines react with perfluoroisobutene to form compounds $(R_2N)_2PF_2.CCl{=}C(CF_3)_2$ containing the CCl= group[73].

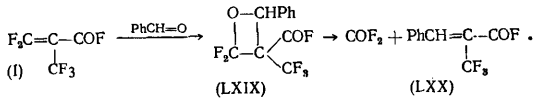
7. Cycloaddition

The appreciably electrophilic properties of PFMA derivatives are responsible for the ease with which they undergo cycloaddition reactions on treatment with various unsaturated compounds having fairly pronounced nucleophilic properties. PFMA derivatives containing the >C=C–C=O bond system can be involved in 1,2- or 1,4-cycloaddition reactions, only the C=C bond, and not the

‡In the process represented in the above scheme, the nucleophilic participation of the carbonyl group, leading to the intermediate formation of 1,2-oxaphospholen structures, may also play an important role.

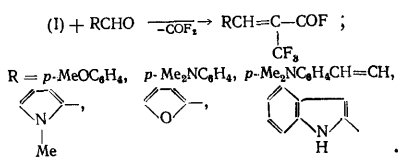
C=O bond, reacting in the former case. Cycloaddition results in the formation of three-, four-, five-, and six-membered rings; it is sometimes possible to isolate only the products of the further reactions of these compounds. The oxygen, nitrogen, and carbon atoms in the reactant can function as the nucleophilic centre.

When perfluoromethacryloyl fluoride reacts with benzaldehyde, a substituted oxetan (LXIX) is formed[9,27,36]. It is relatively unstable, decomposing on heating into carbonyl difluoride and α-trifluoromethylcinnamoyl fluoride (LXX) (a mixture of the *cis*- and *trans*-isomers):



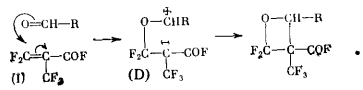
This reaction constitutes a method for the introduction of the substituted methylene group $=C(CF_3)COF$ in place of the oxygen atom of the carbonyl group and, in terms of its final result, it thus resembles the Wittig reaction.

A number of unsaturated acid fluorides have been obtained similarly but without the isolation of the intermediate oxetans[9,74]:



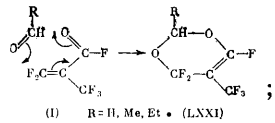
2,6-Dimethyl-γ-pyrone enters into a similar reaction[9].

The mechanism of the 1,2-cycloaddition of carbonyl compounds to perfluoromethacryloyl fluoride probably involves the formation of a dipolar ion (D)[36]:

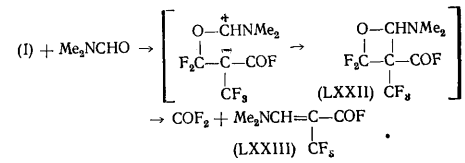


(20)

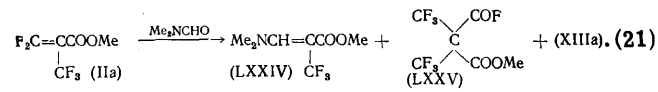
The negative charge in this dipolar ion is stabilised by the electron-withdrawing fluorine-containing groups and the positive charge by the electron-donating mesomeric effect of the group R. On the other hand, if the group R is incapable of stabilising the positive charge on the neighbouring carbon atom, the formation of the dipolar ion becomes unfavourable and synchronous (or almost synchronous) 1,4-cycloaddition takes place instead of the 1,2-cycloaddition. Thus, aliphatic aldehydes add to perfluoromethacryloyl fluoride, giving rise to substituted *m*-dioxins (LXXI)[9,27]:



The presence of the dimethylamino-group, which exhibits a considerable +*M* effect, stabilises the dipolar ion; for this reason, the reaction of perfluoromethacryloyl fluoride with dimethylformamide involves 1,2-cycloaddition with formation of the oxetan (LXXII), which, however, cannot be isolated, since it is immediately cleaved to difluorophosgene and the acid fluoride (LXXIII)[9,74]§:



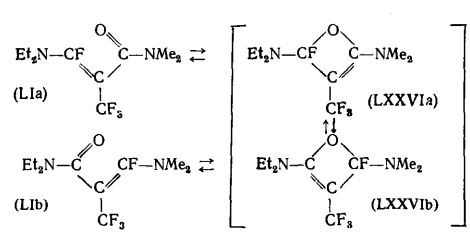
Methyl perfluoromethacrylate reacts more slowly with dimethylformamide than the acid fluoride. Together with the ester (LXXIV), the reaction also leads to the formation of the acid fluoride (LXXV) and of insignificant amounts of the "dimer" (XIIIa)[46]:



Evidently the carbonyl difluoride produced adds to the PFMA ester [see Eqn. (11)]. The analogous reaction of dimethylformamide with perfluoroisobutene leads to the enamine $Me_2NCH=C(CF_3)_2$ and the acid fluoride $(CF_3)_3COF$.[75] Perfluoroisobutene reacts with dimethylformamide somewhat more slowly than does the PFMA ester[46].

In contrast to dimethylformamide, dimethylacetamide and tetramethylurea do not undergo cycloaddition to methyl perfluoromethacrylate. In the latter case, the initial ester is wholly converted into the "dimer" (XIIIa). PFMA dimethylamide does not react with dimethylformamide[46].

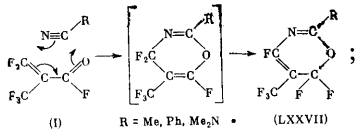
An interesting intramolecular reaction, analogous to the formation of oxetans from PFMA derivatives and dimethylformamide, has been discovered recently. It was found that the dialkylamides of β-dialkylamino-β-fluoro-α-trifluoromethylacrylic acids (LI), containing various alkyl groups at the "amine" and "amide" nitrogen atoms, form on heating to 140°C (or to 100°C in the presence of $Et_3O.BF_3$) an equilibrium mixture containing the isomeric amides (LIa) and (LIb) in proportions of 1 : 1. This evidently involves the intermediate cyclisation of the αβ-unsaturated amides to the substituted oxetens (LXXVI, a and b) (or their adducts with BF_3), the allyl rearrangement with a shift of the F^- ion, and the reverse ring opening reaction[65]:



Methyl β-diethylamino-β-fluoro-α-trifluoromethylacrylate (L) and the dimethylamide of β-fluoro-α-trifluoromethyl-β-phenoxyacrylic acid (XXXVIII) do not undergo this type of isomerisation. Evidently the rearrangement requires both sufficiently pronounced electrophilic properties of the carbonyl oxygen atom attacking the β-carbon atom and sufficient mobility of the fluorine atom, determined by the mesomeric effects of the substituent[65].

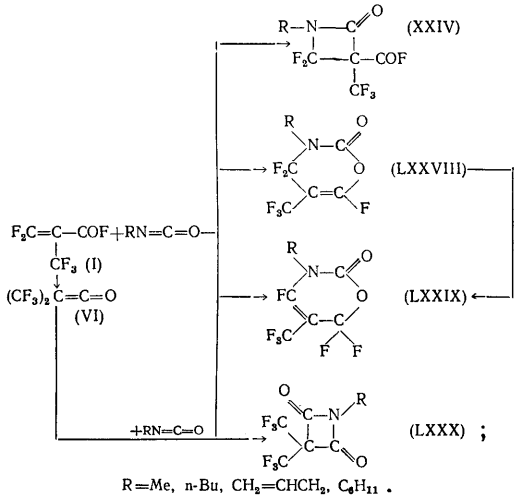
§ A similar reaction of $CF_2=CFCOF$ requires somewhat more severe conditions[9].

In contrast to carbonyl compounds, nitriles are involved in 1,4-cycloaddition on interaction with perfluoromethacryloyl fluoride; the subsequent rearrangement leads to substituted 1,3-oxazines (LXXVII)[27,36]:



The reaction with dimethylcyanamide takes place much more readily than those with acetonitrile and benzonitrile.

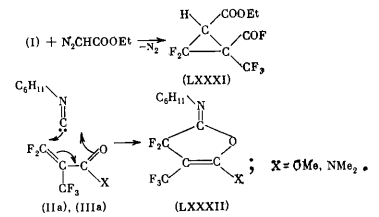
On reaction with perfluoromethacryloyl fluoride, isocyanates form the 1,2-cycloaddition products (XXIV), the 1,4-cycloaddition products (LXXVIII), the allyl rearrangement products (LXXIX), and the products of their cycloaddition to bis(trifluoromethyl)keten (LXXX)[5,27,36]:



An increase in the polarity of the medium favours 1,2-cycloaddition (via a dipolar ion)[5,27,36].

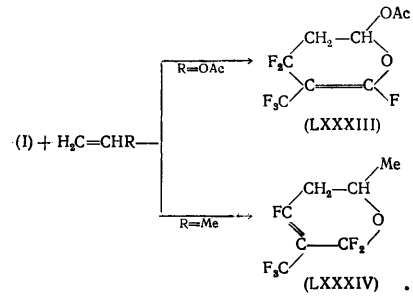
The diazoacetic ester¶, isonitriles, olefins, phenylacetylene and ketens are *C*-nucleophiles capable of being involved in cycloaddition reactions.

The diazoacetic ester reacts with perfluoromethacryloyl fluoride under mild conditions, giving a substituted cyclopropane (LXXXI) (the *erythro*- and *threo*-isomers)[9]. When cyclohexyl isocyanide reacts with PFMA derivatives, substituted iminodihydrofurans (LXXXII) are formed via 1,4-cycloaddition to the system $\rangle C{=}C{-}C{=}O$:[77]

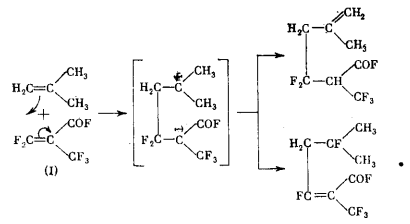


¶The diazoacetic ester may function as an *N*-nucleophile (cf. Gambaryan et al.[76]).

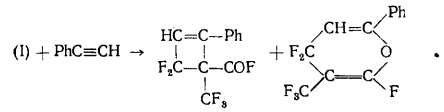
The reaction of perfluoromethacryloyl fluoride with certain olefins leads to six-membered rings via 1,4-cycloaddition; under these conditions, subsequent allyl rearrangement (1,3-migration of the fluorine atom) is frequently observed. The reaction with vinyl acetate leads to the formation of the 1,4-cycloadduct (LXXXIII) and the reaction with propene (and with norbornene) gives the allyl rearrangement product (LXXXIV)[27,36,78]:



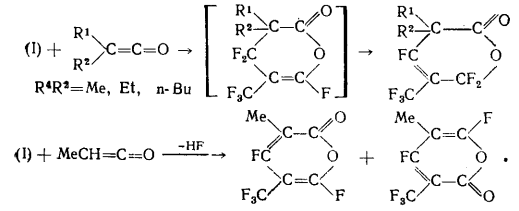
In the reaction with propene, a further two linear products were isolated: $CH_3CHFCH_2CF{=}C(CF_3)COF$ and $CH_3CH{=}CHCF{=}C(CF_3)COF$. Only linear products were obtained after the reaction with isobutene. It may be that, as in the reaction with aromatic aldehydes [Eqn. (20)], a dipolar ion (with the positive charge stabilised by the action of two methyl groups) is formed here as an intermediate, but it does not cyclise to cyclobutane, isomerising with migration of the H^+ or F^- ion[27,36]:



Phenylacetylene adds to perfluoromethacryloyl fluoride, forming 1,2- and 1,4-cycloaddition products[79]:

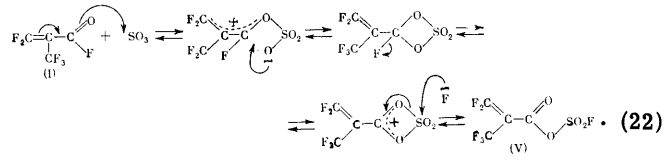


When perfluoromethacryloyl fluoride reacts with dialkylketens, 1,4-cycloaddition to the C=C bond of the keten takes place with subsequent 1,3-migration of the fluorine[27,36]. In the reaction with methylketen, the corresponding dehydrofluorination products were isolated[36]:



8. Other Reactions of PFMA Derivatives

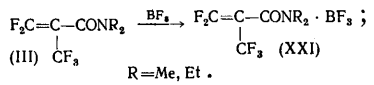
Reactions with electrophilic compounds are completely uncharacteristic of PFMA derivatives. Only sulphur trioxide, a powerful electrophile, is capable of reacting with perfluoromethacryloyl fluoride. In contrast to reactions with nucleophiles, in this case the acyl fluoride group is the most reactive, the product being the mixed anhydride (V). It may be that the reaction begins with attack by the electrophilic SO_3 species on the carbonyl oxygen atom[37]:



(22)

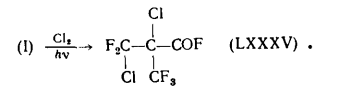
The reaction is reversible—on heating to 125–140° C, the anhydride (V) is cleaved to the initial compounds.

When dialkylamides of PFMA are acted upon by BF_3, the adducts (XXI) are formed [cf. Eqn. (8)][7,33]:



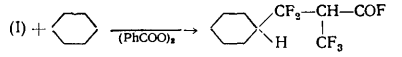
The attempts to brominate the dialkylamides were unsuccessful—only the HBr addition products were obtained [Eqn. (12)][7].

On chlorination, perfluoromethacryloyl fluoride gives rise to $\alpha\beta$-dichloropentafluoroisobutyryl fluoride (LXXXV)[8]:



This reaction is initiated by ultraviolet irradiation and evidently proceeds via a radical mechanism. The use of chlorination for the protection of the reactive $CF_2{=}C\langle$ group is discussed in subsections 1 and 4 of Section II.

In the presence of a radical reaction initiator, cyclohexane readily adds to the C=C bond of perfluoromethacryloyl fluoride[9,27]:



There is little information available about the polymerisation of PFMA derivatives†. Perfluoromethacryloyl fluoride does not apparently polymerise by itself, but it does undergo copolymerisation with other monomers[9,82,83]. The rubber-like copolymer of perfluoromethacryloyl and ethylene, obtained on heating under pressure in the presence of t-butyl peroxide, is soluble in carbon tetrachloride; on treatment with ethylenediamine, a cross-linked polymer, insoluble in carbon tetrachloride, is formed[9,82]. A patent[82] also indicates the possibility of obtaining copolymers from perfluoromethacryloyl fluoride and monomers such as methyl methacrylate, acrylonitrile, tetrafluoroethylene, vinyl fluoride, and vinylidene fluoride. After cross-linking the copolymers can be used for the preparation of films and various coatings, for the impregnation or coating of porous materials, etc. The copolymers of perfluoromethacryloyl fluoride and $CH_2{=}CF_2$, obtained by radiation-induced copolymerisation, are readily cross-linked by bifunctional compounds; they have high thermal stabilities and readily adhere to metals[83].

Ethyl perfluoromethacrylate (IIb) and the diethylamide of PFMA (IIIb) do not polymerise on heating in the presence of benzoyl peroxide, while the dimethylamide (IIIa) forms under these conditions a brittle solid polymer, soluble in acetone and insoluble in carbon tetrachloride. Similar polymers have been obtained from the dimethyl- and diethylamides of PFMA (III, a and b) on γ-irradiation[7].

Examination of the chemical properties of PFMA derivatives reveals distinct electrophilic properties of these compounds. The reactions with very weak nucleophiles, for example with carboxylic acids, which do not require base catalysis, are particularly instructive in this respect. Such reactions are completely uncharacteristic of either perfluoro-olefins or perfluoro-derivatives of $\alpha\beta$-unsaturated carbonyl compounds. Evidently the electrophilic properties of fluoro-olefins and $\alpha\beta$-unsaturated carbonyl compounds are "added together" in the case of PFMA derivatives.

†For the polymerisation and copolymerisation of perfluoroacrylic acid derivatives, see Refs. 9, 80, and 81.

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