Tetrahedron. Vol. 29, pp. 595 to 601. Pergamon Press 1973. Printed in Great Britain

ELECTROPHILIC ELIMINATION OF ALKYL FLUORIDES FROM ALKYL FLUOROALKENYL ETHERS

A NEW WAY OF SYNTHESIZING PERFLUOROMETHACRYLIC ACID DERIVATIVES

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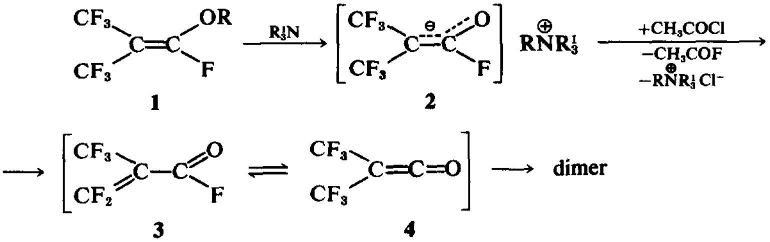
(*Received in the UK* 27 *August* 1972; *Accepted for publication* 25 *September* 1972)

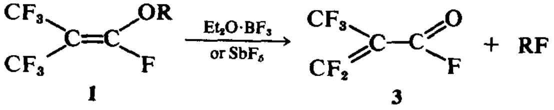
Abstract—A number of perfluoromethacrylic acid derivatives have been prepared by the elimination of alkyl fluoride from substituted alkoxyperfluoroisobutylenes through the action of Lewis acids. Adducts (**11a,b**) containing a mesomeric carbonium-cation and a tetrafluoroborate-anion were obtained by reacting aminoacetals of bis(trifluoromethyl)ketene with BF_3.

Alkyl fluoroalkenyl ethers, particularly alkyl perfluoroisobutenyl ethers (**1**) are easily dealkylated under the action of tertiary amines with the formation of adducts (**2**) which are salts containing a mesomeric fluorocarbanion.[1,2] It was also found that the $F^{\ominus}$ ion could be eliminated from these adducts, e.g. by the action of acyl chloride:[1]



Such a sequence of reactions is, in fact, a method for eliminating alkyl fluoride from alkyl perfluoroisobutenyl ether.*

A similar result may be attained by the action of Lewis acids. Indeed, heating of the ethers (**1**) in the presence of catalytic quantities of antimony pentafluoride or BF_3-etherate gives perfluoromethacrylic fluoride (**3**):



1a: R = CH_3
1b: R = Et

Similarly, methyl perfluoropropenyl ether (**5**) by the action of antimony pentafluoride is converted to perfluoroacrylic fluoride (**6**):

$$\underset{\mathbf{5}}{CF_3CF{=}CFOCH_3} \xrightarrow{SbF_5} \underset{\mathbf{6}}{CF_2{=}CFCOF}$$

The use of ethyl perfluoropropenyl ether results in a mixture of fluoride (**6**) and saturated fluoride $CF_3CFHCOF$.

The elimination of alkyl fluoride from acetals (**7**) and aminoacetals (**8**) of bis(trifluoromethyl)ketene proceeds similarly.† These compounds, on being heated with catalytic quantities of BF_3-etherate, give corresponding perfluoromethacrylic acid derivatives, namely, esters (**9**) and amides (**10**).

This reaction is a convenient method for producing perfluoromethacrylic acid derivatives, which may successfully compete with other methods (*cf*, e.g. Ref. 3–5).

Figure 1 shows the ^{19}F NMR spectra of perfluoromethacrylic acid esters and amides. The set of ^{19}F nuclei in these compounds is, evidently, either an ABC_3- or an ABX_3-system, depending on the nature of the substituent at the carbonyl.

The catalytic effect of the Lewis acid on the elimination of alkyl fluoride may be explained as follows (*cf.* Ref. 6). Lewis acid (A) promotes elim-

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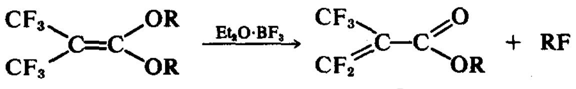
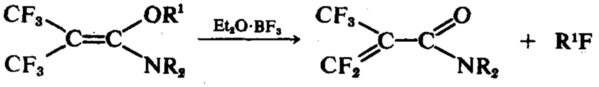
*Under the reaction conditions the resulting fluoride (**3**) or ketene (**4**) which is in equilibrium with it undergoes instantaneous dimerisation.[1]

†The conditions required for the elimination of ethyl fluoride are usually milder than those required for the elimination of methyl fluoride.



7 **9**

7a, 9a: R = CH_3
7b, 9b: R = Et



8 **10**

8a: R = R^1 = CH_3
8b: R = Et, R^1 = Me
8c: R = CH_3, R^1 = Et
8d: R = R^1 = Et

10a: R = Me
10b: R = Et

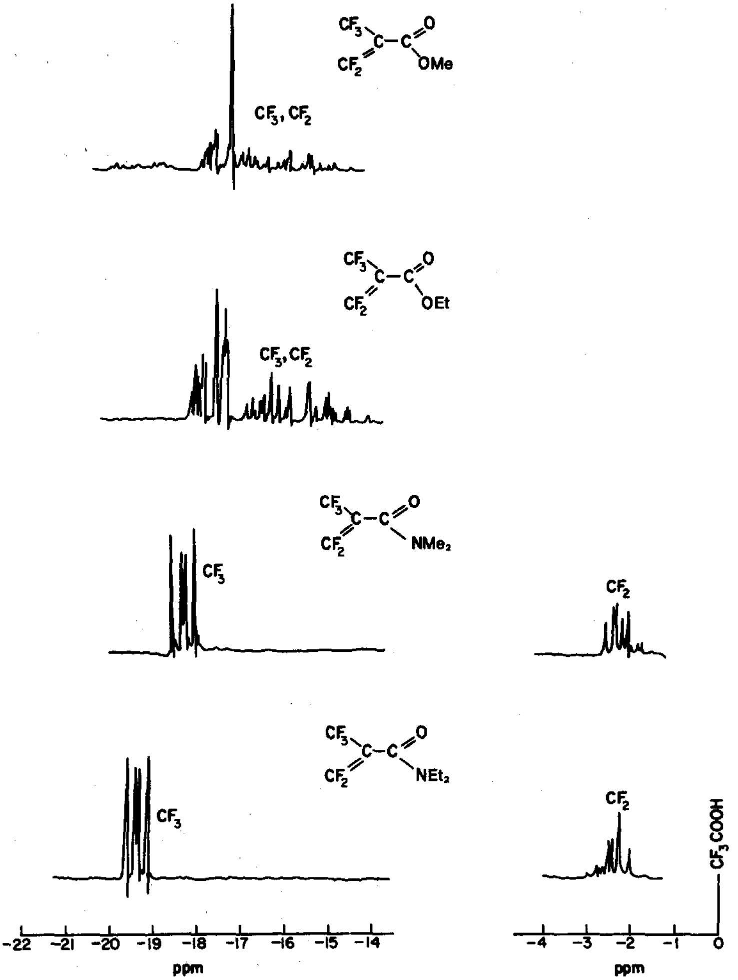
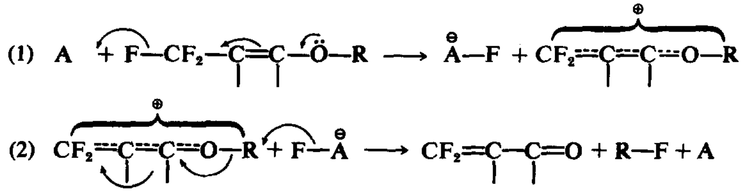


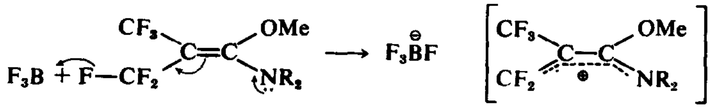
Fig 1. ^{19}F NMR spectra of perfluoromethacrylic acid derivatives.

ination of the fluoride anion from the allyl position of the alkoxyfluoro-olefin, with the formation of a corresponding complex anion (such as $BF_4^{\ominus}$ or $SbF_6^{\ominus}$) and a carbo-cation (*cf* Ref. 7) which is in this case stabilized due to mesomerism. The carbocation which has very strong alkylating properties is capable of further interaction even with weakly nucleophilic fluorine-containing complex anions, with the formation of an α,β-unsaturated carbonyl compound and an alkyl fluoride and regeneration of the Lewis acid. The latter, in accordance with the same scheme, reacts with the next molecule of the alkoxyfluoro-olefin, etc:



This scheme was confirmed by the interaction of aminoacetals of bis(trifluoromethyl)ketene (8) with boron trifluoride.

While aminoacetals (8) on heating with a catalytic quantity of a Lewis acid give perfluoromethacrylic acid amides (10), the mixing of equimolar quantities of the reagents in the cold gives adducts (11) in the form of hygroscopic crystals or viscous liquids:



8a,b.

11

11a: R = Me

11b: R = Et

These unstable compounds are characterized by their NMR spectra. In the ^1H NMR spectra signals are observed from the OMe group and from two non equivalent R groups (Me or Et, respectively; Experimental). The ^{19}F NMR spectra of adducts 11 are presented in Figs 2,3. These spectra, similar to those of perfluoromethacrylic acid amides, evidently, correspond to ABX_3-systems, but here the AB-component (CF_2 group) is found in a lower field than the X_3-component (CF_3 group); the latter circumstance may be attributable to the presence of a partial positive charge at the C atom of the CF_2 group.

The ^{19}F NMR spectra of adducts 11a,b were

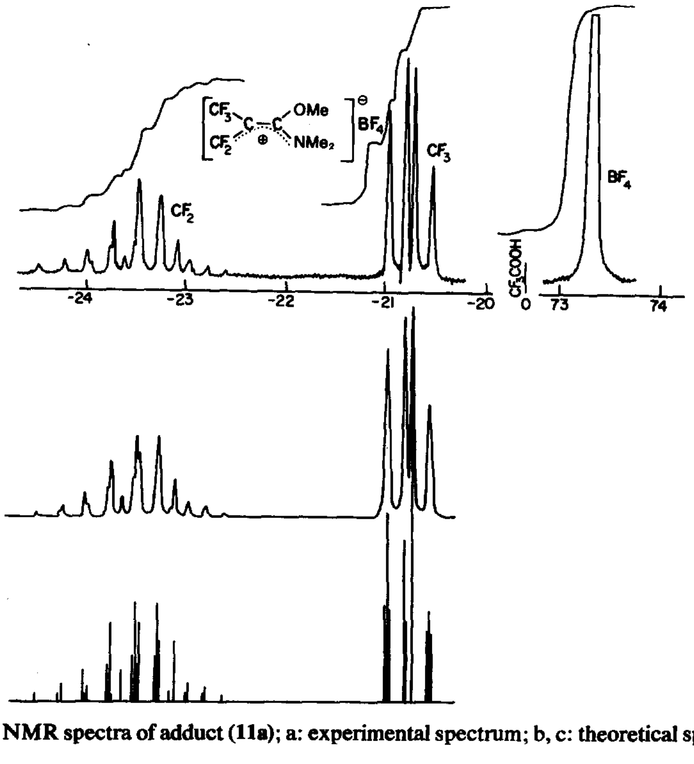


Fig 2. ^{19}F NMR spectra of adduct (11a); a: experimental spectrum; b, c: theoretical spectrum.

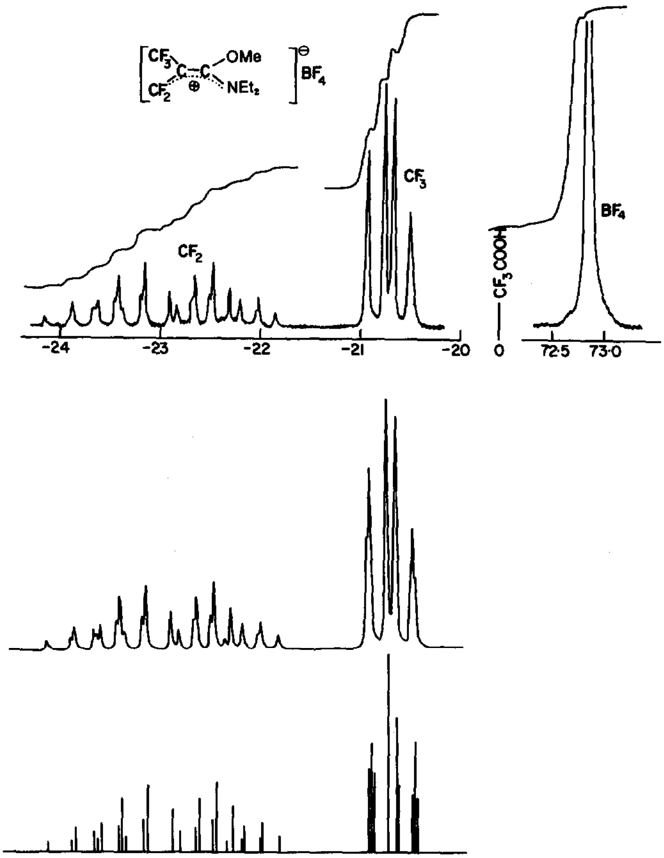


Fig 3. ^{19}F NMR spectra of adduct (**11b**); a: experimental spectrum; b, c: theoretical spectrum.

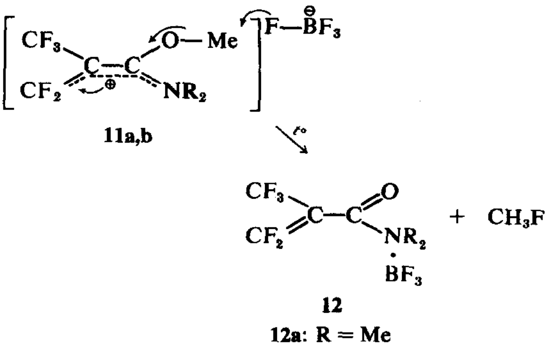
analysed by the simulation method* with the following set of parameters employed:

	11a	**11b**
δ_{X_3}	−20·84 ppm	−20·76 ppm
$\frac{\delta_A+\delta_B}{2}$	−23·72 ppm	−23·10 ppm
$\lvert\delta_A-\delta_B\rvert$	0·58 ppm	1·17 ppm
J_{AX_3}	9·4 Hz	10·2 Hz
J_{BX_3}	16·3 Hz	16·3 Hz
J_{AB}	28·8 Hz	30·1 Hz

As can be seen in Figs 2, 3, the simulated spectra are in good agreement with those obtained experimentally.

Iteration programmes are planned for a more precise estimation of the spin–spin interaction constants and chemical shifts in the AB-region of the spectrum, as well as for the elucidation of the signs of the spin–spin interaction constants. The results will be reported in a special publication.

The heating of compounds **11** to 120–130° results in the elimination of alkyl fluoride and in the formation of adducts of perfluoromethacrylic acid dialkylamides with boron trifluoride (**12**), the products being hygroscopic crystals sublimable in vacuum:



11a,b

12

12a: R = Me

12b: R = Et

These adducts can also be obtained from perfluoromethacrylic acid amides (**10**) and boron trifluoride.

The ^{19}F NMR spectra of adducts **12** are presented in Fig. 4. In contradistinction to amides **10**, here the

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*The spectra were simulated on an electronic computer FABRITEK Model 290 which is in the set of a Fourrier-spectrometer HX-90 "Bruker".

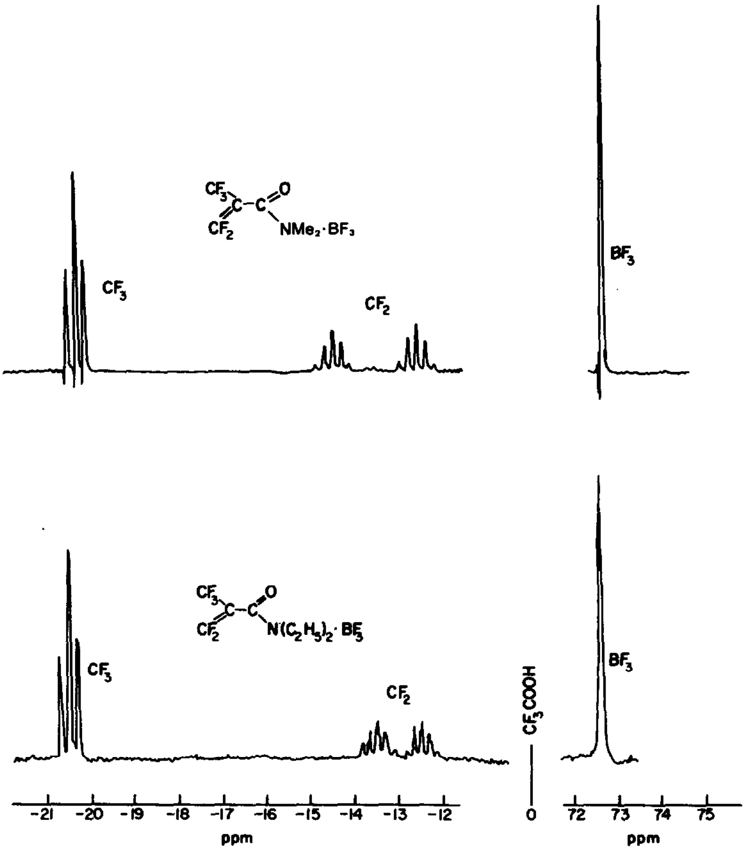
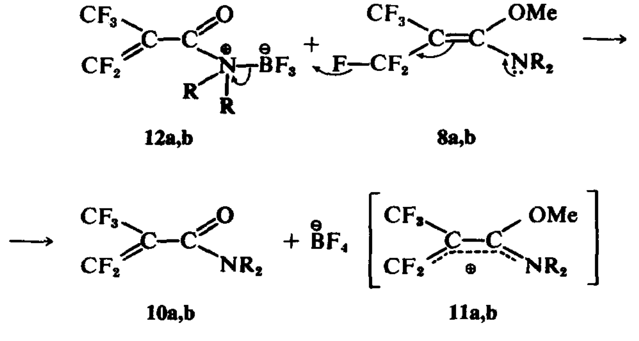


Fig 4. ^{19}F NMR spectra of adducts of perfluoromethacrylic acid dialkylamides with boron trifluoride (**12a,b**).

difference in chemical shifts of the fluorine nuclei of the CF_2 group is sufficiently great and the spectra correspond to AMX_3-systems.

Similarly to the BF_3-etherate, adducts of perfluoromethacrylic acid amides with boron trifluoride are a source of Lewis acid BF_3. Indeed, the interaction of adducts **12** with aminoacetals of bis(trifluoromethyl)ketene (**8**) without heating results in the formation of perfluoromethacrylic acid amides (**10**) and adducts (**11**):

Thus, under the effect of catalytic quantities of Lewis acid on aminacetals of bis(trifluoromethyl)ketene (**8**) a stepwise elimination of alkyl fluoride elements takes place: first the fluoride-anion and then the alkyl-cation. With other alkoxyfluoro-olefins (**1, 5, 7**) this reaction may probably be more or less synchronous in character, due to the lower stability of the intermediate mesomeric carbonium-cation. In any case, the reaction resides in the electrophilic 1,4-elimination of alkyl fluoride and forma-



12a,b **8a,b**

10a,b **11a,b**

Table 1. Elimination of alkyl fluorides from alkyl fluoroalkenyl ethers

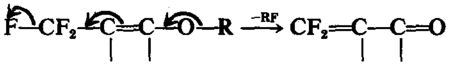
Starting compound	Quantity, g	Lewis acid	Quantity, g	Reaction conditions Temperature, °C	Reaction conditions Duration, hrs	Resulting product	Yield g	Yield per cent of theory
$(CF_3)_2C{=}CFOCH_3$ **(1a)**	10·0	SbF_5	1	b.p.	0·7	$CF_2{=}C(CF_3)COF$ **(3)**	5·7	68
$(CF_3)_2C{=}CFOC_2H_5$ **(1b)**	5·3	$(C_2H_5)_2O{\cdot}BF_3$	0·6	b.p.	3	$CF_2{=}C(CF_3)COF$ **(3)**	2·3	55
$CF_3CF{=}CFOCH_3$ **(5)**	8·1	SbF_5	0·2	b.p.	3	$CF_2{=}CFCOF$ **(6)**	2·5	39
$(CF_3)_2C{=}C(OCH_3)_2$ **(7a)**	16·2	$(C_2H_5)_2O{\cdot}BF_3$	0·2	120–130	1·5	$CF_2{=}C(CF_3)COOCH_3$ **(9a)**	12·2	89
$(CF_3)_2C{=}C(OC_2H_5)_2$ **(7b)**	3·2	$(C_2H_5)_2O{\cdot}BF_3$	0·02	90	2	$CF_2{=}C(CF_3)COOC_2H_5$ **(9b)**	2·2	85
$(CF_3)_2C{=}C(OCH_3)N(CH_3)_2$ **(8a)**	4·4	$(CH_3)_3OBF_4$	0·34	140–150	3	$CF_2{=}C(CF_3)CON(CH_3)_2$ **(10a)**	2·5	66
$(CF_3)_2C{=}C(OCH_3)N(CH_3)_2$ **(8a)**	5·0	$(CH_3)_3O{\cdot}BF_4$	0·40	130	6·5	$CF_2{=}C(CF_3)CON(CH_3)_2$ **(10a)**	3·2	75
$(CF_3)_2C{=}C(OC_2H_5)N(CH_3)_2$ **(8c)**	25·1	$(C_2H_5)_2O{\cdot}BF_3$	0·2	100–115	8	$CF_2{=}C(CF_3)CON(CH_3)_2$ **(10a)**	20·0	99
$(CF_3)_2C{=}C(OC_2H_5)N(C_2H_5)_2$ **(8d)**	4·0	$(C_2H_5)_2O{\cdot}BF_3$	0·2	100–110	2·5	$CF_2{=}C(CF_3)CON(C_2H_5)$ **(10b)**	2·6	78

Table 2. Constants of synthesized compounds

Compound	Boiling point, °C	^{1}H NMR Spectrum δ_{CH_3}	^{1}H NMR Spectrum δ_{CH_2}	^{1}H NMR Spectrum J_{H-H}, Hz	IR-spectrum $\nu_{C=C}$, cm^{-1}	IR-spectrum $\nu_{C=O}$, cm^{-1}	Mol. weight (mass spectrum)	Found, % C	Found, % H	Found, % F	Calculated, % C	Calculated, % H	Calculated, % F
$CF_2{=}C(CF_3)COF^a$ **(3)**	50–51	—	—	—	—	—	—	—	—	—	—	—	—
$CF_2{=}CFCOF^b$ **(6)**	25–28	—	—	—	—	—	—	—	—	—	—	—	—
$CF_2{=}C(CF_3)COOCH_3^c$ **(9a)**	94–95	3·38	—	—	—	—	190	—	—	—	—	—	—
$CF_2{=}C(CF_3)COOC_2H_5$ **(9b)**	106–107	0·89	3·86	7·1	1765	1715	204	35·30	2·42	44·62	35·31	2·47	46·54
$CF_2{=}C(CF_3)CON(CH_3)_2$ **(10a)**	78–80 (39 mm) 40–41 (5 mm)	2·65 and 2·73	—	—	1745	1670	203	35·50	2·92	46·33	35·48	2·98	46·77
$CF_2{=}C(CF_3)CON(C_2H_5)_2$ **(10b)**	75–76 (12 mm)	0·80 and 0·83	3·15	7·3	1750	1665	231	41·39	4·03	41·90	41·57	4·36	41·09

[a] B.p., as reported in Ref. 11, is 51·5°. ^{19}F NMR spectrum is the same as reported in Ref. 12.
[b] B.p., as reported in Ref. 13, is 25·5°. ^{19}F NMR spectrum is the same as reported in Ref. 14.
[c] B.p., as reported in Ref. 3, is 90–92°.

tion of the conjugated system of an α,β-unsaturated carbonyl compound:



Another example of such transformation is the formation of α,β-unsaturated cyclic fluoroketones from the corresponding fluorine-containing alkyl cycloalkenyl ethers.[6,8,9] Such elimination is, obviously, a rather general type of reaction.

EXPERIMENTAL

^1H NMR spectra have been recorded on a "Perkin-Elmer R-12" spectrometer with TMS as an external standard. ^{19}F NMR spectra have been recorded on "Hitachi-Perkin-Elmer R-20" and "Hitachi" spectrometers (working frequency, 56·46 MHz) with trifluoroacetic acid as an external standard. Chemical shifts are given in ppm from TMS or CF_3COOH respectively.

Elimination of alkyl fluorides from alkyl fluoroalkenyl ethers. Acid fluorides (**3** and **6**) were prepared by boiling alkyl perfluoroalkenyl ethers (**1** or **5**) in the presence of antimony pentafluoride or BF_3-etherate, with the resulting products being simultaneously distilled off through a rectification column. Esters **9** and amides **10** were prepared by heating acetals **7** or aminoacetals **8*** and a small quantity of BF_3-etherate and by subsequent distillation. With the use of ethoxy derivatives (**1b**, **7b**, **8c,d**) ethyl fluoride was condensated in a trap (−78°), identified by the ^1H and ^{19}F NMR spectra. The reaction conditions and product yields are presented in Table 1; constants of the compounds are given in Table 2.

*Adducts of aminoacetals of bis(trifluoromethyl)ketene with boron trifluoride (**11a,b**).* Into a soln of **8a** (2·83 g) in 9 ml hexane an excess gaseous BF_3 was passed under cooling, the solvent was distilled off under vacuum (down to 5 mm; bath tempe, to 40°); the residue was a solid colourless hygroscopic adduct (**11a**) with a yield of 3·54 g (97% of theory). ^1H NMR spectrum (in CH_3CN): δ_{CH_3N}, 3·34 and 3·43 (two singlets); δ_{CH_3O}, 4·24 (singlet). ^{19}F NMR spectrum is shown in Fig 2.

By following a similar procedure, from aminoacetal (**8b**) adduct (**11b**) was prepared, the compound being a viscous yellow liquid, with a yield of 98·5% of theory. ^1H NMR spectrum (in CH_3CN): δ_{CH_3C}, 1·18 and 1·20 (two triplets); δ_{CH_2}, 3·76 and 3·80 (two quartets); δ_{CH_3O}, 4·25 (singlet); $J_{CH_3-CH_2}$, 7·3 Hz. ^{19}F NMR spectrum is shown in Fig 3.

Adduct **11a** was also prepared from equimolar quantities of **8a** and BF_3-etherate in the cold.

*Adducts of perfluoromethacrylic acid dialkylamides with boron trifluoride (**12a,b**).* Adduct **11b** (6·7 g) was heated for 1·5 hr at 130–135°, the residue was cooled, sublimated in vacuum (4 mm; bath tempe, up to 120°), and 4·3 g (72% of theory) of colourless hygroscopic solid adduct (**12b**) was obtained. Found: C, 31·61; H, 3·51; F, 49·89. Calc. for $C_8H_{10}BF_8NO$: C, 32·14; H, 3·37; F, 50·84; ^1H NMR spectrum (in CH_3CN): δ_{CH_3}, 1·22 (triplet); δ_{CH_2}, 3·70 (quartet); $J_{CH_3-CH_2}$, 7·2 Hz. ^{19}F NMR spectrum is shown in Fig 4.

Similarly, from **11a** at 115–120° adduct **12a** was obtained. Found: C, 26·24; H, 2·46; F, 56·21; N, 5·61. Calc. for $C_6H_6BF_8NO$: C, 26·60; H, 2·23; F, 56·10; N, 5·17; ^1H NMR spectrum (in CH_3CN): δ_{CH_3}, 2·98 and 3·05 (two singlets). ^{19}F NMR spectrum is shown in Fig 4.

Adduct **12a** was also obtained by heating (120–130°) equimolar quantities of **8a** and trimethyloxonium tetrafluoroborate. Adduct **12b** was formed by reacting **10b** with an equimolar quantity of BF_3-etherate.

*Interaction of adducts (**12**) with aminoacetals of bis(trifluoromethyl)ketene (**8**).* Adduct **12b** (2·30 g), **8b** (2·00 g) and *ca* 0·5 ml abs acetonitrile were mixed. From the resulting soln under vacuum distillation (*ca* 0·001 mm) at room tempe a mixture of acetonitrile and perfluoromethacrylic acid diethylamide (**10b**) was collected in a trap cooled with liquid N_2; the yield of **10b** was 1·32 g (74% of theory). The residue was crude adduct **11b** (identified by the NMR spectra).

^1H and ^{19}F NMR spectra showed that the mixture of **12a** and **8a** in acetonitrile at room temp was completely converted to the mixture of **11a** and **10a**.

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*Acetals and aminoacetals of bis(trifluoromethyl)ketene are prepared by reacting alkyl perfluoroisobutenyl ethers (**1**), correspondingly, with sodium alkoxides or with secondary amines.[10]

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