

PHOTOCHEMICAL ADDITION OF ETHERS TO METHYL TRIFLUOROACRYLATE

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The addition of diethyl ether, 1,2-dimethoxyethane, tetrahydrofuran, 1,4-dioxan, 1,3-dioxolan and 4-methyl-1,3-dioxan to methyl trifluoroacrylate initiated by UV light gave the corresponding, a : 1 adducts in a preparative 36–79% yield. The total relative reactivity of ethers in the investigated addition decreases in the following order: tetrahydrofuran > 4-methyl-1,3-dioxan > 1,3-dioxolan > diethyl ether > 1,2-dimethoxyethane > 1,4-dioxan.

Little attention is given in the literature to radical addition reactions of ethers with fluorinated olefins. These reactions are initiated by organic peroxides^{1–6}, γ -radiation^{7–11} and ultraviolet radiation^{11,12}. Resulting from these reactions are monoadducts (1 : 1 adducts) and the products of telomerisation. In contrast to this the irradiation of a mixture of ether and methyl acrylate with ultraviolet light is also accompanied, as we observed, by the polymerisation of the monomer^{13,14} (taxogen). In connection with this it was interesting to learn which chemical properties would appear in the case of methyl trifluoroacrylate. From some ionic reactions^{14–16} of methyl trifluoroacrylate it follows that it may be compared with highly fluorinated olefins.

In this paper we investigated the reaction of methyl trifluoroacrylate initiated by ultraviolet light with some aliphatic and alicyclic ethers, namely diethyl ether, 1,2-dimethoxyethane, tetrahydrofuran, 1,4-dioxan, 1,3-dioxolan, and 4-methyl-1,3-dioxan. The reaction was carried out in liquid phase in a quartz reactor with an ultraviolet light source at 15–18°C. The molar ratio of ether and methyl trifluoroacrylate 19 : 1 guaranteed according to earlier experiences^{15,17} the preferential formation of a monoadduct.

In the course of the reaction of ethers with methyl trifluoroacrylate the cleavage of the C—H bond on the carbon in the position α to the ether oxygen atom took place as well as the addition of both particles to the olefinic bond of methyl trifluoroacrylate (Scheme 1). In ethers which contain a larger number of α -bonds

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TABLE I
Conditions and Results of the Reaction of Methyl Trifluoroacrylate with Ethers (molar ratio 5 : 95)

No	Ether ^a		Time h	Fraction of monoadduct ^b		Residue ^d g	
	g	mol		g	%		Comp. ^c (% rel.)
1	DE	42.2	0.57	3.02	47	I (100)	1.49
2	DME	51.3	0.57	2.51	36	IIb, IIa (78; 22)	2.08
3	DME	58.7	0.65	1.23	18	IIb, IIa (77; 23)	1.02
4	THF	41.1	0.57	4.09	64.5	III (100)	0.61
5	THF	82.2	1.14	10.04	79	XI, VIII, III (2; 6; 93)	2.37
6	DO	50.2	0.57	2.82	41	VIIa, VIIb, IV (1; 7; 92)	1.79
7	DO	76.8	0.87	2.53	22	VIIb, IV (5; 95)	1.31
8	DOL	42.2	0.57	5.14	79	IXb, Vb, IXa, Va (1; 7.5; 18; 73.5)	1.46
9	MDO	58.1	0.57	3.43	48	Xb, VIc, Xa, VIa—VIIb (1; 17; 6; 76)	2.17
10	MDO	73.0	0.17	3.02	42	Xb, VIc, Xa, VIa—VIIb (3.5; 15.5; 9; 72)	2.71

^a DE diethyl ether, DME 1,2-dimethoxyethane, THF tetrahydrofuran, DO 1,4-dioxan, DOL 1,3-dioxolan, MDO 4-methyl-1,3-dioxan; ^b preparative yield of the monoadduct fraction; ^c sequence of substances according to gas chromatography (see Experimental); ^d distillation residue.

tetrahydrofuran methyl 3-(2-tetrahydrofuryl)-2,3,3-trifluoropropionate (*III*) was formed as a monoadduct. After 20 hours irradiation secondary products *VIII* and *XI* appeared in the reaction mixture. Reaction of 1,4-dioxan gave the secondary reaction products *VIIa*, *VIIb* after 40 hours reaction time in addition to the monoadduct, methyl 3-(1,4-dioxacyclohexyl)-2,3,3-trifluoropropionate (*IV*). The fraction of the monoadduct from the reaction of 1,3-dioxolan contained two isomeric products, methyl 3-[2(1,3-dioxacyclopentyl)]- (*Va*) and methyl 3-[5(1,3-dioxacyclopentyl)]-2,3,3-trifluoropropionate (*Vb*; 91 and 9% rel.), and secondary products *IXa*, *IXb*; we proposed the structure for the second isomer *Vb* on the basis of its mass spectrum (Table IV). 4-Methyl-1,3-dioxan contains three types of C—H bonds in the α -position to the oxygen atom. In the mixture after the photochemical addition reaction of this ether with trifluorochloroethylene three isomeric monoadducts were identified¹² occurring in relative amounts 36, 49 and 15%, which correspond to the relative reactivity of C—H bonds in positions 2, 4, and 6. The analysis of the mixture of isomers *VI* was based on these findings. The fraction contained two waves corresponding to isomers *VI*, in relative amounts 83 and 17%. The PMR spectrum of the main chromatographic wave corresponds to the mixture of methyl 3-[2(4-methyl-1,3-dioxacyclohexyl)]- (*VIa*) and methyl 3-[4(4-methyl-1,3-dioxacyclohexyl)]-2,3,3-tri-

TABLE II
Elemental Analyses of Substances *I*—*VI*

Substance	Formula (m.w.)	Calculated/Found			B.p., °C/Torr	Purity % rel.
		% C	% H	% F		
<i>I</i>	C ₈ H ₁₃ F ₃ O ₃ (214.2)	44.86	6.11	26.62	31—32/0.2	100
		44.63	6.13	26.84		
<i>IIa</i>	C ₈ H ₁₃ F ₃ O ₄ (230.2)	41.74	5.69	24.76	42—43/0.2 ^a	94
		41.53	5.64	24.74		
<i>IIb</i>		41.74	5.69	24.76		95
<i>III</i>	C ₈ H ₁₁ F ₃ O ₃ (212.2)	45.28	5.23	26.28	55—57/0.2	99
		44.97	5.10	27.03		
<i>IV</i>	C ₈ H ₁₁ F ₃ O ₄ (228.2)	42.11	4.86	24.97	58—60/0.2	99
		42.19	4.95	25.07		
<i>Va</i>	C ₇ H ₉ F ₃ O ₄ (214.1)	39.25	4.23	26.63	59—60/0.4	98
		39.30	4.23	26.50		
<i>VI</i>	C ₉ H ₁₃ F ₃ O ₄ (242.2)	44.63	5.41	22.53	42—43/0.2	97 ^b
		44.78	5.04	23.40		

^a Boiling point of a mixture of isomers *IIa*, *IIb*; ^b a mixture of *VIa*, *VIb*.

fluoropropionate (*VIb*) present in approximately equimolar amounts. To the second wave we assign the structure of methyl 3-[6(4-methyl-1,3-dioxacyclohexyl)]-2,3,3-trifluoropropionate (*VIc*) on the basis of our experience with the reaction with trifluorochloroethylene¹². The fraction of monoadducts *VI* always contained secondary products *Xa* and *Xb* (Table I). The structures of adducts *I–VI* follow from elemental analysis (Table II), PMR spectra (Table III), mass spectra (Table IV) and IR spectra (Table V). Monoadducts *I–VI* contain in the molecule at least two asymmetric carbon atoms. However, in contrast to similar cases when the taxogen was trifluorochloroethylene^{11,12,18,19}, we were unable to separate them by gas chromatography to diastereoisomers.

The fraction of monoadduct from some experiments contained other substances which could not be isomers. From experiment 5 of the reaction of tetrahydrofuran (Table I) we isolated by preparative gas chromatography substance *VIII* the structure of which we deduced on the basis of PMR, mass and IR spectra. It was found that

TABLE III
PMR Spectra of Substances *I–VIII* (chemical shift δ (number of protons); s singlet, d doublet, t triplet, m multiplet, ddd doublet of a doublet of doublets, q quasi; coupling constant J c/s)

Substance	Character of peaks
<i>I</i>	dm 5.13 (1), $^2J = 46.5$, $-\text{CF}_2\text{CHF}$; qd 3.85 (3), $-\text{COOCH}_3$; m 3.28–4.02 (4), $-\text{OCH}_3$, $-\text{CH}-\text{O}$; qd 1.28 (3), $-\text{OCH}-\text{CH}_3$; qt 1.16 (3), $-\text{OCH}_2\text{CH}_3$
<i>IIa</i>	qddd 5.13 (1), $^2J_{\text{HF}} = 46.6$, $^3J_{\text{HF}} = 6.4$; 4.5, $-\text{CF}_2\text{CHF}$; qs 3.87 (3), $-\text{COOCH}_3$ m 3.44–4.11 (6), $-\text{CH}_2\text{OCH}_2\text{CH}_2\text{O}$; qs 3.38 (3), $-\text{OCH}_3$
<i>IIb</i>	dm 5.12 (1), $^2J_{\text{HF}} = 46.4$, $-\text{CF}_2\text{CHF}$; s 3.86 (3), $-\text{COOCH}_3$; qs 3.67 (2), $-\text{CH}-\text{CH}_2$; qd 3.52 (3), CH_3O ; s 3.39 (3), CH_3O
<i>III</i>	dm 5.17 (1), $-\text{CF}_2\text{CHF}$; dm 4.32 (1), $-\text{O}-\text{CH}-\text{CF}_2$; qd 3.86 (3), $-\text{COOCH}_3$; 3.73–3.99 (2), $-\text{CH}_2\text{O}$; m 1.79–2.30 (4), $-\text{CH}_2\text{CH}_2-\text{CH}$
<i>IV</i>	dm 5.18 (1), $-\text{CF}_2\text{CHF}$; dm 4.02 (1), $-\text{O}-\text{CH}-\text{CF}_2$; ds 3.87 (3), $-\text{COOCH}_3$; m 3.54–4.18 (6), $-\text{O}-\text{CH}_2\text{CH}_2\text{O}-\text{CH}_2$
<i>Va</i>	qt 5.33 (1), $^3J_{\text{HF}} = 7.6$, $-\text{O}-\text{CH}-\text{O}$; ddd 5.14 (1), $^2J_{\text{HF}} = 45.8$, $^3J_{\text{HF}} = 12.2$; 9.6, $-\text{CF}_2\text{CHF}$; m 3.94–4.17 (4), $-\text{OCH}_2\text{CH}_2\text{O}$; s 3.87 (1), $-\text{COOCH}_3$
<i>VIa, VIb</i>	dm 5.20 (1), $-\text{CF}_2\text{CHF}$ (<i>VI, VIb</i>); qt 5.14 (1), $^3J_{\text{HF}} = 7.4$, $-\text{O}-\text{CH}(\text{CF}_2)-\text{O}$ (<i>VIa</i>); qs 4.84 (2), $-\text{O}-\text{CH}_2-\text{O}$ (<i>VIb</i>); m 4.15–4.50; m 3.56–4.15; qs 3.81, $-\text{COOCH}_3$ (<i>VIa, VIb</i>); m 1.84–2.57; s 1.47 (3), $-\text{C}(\text{CF}_2)-\text{CH}_3$ (<i>VIb</i>); d 1.33 (3), $^3J_{\text{HH}} = 7$, $-\text{CH}-\text{CH}_3$ (<i>VIa</i>)
<i>VIII</i>	dm 4.28 (1), $-\text{O}-\text{CH}-\text{CF}$; m 3.64–3.97 (2), $-\text{CH}_2\text{O}$; s 3.73 (3), $-\text{COOCH}_3$ m 2.82–3.24 (2), $-\text{CHF}-\text{CHF}$; m 1.70–2.30 (4), $-\text{CH}_2\text{CH}_2-\text{CH}$

TABLE IV
Mass Spectra of Substances I—XII (ionic species m/e , relative intensity %)

Substance/ $m.w.$	Main ionic species
<i>I</i> 214	215/0.05 (M + 1) ⁺ ; 214/0.03 (M) ⁺ ; 213/0.06 (M - 1) ⁺ ; 183/3.5 (M - CH ₃ O) ⁺ ; 155/27 (M - C ₂ H ₃ O ₂) ⁺ ; 135/20 (M - C ₂ H ₄ FO ₂) ⁺ ; 107/14.5 (C ₃ HF ₂ O ₂) ⁺ ; 77/16 (C ₃ H ₃ F ₂) ⁺ ; 59/100 (C ₂ H ₃ O ₂) ⁺ ; 45/44 (C ₂ H ₅ O) ⁺ ;
<i>IIa</i> 230	210/5 (M - HF) ⁺ ; 198/0.3 (M - CH ₄ O) ⁺ ; 185/1.6 (M - C ₂ H ₅ O) ⁺ ; 155/26 (M - C ₃ H ₇ O ₂) ⁺ ; 59/46 (C ₂ H ₃ O ₂) ⁺ ; 45/100 (C ₂ H ₅ O) ⁺ ; 32/13 (CH ₄ O) ⁺ ; 30/21 (CH ₂ O) ⁺ ;
<i>IIb</i> 230	229/0.1 (M - 1) ⁺ ; 198/5 (M - CH ₄ O) ⁺ ; 185/8 (M - C ₂ H ₅ O) ⁺ ; 179/3 (M - CH ₄ FO) ⁺ ; 166/24 (M - C ₂ H ₅ FO) ⁺ ; 107/40 (C ₄ H ₅ F ₂ O ₂) ⁺ ; 90/8 (C ₃ H ₃ FO ₂) ⁺ ; 59-24 (C ₂ H ₃ O ₂) ⁺ ; 45/100 (C ₂ H ₅ O) ⁺ ;
<i>III</i> 212	213/0.3 (M + 1) ⁺ ; 211/0.1 (M - 1) ⁺ ; 181/3.5 (M - CH ₃ O) ⁺ ; 133/9 (M - C ₂ H ₄ FO ₂) ⁺ ; 91/9 (C ₃ H ₄ FO ₂) ⁺ ; 71/100 (C ₄ H ₇ O) ⁺ ; 59/18 (C ₂ H ₃ O ₂) ⁺ ; 43/69 (C ₃ H ₇) ⁺ ; 42/16 (C ₃ H ₆) ⁺ ; 41/33 (C ₃ H ₃) ⁺ ; 39/16 (C ₃ H ₃) ⁺ ; 29/18 (CHO) ⁺ ; 27/18 (C ₂ H ₃) ⁺ ;
<i>IV</i> 228	228/2.5 M ⁺ ; 227/2.5 (M - 1) ⁺ ; 188/30 (M - CH ₃ FO) ⁺ ; 137/30 (M - C ₃ H ₄ .FO ₂) ⁺ ; 92/23; 91/30 (C ₃ H ₄ FO ₂) ⁺ ; 87/100 (C ₄ H ₇ O ₂) ⁺ ; 59/77 (C ₂ H ₃ O ₂) ⁺ ; 51/23 (CH ₄ FO) ⁺ ; 43/77 (C ₂ H ₃ O) ⁺ ; 30/85 (CH ₂ O) ⁺ ;
<i>Va</i> 214	215/0.2 (M + 1) ⁺ ; 213/0.3 (M - 1) ⁺ ; 183/2 (M - CH ₃ O) ⁺ ; 154/2 (M - C ₂ H ₄ O ₂) ⁺ ; 91/6 (M - C ₃ H ₄ FO ₂) ⁺ ; 82/6 (C ₂ HF ₃) ⁺ ; 73/100 (C ₃ H ₅ O ₂) ⁺ ; 59/12 (C ₂ H ₃ O ₂) ⁺ ;
<i>Vb</i> 214	213/13.5 (M - 1) ⁺ ; 184/24 (M - CH ₃ O) ⁺ ; 153/8 (M - C ₂ H ₄ O ₂) ⁺ ; 91/17 (C ₃ H ₄ FO ₂) ⁺ ; 73/100 (C ₃ H ₅ O ₂) ⁺ ; 59/81 (C ₂ H ₃ O ₂) ⁺ ;
<i>VIa, VIb</i> 242	243/0.2 (M + 1) ⁺ ; 241/0.6 (M - 1) ⁺ ; 101/77 (C ₅ H ₉ O ₂) ⁺ ; 71/38 (C ₄ H ₇ O) ⁺ ; 59/27 (C ₂ H ₃ O ₂) ⁺ ; 55/71 (C ₃ H ₃ O) ⁺ ; 34/100 (C ₂ H ₅ O) ⁺ ;
<i>VIc</i> 242	241/2.5 (M - 1) ⁺ ; 167/30 (M - C ₃ H ₇ O ₂) ⁺ ; 101/98 (C ₅ H ₉ O ₂) ⁺ ; 71/87 (C ₄ H ₇ .O) ⁺ ; 59/100 (C ₂ H ₃ O ₂) ⁺ ; 55/58 (C ₃ H ₃ O) ⁺ ;
<i>VIII</i> 194	195/0.15 (M + 1) ⁺ ; 193/0.1 (M - 1) ⁺ ; 174/39 (M - HF) ⁺ ; 163/69 (M - CH ₃ O) ⁺ ; 143/17 (M - CH ₄ FO) ⁺ ; 115/100 (M - C ₂ H ₄ FO ₂) ⁺ ; 95/25 (M - C ₂ H ₅ F ₂ O ₂) ⁺ ; 91/24 (M - C ₃ H ₄ FO ₂) ⁺ ; 71/58 (C ₄ H ₇ O) ⁺ ;
<i>IXa</i> 196	197/0.1 (M + 1) ⁺ ; 195/0.1 (M - 1) ⁺ ; 176/0.1 (M - HF) ⁺ ; 165/16 (M - CH ₃ O) ⁺ ; 145/5 (M - CH ₄ FO) ⁺ ; 137/5 (M - C ₂ H ₃ O ₂) ⁺ ; 73/100 (C ₃ H ₅ O ₂) ⁺ ;
<i>IXb</i> 196	195/3 (M - 1) ⁺ ; 176/88 (M - HF) ⁺ ; 165/44 (M - CH ₃ O) ⁺ ; 137/22 (M - C ₂ H ₃ O ₂) ⁺ ; 115/96 (C ₅ H ₄ FO ₂) ⁺ ; 99/44 (C ₅ H ₇ O ₂) ⁺ ; 73/100 (C ₃ H ₅ O ₂) ⁺ ;

TABLE IV
(Continued)

Sub- stance/m.w.	Main ionic species
<i>Xa</i> 224	223/0.25 (M - 1) ⁺ ; 121-20 (C ₄ H ₃ F ₂ O ₂) ⁺ ; 101/100 (C ₅ H ₉ O ₂) ⁺ ; 71/13 (C ₄ H ₇ .O) ⁺ ; 59/17 (C ₂ H ₃ O ₂) ⁺ ; 55/23 (C ₃ H ₃ O) ⁺ ;
<i>Xb</i> 224	225/0.5 (M + 1) ⁺ ; 223/1 (M - 1) ⁺ ; 204/8 (M - HF) ⁺ ; 162/25 (M - C ₂ H ₆ O ₂) ⁺ ; 141/25; 101/100 (M - C ₅ H ₉ O ₂) ⁺ ; 99/63 (C ₅ H ₇ O ₂) ⁺ ; 71/78 (C ₄ H ₇ O) ⁺ ; 59/60 (C ₂ H ₃ O ₂) ⁺ ; 45/70 (C ₂ H ₅ O) ⁺ ;
<i>XI</i>	173/0.4 (M - 1) ⁺ ; 142/10 (M - CH ₃ O) ⁺ ; 84/30 (M - C ₃ H ₃ FO ₂) ⁺ ; 71/100 (C ₄ H ₇ O) ⁺ ; 70/38 (C ₄ H ₆ O) ⁺ ;

this substance contains the CHF—CHF grouping in the fluorinated ligand. Substance *VIII*, methyl 3-(2-tetrahydrofuryl)-2,3-difluoropropionate, appeared in the reaction mixture only after a prolonged reaction (Table I). We suppose, therefore, that the precursor of substance *VIII* is the primary addition product *III* in which on ultra-violet irradiation in tetrahydrofuran substitution of the fluorine atom in the CF₂ group with hydrogen took place, *i.e.* the photochemical reduction of fluorine. From literature cases are known of photochemical reduction of halogens, chlorine^{20,21} or bromine²², which take place easily in secondary alcohols. On the other hand, we know of no case of a similar reaction of fluorine. Secondary reduction products were also found in reactions of other ethers, 1,3-dioxolan and 4-methyl-1,3-dioxan, *i.e.* methyl 3-[2(1,3-dioxacyclopentyl)]- (*IXa*), methyl 3-[5(1,3-dioxacyclopentyl)]-

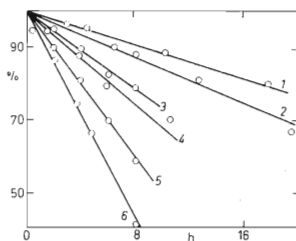


FIG. 1

Decrease of Methyl Trifluoroacrylate Concentration in Time During its Photoinitiated Reaction with Ethers

1 1,4-Dioxan; 2 1,2-dimethoxyethane; 3 diethyl ether; 4 1,3-dioxolan; 5 4-methyl-1,3-dioxan; 6 tetrahydrofuran.

TABLE V
Absorption Maxima (cm^{-1}) in Infrared Spectra of Substances I—VIII (tetrachloromethane)

Substance	$\delta(\text{CH}_3)_a$ s	$\nu(\text{C}=\text{O})$	Other maxima
I	1 438 m 1 775 m	1 760 s 1 775 s	1 010 s, 1 118 s, 1 195 m, 1 236 s, 1 300 m, 1 320 m, 2 875 m, 2 900 m, 2 950 m, 2 980 m
IIa	1 440 m	1 760 s 1 775 s	1 115 s, 1 205 m, 1 232 s, 1 290 m, 1 325 m, 2 875 m, 2 925 w, 2 950 w
IIb	1 440	1 760 s 1 775 s	1 115 s, 1 185 m, 1 232 s, 1 290 m, 1 325 m, 2 825 w, 2 850 w, 2 925 m, 2 950 w
III	1 438 s	1 755 s 1 774 s	935 m, 985 m, 1 010 s, 1 048 m, 1 084 s, 1 112 s, 1 180 s, 1 195 s, 1 228 s, 1 308 s, 1 357 m, 2 875 m, 2 950 s, 2 980 m
IV	1 440 s	1 760 s 1 778 s	893 m, 903 m, 913 m, 920 m, 980 m, 1 008 m, 1 050 m, 1 125 s, 1 194 s, 1 230 s, 1 270 s, 1 295 s, 1 321 s, 1 352 m, 2 860 m, 2 950 m, 2 975 m
Va	1 440 s	1 760 s 1 780 s	940 m, 980 m, 1 010 s, 1 070 s, 1 110 s, 1 190 s, 1 235 s, 1 280 m, 1 315 s, 1 350 m, 2 900 m, 2 950 m, 2 975 m
VIa, VIb	1 440 m	1 760 s 1 775 s	990 s, 1 030 s, 1 115 s, 1 85 s, 1 230 s, 1 285 s, 1 355 m, 2 875 m, 2 950 m, 2 975 m
VIII	1 438 ms	1 753 s 1 774 m(sh)	934 m, 1 003 m, 1 050 m, 1 082 s, 1 127 ms, 1 172 m, 1 218 m, 1 272 m, 1 345 m, 1 357 m, 2 878 m, 2 953 m, 2 982 m

(IXb), and unidentified isomers of methyl 3-(4-methyl-1,3-dioxacyclohexyl)-2,3-difluoropropionate (Xa, Xb). The structures of these substances were deduced from mass spectra (Table IV) and the structures of isomers IXa and IXb were assigned on the basis of their relative amounts in relation to the primary adducts Va and Vb.

In the fraction of monoadducts of tetrahydrofuran we found substance XI after a prolonged reaction to which we assigned on the basis of its mass spectrum the structure of methyl 3-(2-tetrahydrofuryl)-2-fluoroacrylate. The formation of substance XI can be explained by dehydrofluorination of the difluoro derivative VIII under the effect of ultraviolet radiation. The position of fluorine in α -position to the methoxycarbonyl group seems to us more probable than in the β -position. Therefore we consider that β -fluorine in the molecule of fluoropropionates is very reactive²³, because in the mass spectrum (Table IV) the fragment m/e 84 ($M - C_3H_3O_2F$)⁺ is present among the main ionic species, while the fragment ($M - HF$)⁺ is absent.

After a prolonged reaction of 1,4-dioxan we also found two secondary products, VIIa and VIIb in the reaction mixture. The mass of the highest ionic species of both substances in their mass spectra (213 and 227) does not exceed the mass of the 1 : 1 adduct (IV; 228). In both spectra the main ionic species m/e 81 ($C_4H_7O_2$)⁺ dominates as in the spectrum of the monoadduct IV. Therefore we suppose that both substances, VIIa and VIIb, are derivatives of 1,4-dioxan.

In the literature⁷ the reactivity of some ethers during their reaction with fluoroethylenes, initiated with γ -radiation, is evaluated qualitatively. We were interested to learn whether the order⁷ obtained, tetrahydrofuran > diethyl ether > 1,4-dioxan, would remain unchanged in photochemical addition reactions with methyl trifluoroacrylate too. In the study of total reactivity of ethers we measured the concentration decrease of methyl trifluoroacrylate in the reaction mixture by means of gas chromatography (Fig. 1). We supposed that the transfer constants are approximately equal for all ethers and for the same taxogen. From the dependences obtained (Fig. 1) it followed that the general order of reactivity is: tetrahydrofuran > 4-methyl-1,3-dioxan > 1,3-dioxolan > diethyl ether > 1,2-dimethoxyethane > 1,4-dioxan. Hence, the order corresponds to that previously found for the three mentioned ethers for a reaction initiated by radiation.

EXPERIMENTAL

The temperature data were not corrected. Gas chromatography was carried out on a Chrom 3 apparatus (Laboratorní přístroje, Prague; FID, analytical columns of 0.6 cm diameter, preparative columns of 1 cm diameter, length 500 cm, carrier gas nitrogen; support of the stationary phase Chromaton N-AW-DMCS, Lachema, Brno). The infrared spectra were measured on a Perkin-Elmer 325 apparatus (Bodenseewerk); the PMR spectra were recorded with a Varian XL-100-15 apparatus (Palo Alto; deuteriochloroform). The mass spectra were measured on a Gas Chromatograph-Mass Spectrometer LKB 9 000 (Stockholm; single focus, electron energy 70 eV; gas chromatographic inlet: poly(ethyleneglycol adipate), support Chromaton N-AW, glass column of 250 cm length, diameter 0.23 cm, 170—180°C, helium 10 ml/min).

Chemicals Used

1,3-Dioxolan was prepared from ethylene glycol and paraformaldehyde²⁴. 4-Methyl-1,3-dioxan was prepared by reaction of 1,3-butanediol with paraformaldehyde²⁵. The chemicals used were dried over sodium and distilled in the presence of sodium under argon. Methyl trifluoroacrylate was prepared according to the described procedure²⁶.

Photochemical Addition of Ethers

A. Preparative reaction: A mixture of ether and methyl trifluoroacrylate (Table I) was irradiated with a UV lamp (Tesla, 125 W) in a stream of argon at 15–18°C in a quartz reactor. After elimination of unreacted components by distillation the products were distilled *in vacuo* to give a fraction of monoadduct (for composition and yields see Table I). Gas chromatography: poly(propylene sebacate) 15%, column 120 cm, 180–210°C.

B. Relative reactivity of ethers: A mixture of methyl trifluoroacrylate (4.20 g; 30 mmol), tert-butyl alcohol (1.21 g; 16 mmol; internal standard), and ether (570 mmol) was irradiated as under *A*. The samples withdrawn were analysed by gas chromatography (see *A.*, temperature programme 80–120°C). The concentration decrease of methyl trifluoroacrylate was calculated using a calibration graph tert-butyl alcohol–methyl trifluoroacrylate.

The spectra were measured in the Department of Infrared Spectroscopy (head Dr P. Adámek), in the Department of Mass Spectrometry (head Dr V. Kubelka), and in the Department of NMR spectra; elemental analyses were determined in the Department of Organic Analysis (head Dr L. Helešic) of the Institute of Chemical Technology. We thank them all for the analyses.

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