

## PHOTOINITIATED ADDITION OF 1,3-DIOXOLANES TO CHLOROTRIFLUOROETHYLENE

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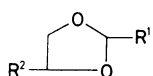
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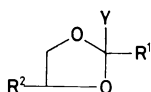
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Within the framework of our investigations on radical-initiated additions of ethers<sup>1-2</sup> and acetals<sup>3-6</sup> to olefins we performed this reaction with some 1,3-dioxolanes. Besides obtaining monomers for modified polymethylene oxides, we aimed at a study of the reactivity of individual C—H bonds in 1,3-dioxolanes in the photochemically initiated addition to chlorotrifluoroethylene.

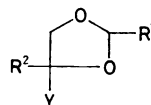
As telogenes we chose 1,3-dioxolane (*I*), 2-methyl-1,3-dioxolane (*II*), and 4-methyl-1,3-dioxolane (*III*). We have found that in the photochemically initiated addition to chlorotrifluoroethylene the C—H bonds in positions 4 and 5 are substantially less reactive: the reaction afforded about 90% of compounds arising by fission of the C—H bond in position 2 of the dioxolane and only 4–15% were products of addition in position 4 or 5. The yields of 1 : 1 adducts (related to the reacted chlorotrifluoroethylene) amounted to 53–60% (Table I) whereas the addition of 1,3-dioxolane to 1-heptene, 1-hexene or 1-octene is reported<sup>4</sup> to give only about 20–34% of 1 : 1 adducts.



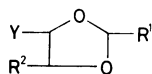
- I*, R<sup>1</sup> = R<sup>2</sup> = H  
*II*, R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = H  
*III*, R<sup>1</sup> = H; R<sup>2</sup> = CH<sub>3</sub>



- IV*, R<sup>1</sup> = R<sup>2</sup> = H; Y = CF<sub>2</sub>CFCIH  
*V*, R<sup>1</sup> = R<sup>2</sup> = H; Y = (CF<sub>2</sub>CFCI)<sub>2</sub>H  
*VI*, R<sup>1</sup> = R<sup>2</sup> = H; Y = (CF<sub>2</sub>CFCI)<sub>3</sub>H  
*VII*, R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = H; Y = CF<sub>2</sub>CFCIH  
*VIII*, R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = H; Y = (CF<sub>2</sub>CFCI)<sub>2</sub>H  
*IX*, R<sup>1</sup> = H; R<sup>2</sup> = CH<sub>3</sub>; Y = CF<sub>2</sub>CFCIH  
*X*, R<sup>1</sup> = H; R<sup>2</sup> = CH<sub>3</sub>; Y = (CF<sub>2</sub>CFCI)<sub>2</sub>H  
*XI*, R<sup>1</sup> = H; R<sup>2</sup> = CH<sub>3</sub>; Y = (CF<sub>2</sub>CFCI)<sub>3</sub>H



- IVa*, R<sup>1</sup> = R<sup>2</sup> = H; Y = CF<sub>2</sub>CFCIH  
*Va*, R<sup>1</sup> = R<sup>2</sup> = H; Y = (CF<sub>2</sub>CFCI)<sub>2</sub>H  
*VIIa*, R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = H; Y = CF<sub>2</sub>CFCIH  
*VIIIa*, R<sup>1</sup> = CH<sub>3</sub>; R<sup>2</sup> = H; Y = (CF<sub>2</sub>CFCI)<sub>2</sub>H  
*IXb*, R<sup>1</sup> = H; R<sup>2</sup> = CH<sub>3</sub>; Y = CF<sub>2</sub>CFCIH  
*Xa*, R<sup>1</sup> = H; R<sup>2</sup> = CH<sub>3</sub>; Y = (CF<sub>2</sub>CFCI)<sub>2</sub>H



- IXa*, R<sup>1</sup> = H; R<sup>2</sup> = CH<sub>3</sub>; Y = CFCFCIH

TABLE I  
Addition of 1,3-dioxolanes I—III to chlorotrifluoroethylene

Dioxolane	Amount mol	CF <sub>2</sub> =CFCl mol	Reaction time, h	Products, mole % <sup>a</sup>			Residue <sup>b</sup>		
I	1.64	0.812	30	IV (56.3)	IVa (2.5)	V (6.8)	Va (1.9)	VI (0.8)	1.2
I <sup>c</sup>	1.74	0.600	30	IV (53.1)	IVa (5.6)	V (10.9)	Va (2.6)	VI (0.45)	1.7
II	0.794	0.670	30	VII (63.1)	VIIa (11.4)	VIII (13.7)	VIIIa (0.7)	—	3.2
II <sup>c</sup>	0.920	0.962	30	VII (53.1)	VIIa (9.0)	VIII (12.3)	VIIIa (5.9)	—	16.7
III	1.066	0.75	46	IX (58.9)	IXa (2.2)	X (17.0)	Xa (1.4)	XI (1.5)	1.9
					IXb (0.9)				
III <sup>c</sup>	3.22	2.34	55	IX (60.0)	IXa (2.9)	X (11.6)	Xa (3.0)	XI (1.7)	14.2
					IXb (1.0)				

<sup>a</sup> Mole %, calculated for the reacted chlorotrifluoroethylene; <sup>b</sup> in g; <sup>c</sup> in the presence of acetone (8.0 g; 0.13 mol).

Neither the reactivity of the individual C—H bonds nor the total yields (Table I) were affected dramatically when the reaction was carried out in the presence of acetone as sensitizer (Table I). Besides the products of addition of dioxolane to chlorotrifluoroethylene, this reaction modification gave also the products of addition of 2-propanol to chlorotrifluoroethylene, i.e. 2-methyl-4-chloro-3,3,4-trifluoro-2-butanol and 2-methyl-4,6-dichloro-3,3,4,5,5,6-hexafluoro-2-hexanol<sup>7</sup>. Structure of the adducts and telomers *IV–XI* has been proven by elemental analyses (Table II) and NMR and mass spectra (Tables III and IV), the minor products *IVa*, *Va*, *VIIa*, *VIIIa*, *IXa* and *Xa* being not isolated in the pure state. The structures *IVa*, *VIIa*, *IXa* and *IXb* were derived from GC-MS spectra, the molecular weight of telomers *Va*, *VIIIa* and *Xa* was confirmed by their molecular ions ( $M^+$  307 or 321).

### EXPERIMENTAL

The temperature data are uncorrected. Proton NMR spectra were measured in tetrachloromethane on a Tesla BF 477 instrument at 60 MHz. Gas-liquid chromatographic analyses were

TABLE II  
Boiling points and elemental analyses of compounds *IV–XI*

Compound	M.w.	B.p., kPa	Calculated/Found			
			% C	% H	% Cl	% F
<i>IV</i>	190.6	89.5/6.9	31.52	3.17	18.61	29.91
			31.58	3.28	18.41	29.76
<i>V</i>	307.0	106/1.33	27.39	1.97	23.10	37.13
			27.53	1.94	22.69	39.04
<i>VI<sup>a</sup></i>	423.5	130–131/1.47	25.53	1.43	25.12	40.38
			26.12	1.84	22.46	40.67
<i>VII</i>	204.6	91–91.5/4.66	35.23	3.94	17.33	27.86
			35.31	3.79	16.67	27.95
<i>VIII</i>	321.0	102–103/1.33	29.93	2.51	22.09	35.51
			30.71	2.16	21.66	35.44
<i>IX</i>	204.6	60–61/1.33	35.23	3.94	17.33	27.86
			35.04	4.07	16.90	28.97
<i>X<sup>a</sup></i>	321.0	101.5/1.47	29.93	2.51	22.09	35.51
			30.37	2.67	21.08	35.09
<i>XI<sup>a</sup></i>	437.5	148.5–149/1.87	27.46	1.84	24.31	39.08
			27.62	2.05	23.65	43.34

<sup>a</sup> Purity 90–95%.

performed on a Griffin & George Ltd. instrument (Model Mk IIB), equipped with a flame-ionization detector. Preparative gas-liquid chromatography was carried out on a chromatograph model 3002 (Developmental Workshops of Czechoslovak Academy of Sciences; 1.5 m column of 10 mm diameter). In both cases the stationary phase was poly(propylene sebacate) on Celite 545, carrier gas hydrogen. Mass spectra were measured on a mass spectrometer LKB 9000.

### Chemicals

Chlorotrifluoroethylene (purity 99.5%, Spolek pro chemickou a hutní výrobu, Ústí nad Labem, Czechoslovakia) was dried over calcium chloride prior to use. 1,3-Dioxolane (b.p. 74°C/101.3 kPa), 2-methyl-1,3-dioxolane (b.p. 84.5°C/101.3 kPa) and 4-methyl-1,3-dioxolane (b.p. 84.5°C/101.3 kPa) were prepared according to Astle and collaborators<sup>8</sup>.

### General Procedure

The reactions were performed in a 200 ml glass photochemical reactor equipped with a reflux condenser and a water-cooled high-pressure quartz lamp (TESLA RVC 80 W). The given dioxo-

TABLE III  
Proton NMR spectra ( $\delta$ , ppm;  $J$ , Hz) of compounds IV–XI

Compound	CHClF	O–CH–O	CH <sub>2</sub>	CH <sub>3</sub>	CH–CH <sub>3</sub>
IV	6.26 dm $^2J(\text{H, F}) = 49.0$	5.20 td $^3J(\text{HF}) = 8.0$ 1.6	4.18 s	—	—
V	6.52 dm $^2J(\text{H, F}) = 48.0$	5.46 t	4.06 s	—	—
VI	6.16 m	6.16 m	4.25 s	—	—
VII	6.07 dm $^2J(\text{H, F}) = 48.0$ $^3J(\text{H, F}) = 14.0$ 2.0	—	3.81 s	1.17 q $J(\text{H, H}) = 2.0$	—
VIII	6.68 dm $^2J(\text{H, F}) = 47.0$	—	4.12 s	1.47 s, 1.67 s	—
IX	6.26 dt $^2J(\text{H, F}) = 48.5$	5.30 td $^3J(\text{H, F}) = 8.0$ 1.5	3.84–4.55 m	1.08–1.45 dd	3.43 t $J(\text{H, H}) = 6.5$
X	5.72–7.1 dm $^2J(\text{H, F}) = 48.0$	5.12–5.68 m	3.78–4.44 m	1.1–1.55 dd $J(\text{H, H}) = 6.0$	3.43 t $J(\text{H, H}) = 6.5$
XI	5.7–7.16 m	—	3.97–4.94 m	1.39 d $J(\text{H, H}) = 6.0$	3.42–3.85 m

TABLE IV  
Mass spectra ( $m/z$ ; relative intensity, %) of 1 : 1 adducts IV, VII, and IX

Adduct	$M^+$	$(M-1)^+$	$(M-CH_3)^+$	$(M-Y^a)^+$	$(M-Y^a-CO)^+$	$(M-Y^a-CH_2O)^+$	$(M-CICH_2O)^+$	$(M-HCFClCH_2O)^+$
IV	190/1	—	—	73/100	45/79	43/17	125/9	93/5
IV <sup>a</sup>	190/9	189/<1	—	73/100	45/43	43/31	125/12	93/8
VII <sup>b</sup>	204/<1	203/<1	189/4	87/50	59/1	57/3	139/7	107/4
VII <sup>a</sup> <sup>b</sup>	204/<1	203/5	189/46	87/16	59/10	57/4	—	107/4
IX	204/<1	203/1	189/<1	87/100	59/64	57/19	139/2	107/3
IX <sup>a</sup>	204/<1	203/6	189/<1	87/100	59/29	57/60	139/12	107/10
IX <sup>b</sup>	204/<1	203/5	189/4	87/3	59/11	57/100	—	—

<sup>a</sup> Y = CF<sub>2</sub>CFCIH; <sup>b</sup> parent ion:  $m/z$  43.

lane (*I–III*), either alone or with acetone, was placed into the reactor and chlorotrifluoroethylene was introduced at the rate 0.5–0.7 l/h at 9–12°C for 30–55 h (Table I). After the end of the reaction, the strongly acidic reaction mixture was adjusted to pH 5–6 by addition of Amberlite IR-45 (6 g), the unreacted dioxolane was distilled off through a Vigreux column (20 cm) and the distillation residue was analyzed by gas-liquid chromatography. The individual compounds were isolated by fractionation or preparative gas-liquid chromatography. The boiling points and elemental analyses of the products are given in Table II, their proton NMR spectra in Table III and mass spectra of the 1 : 1 adducts in Table IV.

In the experiment with 1,3-dioxolane (*I*) performed in the presence of acetone as photosensitizer, also products of addition of 2-propanol to chlorotrifluoroethylene, i.e. 2-methyl-3,3,4-trifluoro-4-chloro-2-butanol and 2-methyl-3,3,4,5,5,6-hexafluoro-4,6-dichloro-2-hexanol<sup>7</sup>, were proven by comparison with authentic samples.

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