

PHOTOCHEMICAL CHLOROTRIFLUOROETHYLATION OF 1,2-, 1,3-, AND 1,4-DIOLS*

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The UV light-initiated reaction of chlorotrifluoroethylene with 1,2-ethanediol (*I*) proceeds only in the presence of acetone and affords 2-(2-chloro-1,1,2-trifluoroethyl)-2-methyl-1,3-dioxolane (*VI*). It has been proved that *I* is first photolyzed to acetaldehyde. Its acetalization in the reaction mixture gives 2-methyl-1,3-dioxolane (*V*) which then undergoes chlorotrifluoroethylation. The chlorotrifluoro derivative of 1,2-ethanediol *XII* was prepared by hydrolysis of 4-(2-chloro-1,1,2-trifluoroethyl)-2,2-dimethyl-1,3-dioxolane (*XIII*). 1,3-Propanediol (*II*) reacted to give 5-chloro-4,4,5-trifluoro-1,3-pentanediol (*XVI*). Analogous reaction of 1,4-butanediol (*III*) and 1,3-butanediol (*IV*) afforded, in addition to derivatives with chlorotrifluoroethyl group at the hydroxyl-bearing carbon atom (*XVII* from *III*, *XIX* and *XX* from *IV*), also the respective bis-chlorotrifluoroethyl derivatives *XVIII* and *XXI* as products arising by the 1,5- or 1,6-transfer in the radical intermediates.

In our previous papers¹⁻⁵ we have described radical-induced reactions of chlorotrifluoroethylene with primary and secondary alcohols. These reactions proceed regioselectively, affording chlorotrifluoroethyl derivatives or telomeric chlorofluoroalkyl derivatives at the hydroxyl-bearing α -carbon. We have found that primary alcohols add to chlorotrifluoroethylene less readily than the secondary ones and among the minor products we detected branched α,α -bis-chlorofluoroalkyl derivatives whose formation indicates an intramolecular transfer in a cyclic transition state of the radical intermediate². The present communication concerns the photochemically initiated reaction of chlorotrifluoroethylene with diols: 1,2-ethanediol (*I*), 1,3-propanediol (*II*) and 1,4-butanediol (*III*) as representatives of diols with primary alcoholic groups in the α,β and γ positions, and 1,3-butanediol (*IV*) in which the primary and secondary hydroxyl groups can compete in the reaction.

The UV radiation-initiated reaction of chlorotrifluoroethylene with 1,2-ethanediol (*I*) proceeded satisfactorily only after addition of acetone as photoinitiator, however, its result was unexpected. As the principal reaction product we identified 2-(2-chloro-1,1,2-trifluoroethyl)-2-methyl-1,3-dioxolane (*VI*). This com-

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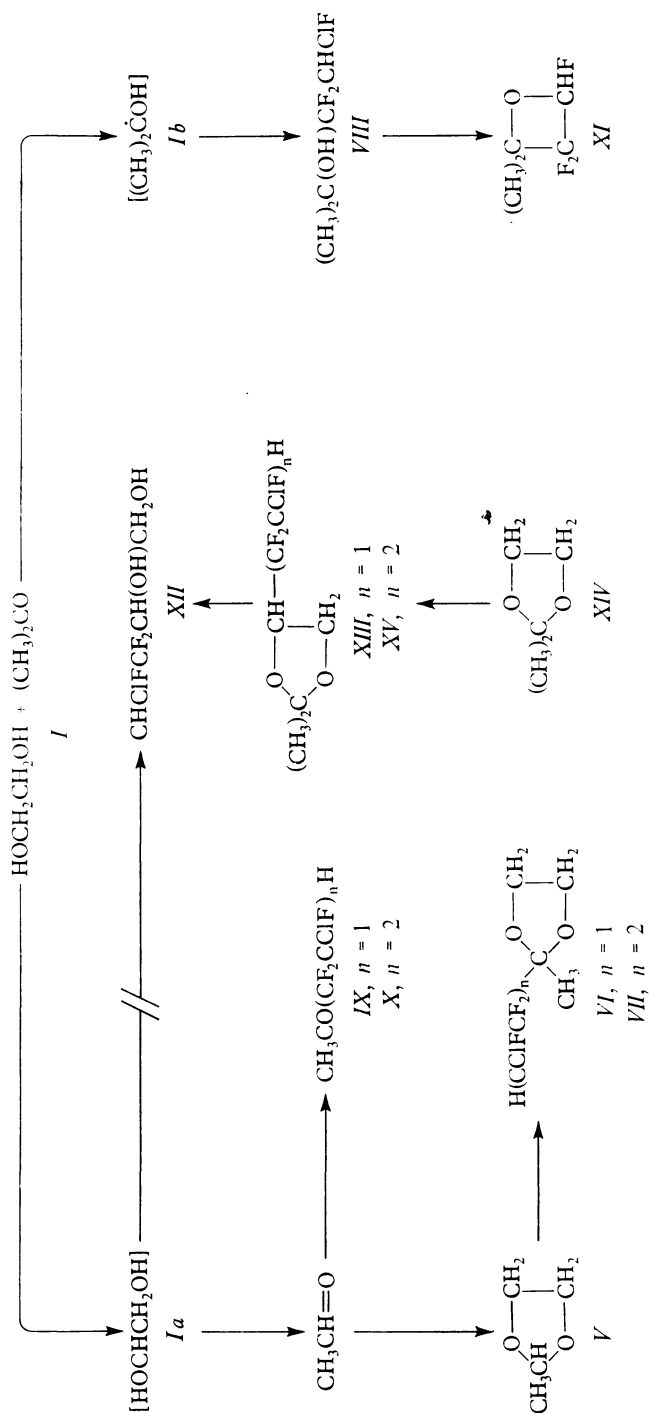
pond was identical with the compound obtained by photochemical addition of 2-methyl-1,3-dioxolane (*V*) to chlorotrifluoroethylene⁶. Among the minor reaction products we isolated the 1:2 telomer, *i.e.* 2-(2,4-dichloro-1,1,2,3,3,4-hexafluorobutyl)-2-methyl-1,3-dioxolane (*VII*) and 4-chloro-3,3,4-trifluoro-2-methyl-2-butanol (*VIII*). As detected by gas-liquid chromatography, the reaction mixture contained acetaldehyde, ethanol, 2-methyl-1,3-dioxolane (*V*), 4-chloro-3,3,4-trifluoro-2-butanone² (*IX*), the telomeric 4,6-dichloro-3,3,4,5,5,6-hexafluoro-2-hexanone² (*X*), and acetone used as the photoionitiator. Most probably, the 1,2-dihydroxyethyl radical *Ia*, formed in the photochemical reaction of 1,2-ethanediol with chlorotrifluoroethylene, is preferentially cleaved to give acetaldehyde and water without reacting with chlorotrifluoroethylene. The arising acetaldehyde is acetalized with ethylene glycol (*I*) under formation of 2-methyl-1,3-dioxolane (*V*) which then is converted to the chlorotrifluoroethyl derivative *VI* or the telomeric dichlorohexafluorobutyl derivative *VII*. This reaction scheme is in accord with the described⁷ photolysis of 1,2-ethanediol (*I*) and with the fact that the addition of acetone as initiator and acidification of the reaction mixture enhance substantially the photolysis of 1,2-ethanediol itself. The suggested reaction course is also supported by the presence of acetaldehyde, ethanol, the dioxolane *V* and the already described fluoro ketones *IX* and *X* which arise by radical addition of acetaldehyde to chlorotrifluoroethylene².

The main reaction product, the dioxolane *VI*, cannot be completely separated by fractionation from 4-chloro-3,3,4-trifluoro-2-methyl-2-butanol (*VIII*), formed by reaction of chlorotrifluoroethylene with the 1-methyl-1-hydroxyethyl radical (*Ib*) arising by reduction of acetone. Complete separation was achieved after conversion of the alcohol *VIII* to the more volatile 2,2-dimethyl-3,3,4-trifluorooxetane (*XI*) by heating with aqueous sodium hydroxide according to ref.⁸ (Scheme 1).

The intended synthesis of 4-chloro-3,3,4-trifluoro-1,2-butanediol (*XII*) was realized by hydrolysis⁹ of 4-(2-chloro-1,1,2-trifluoroethyl)-2,2-dimethyl-1,3-dioxolane (*XIII*) with dilute hydrochloric acid. The dioxolane *XIII* was isolated as the main product of the reaction of 2,2-dimethyl-1,3-dioxolane (*XIV*) with chlorotrifluoroethylene. Among the side-products we identified 4-(2,4-dichloro-1,1,2,3,3,4-hexafluorobutyl)-2,2-dimethyl-1,3-dioxolane (*XV*) and the butanol *VIII*. The latter compound was separated from the dioxolane *XIII* also by the above-mentioned procedure⁸ (Scheme 1).

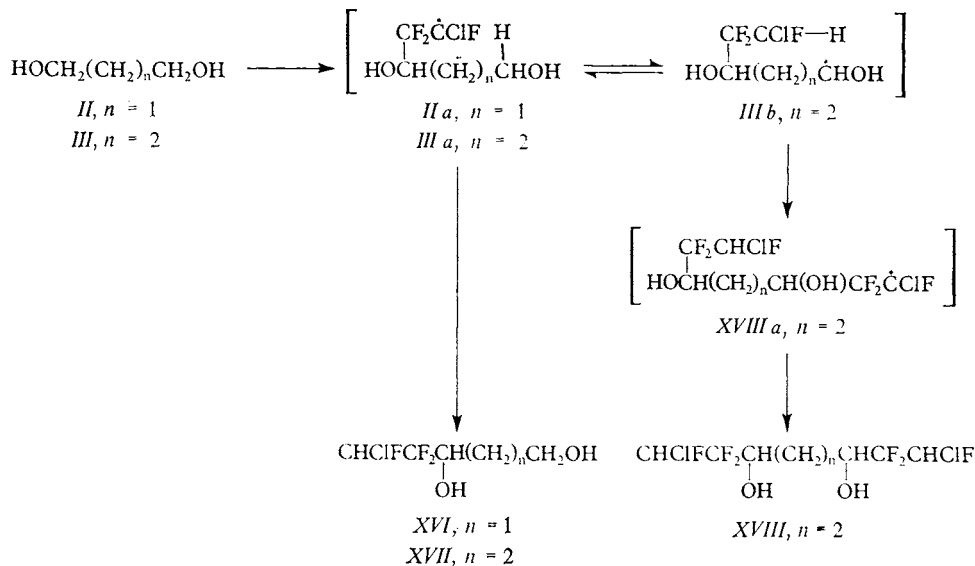
Contrary to 1,2-ethanediol (*I*), 1,3-propanediol (*II*) reacted in the expected manner, affording after distillation solely the 1 : 1 adduct, *i.e.* 5-chloro-4,4,5-trifluoro-1,3-pentanediol (*XVI*). With acetone as photoinitiator, the yield increased by about one half (Scheme 2).

In the reaction of 1,4-butanediol (*III*) and 1,3-butanediol (*IV*) with chlorotrifluoroethylene the distillable portions contained significant amounts of the respective bis-chlorotrifluoroethyl derivatives *XVIII* and *XXI* (Scheme 2 and 3); no telomeric 1 : 2 adduct was observed. From the mixture after reaction with *III* we isolated



SCHEME 1

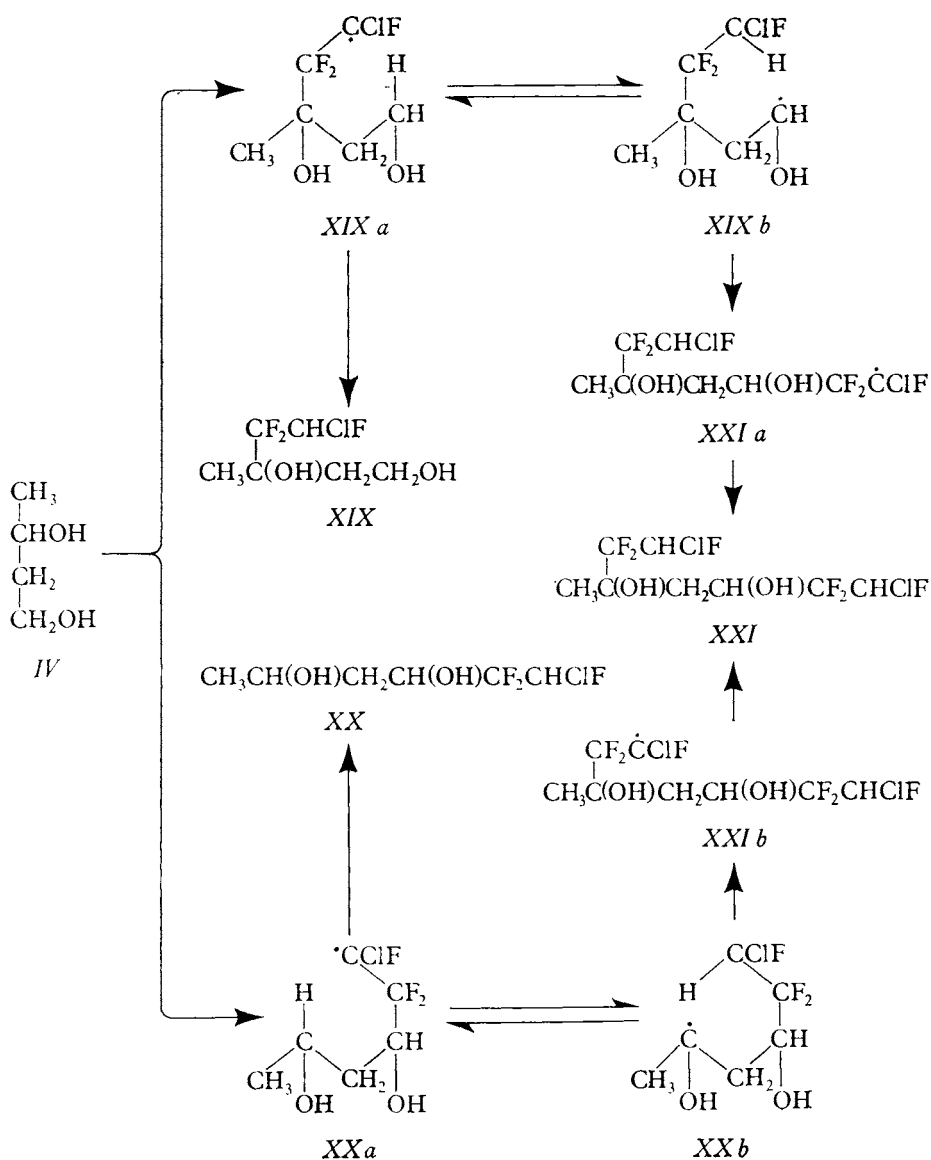
the 1 : 1 adduct, *i.e.* 6-chloro-5,5,6-trifluoro-1,4-hexanediol (*XVII*), together with 1,8-dichloro-1,2,2,7,7,8-hexafluoro-3,6-octanediol (*XVIII*) in the ratio 2·86 : 1 without acetone as initiator and 1·94 : 1 with acetone (Scheme 2).



SCHEME 2

In the addition of 1,3-butanediol (*IV*), the bis-chlorotrifluoroethyl derivative *XXI*, *i.e.* 1,7-dichloro-1,2,2,6,6,7-hexafluoro-3,5-heptanediol, was even the principal product and both the possible 1 : 1 adducts *XIX* and *XX* only side-products. Without the initiator the ratio *XXI* : *XX* : *XIX* was 3·9 : 1·3 : 1, in its presence 13·3 : 2·4 : 1 (Scheme 3).

The high proportion of the respective bis-chlorotrifluoroethyl derivatives *XVIII* and *XXI* arising in the reaction of the diols *III* and *IV* indicates that propagation and formation of the telomers, as well as termination of the adduct-radicals *IIIa* or *XIXa* and *XXa* by intramolecular transfer to the 1 : 1 adducts *XVII* or *XIX* and *XX*, compete with the intramolecular, 1,5- or 1,6-transfer^{10,11} to the isomeric adduct-radicals *IIIb* or *XIXb* and *XXb* (Scheme 2 and 3). The addition of *IIIb* or *XIXb* and *XXb* to another molecule of chlorotrifluoroethylene leads to the radicals *XVIIIa* or *XXIa,b* which give rise to the bis-chlorotrifluoroethyl derivatives *XVIII* or *XXI*. We have found that acetone as initiator markedly supports the intramole-



SCHEME 3

cular transfer in the radical intermediates. Our experiments also show that the reaction of chlorotrifluoroethylene with the primary diols *II* and *III*, leading to low-molecular adducts, is more facile than the reaction with primary monohydric alcohols^{2,3,12,13}. On the other hand, in the reaction of the 1,4-diol *III* there is more

intramolecular transfer in the cyclic transition state of the adduct-radical than in the reaction of primary alcohols; this pathway leads to disubstitution products with the chlorotrifluoroethyl groups on the hydroxyl-bearing carbon atoms. In the case of the 1,3-diol *IV* with the competing primary and secondary hydroxyl groups, the disubstitution derivative becomes the principal product, undoubtedly because the intermediate with radical at the secondary carbon atom is more populated.

EXPERIMENTAL

The temperature data are uncorrected. ^1H NMR spectra were measured in deuteriochloroform on a Tesla BS 477 (60 MHz) instrument. Gas-liquid chromatographic analyses were performed on a Chrom II (Laboratorní přístroje, Prague) chromatograph on 160×0.5 cm columns packed with A) 15% poly(propylene sebacate) on Celite 545, or B) 10% Carbowax 20M on Chromaton N; flame ionization detector, carrier gas nitrogen, temperature 40–190°C. Preparative gas-liquid chromatography was carried out on a home-made instrument¹⁴ on a 190×1.3 cm column packed with 10% Carbowax 20M on Celite 545, carrier gas nitrogen, temperature 170–180°C. As the UV light source we used RVC 125 or RVC 80 high-pressure mercury lamps (Tesla, Prague).

TABLE I
Photochemically initiated reaction of diols *I–IV* and dioxolane *XIV* with chlorotrifluoroethylene

Compound	Acetone	$\text{CF}_2=\text{CFCl}$	Time	Products			
g	g	g	h	g (%)			
				<i>VI</i>	<i>VII</i>	<i>VIII</i>	
<i>I</i> ^a	266.3	23.8	152.2	40	88.9 (33)	8.0(4)	37.6 (16)
<i>I</i> ^b	991.0	72.0	253.0	40	183.0 (41)	3.9 (1)	82.4 (21.5)
				<i>XVI</i>	<i>VIII</i>		
<i>II</i> ^c	89.7	—	6.1	30	3.3 (33)	—	
<i>II</i> ^d	103.7	9.8	29.5	30	24.1 (49.5)	20.5 (46)	
				<i>XVII</i>	<i>XVIII</i>	<i>VIII</i>	
<i>III</i> ^c	163.0	—	40.0	30	34.1 (48)	9.3 (17)	—
<i>III</i> ^d	330.0	39.6	136.2	43	95.9 (40)	38.7 (20)	36.8 (18)
				<i>XIX</i>	<i>XX</i>	<i>XXI</i>	<i>VIII</i>
<i>IV</i> ^c	84.2	—	14.7	30	2.8 (11)	3.6 (14)	8.6 (42)
<i>IV</i> ^d	318.3	34.1	124.6	30	7.4 (3)	17.9 (8)	78.0 (45)
				<i>XIII</i>	<i>XV</i>	<i>VIII</i>	
<i>XIV</i> ^c	151.0	—	83.9	33	48.5 (31)	8.7 (7)	3.0 (2)
<i>XIV</i> ^d	151.3	15.2	90.3	30	40.6 (24)	14.1 (11)	9.1 (7)

^a Procedure A); ^b procedure B); ^c without acetone; ^d with acetone.

Chemicals: Chlorotrifluoroethylene was of technical grade (Spolek pro chemickou a hutní výrobu, Ústí nad Labem) and was dried by passing through a column filled with anhydrous calcium chloride. 2,2-Dimethyl-1,3-dioxolane (*XIV*) was prepared by reaction of 1,2-ethanediol (*I*) with acetone in the presence of anhydrous cupric sulfate¹⁵.

Reaction of 1,2-Ethanediol (*I*) with Chlorotrifluoroethylene

The reaction was performed in glass reactors with an inside high-pressure mercury lamp⁴ cooled with water. Gaseous chlorotrifluoroethylene was introduced through a flow-meter at 20–30°C into a mixture of 1,2-ethanediol (*I*) and acetone with simultaneous irradiation until the absorption ceased. The amounts of reactants and reaction conditions are specified in Table I. During the reaction the mixture was separated into two layers. The upper layer contained the unreacted 1,2-

TABLE II
Boiling points and elemental analyses of the products

Compound	B.p., °C/kPa	Calculated/Found			
		% C	% H	% Cl	% F
<i>VI</i>	69/1.7	35.23	3.94	17.33	27.86
		35.41	3.72	16.90	27.65
<i>VII</i>	90/1.5	29.93	2.51	22.09	35.51
		30.21	2.45	21.74	35.14
<i>XII</i>	112/2.1	26.91	3.39	19.86	31.92
		27.07	3.67	19.71	32.06
<i>XIII</i>	84/6.0	38.46	4.61	16.22	26.07
		38.72	4.45	15.98	26.13
<i>XV</i>	45/0.04	32.26	3.01	21.16	34.02
		32.48	2.99	20.94	33.91
<i>XVI</i>	66/0.04	31.18	4.18	18.41	29.60
		31.34	4.38	18.54	30.03
<i>XVII</i>	99/0.04	34.88	4.88	17.16	27.59
		34.73	4.89	17.60	27.68
<i>XVIII</i>	120/0.09	29.74	3.12	21.95	35.28
		30.12	3.38	21.80	34.91
<i>XIX</i>	129–134/1.9 ^a	34.88	4.88	17.16	27.59
		34.83	4.68	17.17	27.14
<i>XX</i>	129–134/1.9 ^{a,b}	34.88	4.88	17.16	27.59
		35.14	4.87	17.43	27.91
<i>XXI</i>	88/0.04	29.74	3.12	21.95	35.29
		29.86	3.16	21.55	35.51

^a B.p. of a 1 : 1 mixture of *XIX* and *XX*; ^b b.p. of *XX* 73°C.

-ethanediol (*I*) and a part of the side-products which were determined in the procedure *B*). The reaction mixture was worked up by one of the two following procedures:

A) The (lower) organic layer was washed to neutrality with water, aqueous sodium hydrogen carbonate and water, dried over anhydrous potassium carbonate and distilled on a Vigreux column (20 × 1 cm). The products were purified by repeated fractionation. The boiling points, elemental analyses and spectral characteristics are given in Tables II and III.

TABLE III
¹H NMR spectra of the prepared diols and dioxolanes. Chemical shifts δ (ppm) and coupling constants *J* (Hz)

Compound	CH ₃	CH ₂	CH	CHCIF	OH
<i>VI</i>	1.59 m, 3 H	4.21 s, 4 H	—	6.48 ddd, 1 H ² <i>J</i> _{HF} = 48.0 ³ <i>J</i> _{HF} = 14.0 2.0	—
<i>VII</i>	1.57 m, 3 H	4.08s, 4 H	—	6.54 dm, 1 H ² <i>J</i> _{HF} = 48.0	—
<i>XII</i>	—	3.65—4.05 m, 2 H	4.05—4.55 m, 1 H	6.37 dm, 1 H ² <i>J</i> _{HF} = 48.0	3.10—3.65 b, 2 H
<i>XIII</i>	1.46 2 × s, 6 H 1.60	3.60—4.95 m, 3 H	—	6.70 dm, 1 H ² <i>J</i> _{HF} = 48	—
<i>XV</i>	1.42 2 × s, 6 H 1.48	4.00—4.95 m, 3 H	—	6.67 dm, 1 H ² <i>J</i> _{HF} = 40.0	—
<i>XVI</i>	—	1.90 m, 2 H 3.88 t, 2 H ³ <i>J</i> _{HH} = 4	4.25 m, 1 H	6.40 dm, 1 H ² <i>J</i> _{HF} = 49.0	3.15 b, 2 H
<i>XVII</i>	—	1.50—2.00 m, 4 H 3.50—4.40 m, 3 H	—	6.45 dm, 1 H ² <i>J</i> _{HF} = 50.0	4.28 s, 2 H
<i>XVIII</i>	—	1.50—2.20 m, 4 H	3.50—4.50 m, 2 H	6.40 dm, 2 H ² <i>J</i> _{HF} = 49.0	3.05 s, 2 H
<i>XIX</i>	1.42 s, 3 H	2.07 t, 2 H 3.97 t, 2 H ³ <i>J</i> _{HH} = 6.5	—	6.50 dm, 1 H ² <i>J</i> _{HF} = 49.0	3.55 s, 2 H
<i>XX</i>	1.30 d, 3 H ³ <i>J</i> _{HH} = 6	1.67—2.00 m, 2 H	3.90—4.75 m, 2 H	6.47 dm, 1 H ² <i>J</i> _{HF} = 48.0	2.35—3.20 b, 2 H
<i>XXI</i>	1.46 s, 3 H	2.10 d, 2 H ³ <i>J</i> _{HH} = 10.0	4.10—4.95 m, 1 H	6.47 dm, 2 H ² <i>J</i> _{HF} = 48.0	3.40—4.50 b, 2 H

B) The whole reaction mixture, containing two layers, was neutralized with solid potassium carbonate and steam-distilled. The lower layer of the distillate was dried over anhydrous potassium carbonate and distilled through a Vigreux column (45 × 2 cm). The products were purified by repeated fractionation or identified by gas-liquid chromatography (Tables II and III). The upper layer of the distillate was again subjected to distillation until the distillate no longer formed two layers on saturation with potassium carbonate. The upper organic layer (35.3 g) was separated, dried over anhydrous potassium carbonate and analyzed by gas-liquid chromatography. It contained acetaldehyde (3.8%), acetone (29.8%), ethanol (27.0%), VIII (31.5%), I (4.5%), and VI (3.4%).

Isolation of pure dioxolane VI: The crude dioxolane VI (68.6 g; content of VIII: 18.5%) was added to a solution of sodium hydroxide (20 g) in water (50 ml). The stirred mixture was heated with an infrared lamp under simultaneous distillation of the lower-boiling product and water through a Vigreux column (15 × 1 cm) so as the boiling point did not exceed 70°C. After 6 h, when even after increase in temperature only water distilled, the reaction was ended. The lower organic layer of the distillate (10.9 g) contained only 2,2-dimethyl-3,3,4-trifluorooxetane⁸ (XI). The residue in the flask was washed with water, the lower layer (51.5 g) was dried over anhydrous potassium carbonate and distilled affording the pure dioxolane VI, b.p. 69°C/1.7 kPa.

Reaction of Diols II–IV and Dioxolane XIV with Chlorotrifluoroethylene

The reaction was performed in the same apparatus as described for the diol I, in the absence of acetone (procedure C) or with acetone as initiator (procedure D) (Table I). The homogeneous reaction mixtures were neutralized with Amberlite IR-45, filtered and distilled through a Vigreux column (20 × 1 cm). The products were purified by repeated fractionation. Even repeated distillation of reaction products from the diol IV gave only about 1 : 1 mixtures of the isomeric diols XIX and XX. The solid diol XX crystallized from the mixture after several days and was purified by crystallization from tetrachloromethane. The NMR spectrum of the diol XIX was obtained by subtracting the spectrum of pure XX from that of the 1 : 1 mixture of XIX and XX. Gas-liquid chromatography showed the diol XXI to consist of two components in an approximately 1 : 1 ratio; they were separated by preparative gas-liquid chromatography¹⁴. Their identical elemental analyses as well as very similar spectral data indicated diastereoisomeric relationship. Results of the experiments and properties of the products are given in Tables I–III.

4-Chloro-3,3,4-trifluoro-1,2-butanediol (XII)

A stirred mixture of the dioxolane XIII (11.0 g; 50.3 mmol) and 20% hydrochloric acid (30 ml) was heated to 120°C for 3 h. During the reaction the mixture became homogeneous and on distillation gave 8.0 g (45 mmol; 89%) of the diol XII, b.p. 112°C/2.1 kPa.

Photolysis of 1,2-Ethanediol (I)

1,2-Ethanediol (I) was photolyzed in the same apparatus as described for its reaction with chlorotrifluoroethylene, using *a*) 88.2 g of I, *b*) I (88.2 g) and acetone (6.4 g), *c*) I (88.2 g), acetone (6.4 g) and concentrated hydrochloric acid (3 ml) with stirring by introduction of nitrogen (0.2–0.3 l h⁻¹) for 30 h. No low-boiling products were collected in the dry ice trap connected to the apparatus. After the reaction, the mixture in experiment *c*) was neutralized with solid potassium carbonate and all the reaction mixtures were analyzed by gas-liquid chromatography. In addition to the diol I, the products contained: *a*) acetaldehyde, ethanol; *b*) acetaldehyde, acetone, ethanol, 2-propanol, 2-methyl-1,3-dioxolane (V) and 2,2-dimethyl-1,3-dioxolane (XIV); *c*) acetaldehyde, acetone, acetaldehyde diethyl acetal, ethanol, 2-propanol, and compounds V and XIV. The reaction *c*) gave 2–3 times higher yields than the reactions *a*) and *b*).

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