Photochemical addition of diethyl ether to β,β,β',β'-tetrakis(trifluoromethyl)divinyl ether

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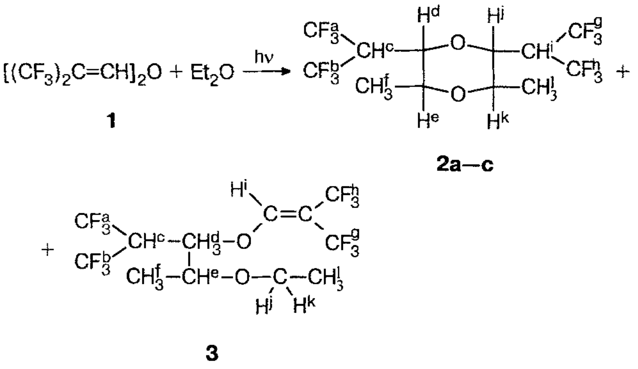
The 1:1 adducts of diethyl and β,β,β',β'-tetrakis(trifluoromethyl)divinyl ether (**1**), *i.e.*, 3,5-(*ee*)-bis[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-2,6-dimethyl-1,4-dioxane (**2**) (3 isomers) and 4-ethoxy-1,1,1-trifluoro-2-trifluoromethyl-3-[3,3,3-trifluoro-2(trifluoromethyl)propenyloxy]pentane (**3**), have been obtained by UV-irradiation of a solution of divinyl ether **1** in diethyl ether. The X-ray structural investigation of the all-(e)-isomer of dioxane (**2**) has been carried out.

Key words: photochemistry, diethyl ether, β,β,β',β'-tetrakis(trifluoromethyl)divinyl ether.

There are in literature examples of photochemical addition of ethers to fluorine-containing olefins.[1–3] It is assumed that the reaction starts with the generation of an α-alkoxyalkyl radical and proceeds by a radical-chain mechanism. Radical addition reactions are also known for vinyl ethers. Here the attacking C radical can be added both in the α- [4] and β-position of the double bond[5–7] (cf. Refs. 8(a)—11). The possibility of radical addition of ethers to fluorine-containing vinyl and divinyl ethers has not been mentioned anywhere.

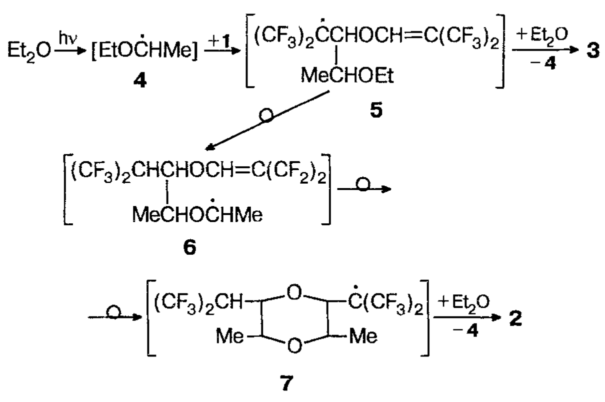
The UV-irradiation of a β,β,β',β'-tetrakis(trifluoromethyl)divinyl ether (**1**) solution in diethyl ether has been found to lead to the products of the addition of diethyl ether to divinyl ether **1** — dioxane **2a**—**c** and diether **3** (Scheme 1), in high yield.

Scheme 1



The ratio of compounds **2**/**3** remains constant in the course of the reaction and is not changed by continuous irradiation of the reaction mixture after full conversion of the initial divinyl ether **1**. Thus, diether **3** is not an intermediate product in the synthesis of dioxane **2**. To explain the above, we propose the following scheme of radical-chain reactions (Scheme 2) covering the stage of addition of α-alkoxyalkyl radical **4** to the α-position of vinyl ether **1** to give radical **5**, which is either converted into product **3** or rearranged with 1,5-migration of a hydrogen atom (cf. Refs. 1, 8b, 12) into radical **6**. The latter undergoes intramolecular cyclization into radical **7**, which preceeds product **2**. Probably divinyl ether **1** can also play here the role of a radical photoinitiator [UV spectrum (Et_2O) λ_{max}: 222 nm] to form primary α-etoxyethyl radicals **4** (see Ref. 13).

Sheme 2



Dioxane **2** is formed as three possible isomers: 2,6-(*ee*) (**2a**), 2,6-(*ea*) (**2b**), 2,6-(*aa*) (**2c**) (the $(CF_3)_2CH$-

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† Deceased.

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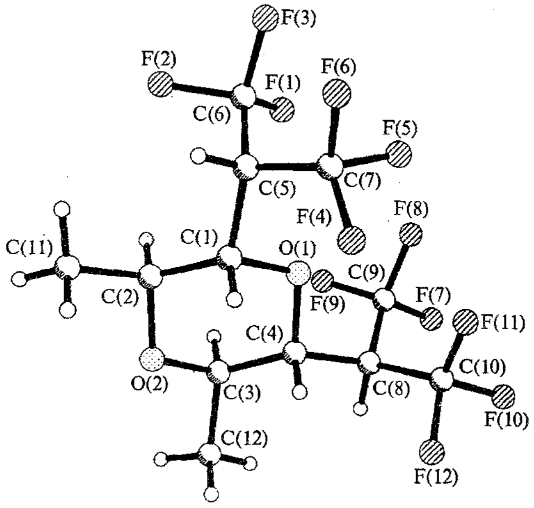

Fig.1. General view and atomic numberings of molecule **2a**.

Table 1. Characteristics of the synthesized compounds

Compound	^{a}M.p./°C ^{b}B.p./°C (p/Torr)	$\frac{\text{Found}}{\text{Calculated}}$ (%) C	H	F	Elemental Formula	Yield (%)
2a	^{a}44—45 (from C_6F_{14})	34.7 34.6	2.96 2.91	54.4 54.8	$C_{12}H_{12}F_{12}O_2$	35.3
2b	^{b}49—51 (1)	34.5 34.6	2.95 2.91	54.8 54.8	$C_{12}H_{12}F_{12}O_2$	24.4
2c	^{a}93—95*	34.7 34.6	3.06 2.91		$C_{12}H_{12}F_{12}O_2$	~0.6
3	^{b}187—190 (760)	34.3 34.6	2.85 2.91	54.8 54.8	$C_{12}H_{12}F_{12}O_2$	2.4

* For fast heating, sublimation is above 70 °C.

groups are all in the equatorial position, probably for steric reasons), and diether **3** is in the form of one diastereomer. The structures of compounds **2a—c** and **3** were confirmed by the data of elemental analysis, NMR, IR, Raman, UV and mass-spectra, while the structure of all-(e)-isomer **2a** was determined with an X-ray analysis. The general view of molecule **2a** and atomic numberings are shown in Fig. 1.

The six-membered heterocycle has a chair conformation: atoms C(1), C(2), C(3) and C(4) are coplanar within 0.0014 Å, and atoms O(1) and O(2) are similarly ±0.567 Å out of the plane, respectively. The orientation of the $(CF_3)_2CH$ substituents towards the heterocycle atoms is characterized by the following torsion angles: O(1)C(1)C(5)C(6) 68.1°, O(1)C(1)C(5)C(7) −63.5°, O(1)C(4)C(8)C(9) −51.9° and O(1)C(4)C(8)C(10) 76.1°. The bond lengths and angles in molecule **2a** have standard values. It should be noted that shortening of the C—F bonds, together with the high thermal parameters of the F atoms, is indicative of significant thermal vibrations of the CF_3 groups. It is possible that the relatively high R factor is accounted for by unexposed disorder in these groups.

Experimental

The ^1H, ^{19}F, $^1H\{^1H\}$ and $^{19}F\{^1H\}$ spectra were recorded using a Bruker WP-200SY NMR spectrometer for 25-30 % solutions in C_6D_6. The chemical shifts are given in p.p.m. from the $SiMe_4$ and CF_3COOH (δ-scale) external standards. The IR spectrum was taken on an UR-20 spectrometer, the Raman spectrum — on a Ramanor HG-2S spectrometer, the UV spectrum — on a Specord UV VIS spectrophotometer, mass-spectra — on a VG 7070E mass-spectrometer (IP, 70 eV). The preparative gas-liquid chromatography (PGLC) was carried out on a column (3.6 m long, diameter 25 mm) with krytox on chromosorb. Diethyl ether was purified by distillation over benzophenone ketyl, and irradiation was performed with a DRL-125 inner-plunge lamp under an Ar atmosphere. For mixtures, everywhere the molar ratios of the specific components are given. The characteristics of the synthesized compounds are given in Table 1, the NMR and mass-spectra are given in Tables 2 and 3.

The crystals of compound **2a** are monoclinic, at −60°C a = 6.669(2), b = 13.593(3), c = 17.672(4) Å, β = 90.93(4), V = 1602(1) Å^3, d_{calc} = 1.726 g/cm^3, Z = 4, space group $P2_1/n$.

Table 2. NMR spectra of the synthesized compounds (δ) (J/Hz)

Compound	NMR (δ_H)	NMR ^{19}F (δ_F)	J/Hz
2a	2.67 br.h ($2H^{c,i}$); 3.47 br.d ($2H^{d,j}$); 3.55 br.d.q ($2H^{e,k}$); 0.76 br.d ($6H^{f,l}$)	12.3 br.d.q ($6F^{a,g}$); 16.9 br.d.q ($6F^{b,h}$)	$J_{a-b(g-h)}$ = 9.4; $J_{a-c(g-i)} = J_{b-c(h-i)}$ = 8.0; $J_{d-e(j-k)}$ = 9.2; $J_{e-f(k-l)}$ = 5.9
2b	2.74 d.h ($1H^c$); 3.52 d.d.q ($1H^d$); 3.87 br.d.q ($1H^e$); 0.77 d ($3H^f$); 2.67 d.q.q ($1H^i$); 4.04 d.d ($1H^j$); 3.90 q.d.q ($1H^k$); 1.05 d ($3H^l$)	11.9 br.q.d.q ($3F^a$); 16.9 q.d.q.d ($3F^b$); 15.4 q.d.q.q ($3F^g$); 13.5 q.d.d ($3F^h$)	J_{a-b} = 9.0; J_{a-g} = 3.6; $J_{b-g} = J_{b-d} = J_{c-d}$ = 1.7; J_{g-h} = 11.6; $J_{a-c} = J_{b-c}$ = 8.3; J_{g-i} = 7.1; J_{h-i} = 8.1; J_{h-k} = 1.3; J_{d-e} = 9.9; J_{e-f} = 6.1; J_{i-j} = 9.8; J_{j-k} = 2.8; J_{k-l} = 6.7
2c	2.72 br.d.h ($2H^{c,i}$); 3.86 d.d ($2H^{d,j}$); 3.61 d.q.q ($2H^{e,k}$); 0.90 br.d ($6H^{f,l}$)	16.3 m ($6F^{a,g}$); 13.1 d.q.d ($6F^{b,h}$)	$J_{a-b(g-h)}$ = 11.4; $J_{a-c(g-i)} \approx J_{b-c(h-i)} \approx J_{c-d(i-j)} \approx$ 8; $J_{b-e(h-k)}$ = 1.3; $J_{d-e(j-k)}$ = 4.2; $J_{e-f(k-l)}$ = 6.8
3	2.82 d.h ($1H^c$); 3.68 d.d.q ($1H^d$); 3.41 d.q.q ($1H^e$); 0.64 d ($3H^f$); 7.08 m ($1H^i$); 3.02 d.q ($1H^j$); 3.23 d.q ($1H^k$); 1.05 d.d ($3H^l$)	11.6 d.q ($3F^a$); 16.4 q.d.q.d.d ($3F^b$); 18.3 q.q.d ($3F^g$); 16.3 d.q ($3F^h$)	J_{a-b} = 9.2; $J_{b-g} = J_{b-d}$ = 1.5; J_{g-h} = 6.4; $J_{a-c} = J_{b-c}$ = 8.0; J_{b-e} = 1.25; $J_{g-i} \approx$ 1; J_{h-i} = 1.6; J_{c-d} = 1.7; $J_{d-e} = J_{j-k}$ = 8.9; J_{e-f} = 6.2; $J_{j-l} = J_{k-l}$ = 7.0

Table 3. Mass-spectra of the synthesized compounds

Compound	m/z (I_{rel}(%))
2a	416 $[M]^+$ (5.6); 209 $[C_6H_7F_6O]^+$ (1.2); 192 $[C_6H_6F_6]^+$ (10.1); 123 $[C_5H_6F_3]^+$ (19.1); 103 $[C_5H_5F_2]^+$ (8.0); 59 $[C_3H_7O]^+$ (9.1); 57 $[C_3H_5O]^+$ (12.9); 45 $[C_2H_5O]^+$ (100)
2b	416 $[M]^+$ (4.9); 209 $[C_6H_7F_6O]^+$ (2.4); 192 $[C_6H_6F_6]^+$ (9.8); 123 $[C_5H_6F_3]^+$ (19.7); 103 $[C_5H_5F_2]^+$ (8.4); 59 $[C_3H_7O]^+$ (9.6); 57 $[C_3H_5O]^+$ (13.0); 45 $[C_2H_5O]^+$ (100)
2c	416 $[M]^+$ (2.3); 209 $[C_6H_7F_6O]^+$ (2.3); 192 $[C_6H_6F_6]^+$ (10.8); 123 $[C_5H_6F_3]^+$ (20.8); 103 $[C_5H_5F_2]^+$ (9.8); 59 $[C_3H_7O]^+$ (10.7); 57 $[C_3H_5O]^+$ (13.0); 45 $[C_2H_5O]^+$ (100)
3	415 $[M-H]^+$ (0.1); 401 $[M-Me]^+$ (0.2); 397 $[M-F]^+$ (0.2); 371 $[M-EtO]^+$ (1.4); 329 $[C_8H_4F_{12}]^+$ (3.2); 237 $[M-(CF_3)_2C{=}CHO]^+$ (2.0); 209 $[C_6H_7F_6O]^+$ (11.9); 73 $[C_4H_9O]^+$ (88.0) 45 $[C_2H_5O]^+$ (100); 29 $[C_2H_5]^+$ (20.4)

The unit cell dimensions and intensities of 2719 independent reflections were measured at —60°C on an automatic four-circle Siemens P3/PC diffractometer (MoK$_\alpha$-radiation, graphite monochromator, $\theta/2\theta$ scan technique, $2\theta \leq 46°$). A total of 1707 observed reflections with $|F| > 4\sigma(F)$ were used for further calculations and refinement. The structure was solved by direct methods and refined by least-squares in full-matrix anisotropic approximation. The positions of the H atoms were determined from a difference synthesis by the electron density and were included in the refinement with fixed coordinates and with isotropic thermal factors U_{iso} = 0.05 Å^2. The final refinement was reduced to R = 0.082, R_w = 0.092, GOF = 2.50. Table 4 gives the coordinates of the non-hydrogen atoms and their equivalent temperature factors. Tables 5 and 6 give bond lengths and angles. All the calculations were performed on an IBM PC/AT computer using the SHELXTL PLHS package of programs.

Table 4. Coordinates of non-hydrogen atoms in structure **2a** ($\times 10^4$) and their isotropic equivalent temperature factors U (Å$^2 \cdot 10^2$)

Atom	x	y	z	U
F(1)	−1895(9)	5883(6)	2204(4)	155(4)
F(2)	−297(13)	4542(5)	2223(4)	155(4)
F(3)	−717(9)	5345(4)	3229(3)	108(2)
F(4)	3354(10)	7412(4)	2686(3)	120(3)
F(5)	366(10)	7414(4)	2917(3)	109(3)
F(6)	2310(9)	6534(4)	3594(2)	100(2)
F(7)	−3737(6)	8840(4)	418(3)	90(2)
F(8)	−3048(8)	8035(4)	1383(3)	109(2)
F(9)	−3138(8)	7312(4)	345(4)	141(3)
F(10)	−687(7)	9990(3)	862(3)	75(2)
F(11)	414(11)	9047(3)	1708(3)	132(3)
F(12)	2177(8)	9435(4)	735(4)	131(3)
O(1)	639(6)	7023(3)	1360(2)	37(1)
O(2)	2531(6)	5954(3)	253(2)	48(2)
C(1)	2004(12)	6246(5)	1552(4)	61(3)
C(2)	2165(13)	5500(6)	963(4)	69(3)
C(3)	1162(12)	6708(6)	33(4)	66(3)
C(4)	1029(12)	7429(5)	638(4)	59(3)
C(5)	1563(11)	5960(5)	2361(4)	50(2)
C(6)	−381(18)	5480(7)	2501(6)	93(4)
C(7)	1995(16)	6809(7)	2880(4)	74(3)
C(8)	−392(9)	8316(4)	535(3)	41(2)
C(9)	−2573(12)	8127(6)	670(5)	62(3)
C(10)	333(12)	9170(6)	982(5)	66(3)
C(11)	3678(12)	4712(5)	1093(4)	63(3)
C(12)	1765(12)	7083(6)	−720(4)	65(3)

Table 5. Bond length (Å) in molecule **2a**

Bond	d	Bond	d
F(1)—C(6)	1.26(1)	O(1)—C(4)	1.418(8)
F(2)—C(6)	1.37(1)	O(2)—C(2)	1.422(9)
F(3)—C(6)	1.32(1)	O(2)—C(3)	1.422(9)
F(4)—C(7)	1.27(1)	C(1)—C(2)	1.46(1)
F(5)—C(7)	1.37(1)	C(1)—C(5)	1.514(9)
F(6)—C(7)	1.328(9)	C(2)—C(11)	1.49(1)
F(7)—C(9)	1.314(9)	C(3)—C(4)	1.45(1)
F(8)—C(9)	1.31(1)	C(3)—C(12)	1.49(1)
F(9)—C(9)	1.30(1)	C(4)—C(8)	1.543(9)
F(10)—C(10)	1.321(9)	C(5)—C(6)	1.48(1)
F(11)—C(10)	1.29(1)	C(5)—C(7)	1.50(1)
F(12)—C(10)	1.36(1)	C(8)—C(9)	1.50(1)
O(1)—C(1)	1.431(8)	C(8)—C(10)	1.48(1)

3,5-(*ee*)-Bis[2,2,2-trifluoro-1-(trifluoromethyl)ethyl]-2,6-dimethyl-1,4-dioxane (2a—c) and 4-ethoxy-1,1,1-trifluoro-2-trifluoromethyl-3-[3,3,3-trifluoro-2-(trifluoromethyl)propenyloxy]pentane (3). Divinyl ether **1** (purity 98.6—99 %) in ~180 mL of diethyl ether in portions of 2.4, 5.08, 5.3 g (totally 12.78 g, 37.4 mmol) was irradiated with cooling (10 °C) and mixed untill the initial ether **1** vanished (4—4.5 h) (GLC). The solution contained compounds **2a**, **2b**, **2c** and **3** (1.0:0.87:0.02:0.10) with an admixture of some low-boiling

Table 6. Bond angles (deg.) in molecule **2a**

Angle	ω	Angle	ω
C(1)—O(1)—C(4)	112.1(5)	F(3)—C(6)—C(5)	112.8(8)
C(2)—O(2)—C(3)	115.8(5)	F(4)—C(7)—F(5)	101.3(7)
O(1)—C(1)—C(2)	113.4(6)	F(4)—C(7)—F(6)	109.6(8)
O(1)—C(1)—C(5)	106.3(5)	F(5)—C(7)—F(6)	103.8(7)
C(2)—C(1)—C(5)	120.9(6)	F(4)—C(7)—C(5)	117.4(7)
O(2)—C(2)—C(1)	110.1(6)	F(5)—C(7)—C(5)	110.3(7)
O(2)—C(2)—C(11)	108.9(6)	F(6)—C(7)—C(5)	113.0(7)
C(1)—C(2)—C(11)	116.6(7)	C(4)—C(8)—C(9)	116.3(6)
O(2)—C(3)—C(4)	109.3(6)	C(4)—C(8)—C(10)	110.8(6)
O(2)—C(3)—C(12)	108.1(6)	C(9)—C(8)—C(10)	111.0(6)
C(4)—C(3)—C(12)	116.6(6)	F(7)—C(9)—F(8)	104.2(6)
O(1)—C(4)—C(3)	114.4(6)	F(7)—C(9)—F(9)	108.3(7)
O(1)—C(4)—C(8)	106.8(5)	F(8)—C(9)—F(9)	105.7(7)
C(3)—C(4)—C(8)	119.0(6)	F(7)—C(9)—C(8)	112.9(6)
C(1)—C(5)—C(6)	117.2(6)	F(8)—C(9)—C(8)	114.8(6)
C(1)—C(5)—C(7)	110.0(6)	F(9)—C(9)—C(8)	110.5(6)
C(6)—C(5)—C(7)	113.4(7)	F(10)—C(10)—F(11)	106.4(7)
F(1)—C(6)—C(2)	107.1(9)	F(10)—C(10)—F(12)	101.0(6)
F(1)—C(6)—C(3)	108.7(9)	F(11)—C(10)—F(12)	109.2(7)
F(2)—C(6)—C(3)	103.2(8)	F(10)—C(10)—C(8)	114.4(6)
F(1)—C(6)—C(5)	116.0(8)	F(11)—C(10)—C(8)	115.8(6)
F(2)—C(6)—C(5)	108.1(9)	F(12)—C(10)—C(8)	109.0(7)

(totally 2—3 % (GLC)) and high-boiling (3-4 % (GLC)) products. The distillation gave: 1) fraction, b.p. 24—42 °C (1 Torr), 0.11 g, purity 64 %, **2a/2b/2c/3** = 1.0/0.66/0.004/0.12; 2) fraction, b.p. 42—48 °C (1 Torr), 12.55 g (~80 %), purity 96.5 %, **2a/2b/2c/3** = 1.0/0.94/0.02/0.11; 3) fraction, b.p. 48—71 °C (1 Torr), 0.86 g, purity 88 %, **2a/2b/2c/3** = 1.0/1.27/0.11/0.10. Using the PGLC (110°C) of joint fractions there were separated: a) 5.5 g of (ee) isomers **2a**, purity 96 %, crystals for X-ray analysis were obtained from C_6F_{14}; b) 3.8 g of (ea) isomer **2b**, purity 98 %, c) ~0.1 g of (aa) isomer **2c**, purity ~90 %, d) 0.4 g of diether **3**, purity ~94 %, IR (Raman) spectrum (ν/cm^{-1}): 1682 av (1682.0) (C=C), UV spectrum (Et_2O): λ_{max}: 219 nm (ε 50000).

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