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PHOTOCHEMICAL SYNTHESIS OF FLUOROALKANOLS BASED ON TETRAFLUOROETHYLENE

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SUMMARY

The conditions of the photochemical synthesis of fluoroalkanols $H(C_2F_4)_nC(OH)R^1R^2$ (n = 1, 2) by the reaction of tetrafluoroethylene with alcohols in the presence of photoinitiators and sensitisers are described. The reaction is initiated by UV radiation and is performed under atmospheric pressure. The yields of alkanols were 0.1-0.39 mol using 250 W UV lamp after 6-8 hours and 73-82 % relatively to the converted tetrafluoroethylene.

INTRODUCTION

Synthesis of fluorinated alkanols by thermal initiated free-radical addition of aliphatic alcohols to tetrafluoroethylene has been reported in the literature [1,2]. Such addition can also be performed [3,4] photochemically without any initiator and practically under atmospheric pressure, provided that there is no oxygen present and chemicals of high purity are used. Further disadvantage of the "direct"

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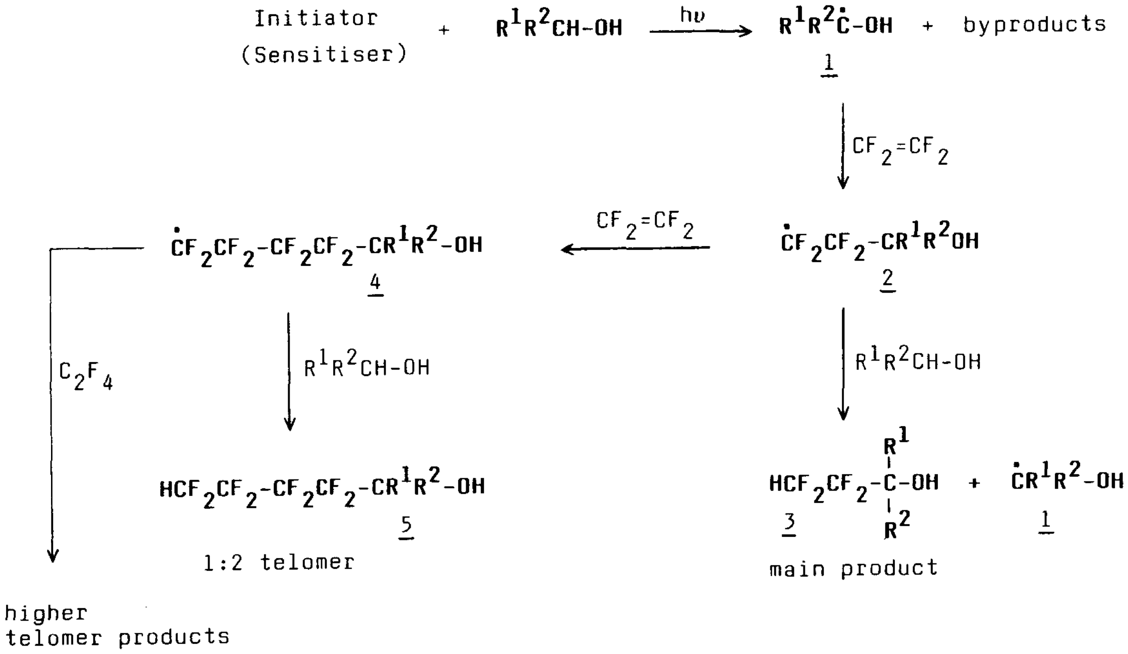
photochemical method is the fact that only a very small part of the radiation of a medium- or high-pressure UV-lamp is exploited, because the reactions are started by absorption of short-wavelength UV light by olefin.

Another preparative way, more suitable for obtaining the fluoroalkanols on a laboratory scale, exploits a longer-wavelength region of UV radiation to cause a relative slow decomposition of free-radical reaction initiators; tetrafluoroethylene is introduced [5] into the reaction system at the same time. The reaction is performed with advantage in an immersion-well photoreactor which can be easily cooled from the outside to ensure a higher concentration of tetrafluoroethylene in the reaction mixture.

RESULTS AND DISCUSSION

As shown in the Scheme, the reactions leading to the fluoroalkanols are: - 1) Absorption of UV light by an initiator or sensitiser and formation of free radicals 1, the C-H bond in the α-position of the starting alkanols being cleaved. 2) A set of consecutive free-radical chain reactions: the adduct-radical 2 is converted by a chain transfer to the main product 3, or undergoes a telomerisation to give the telomeric product 5. Higher telomers are formed in only very low yields. The most important step in the synthesis of fluoroalkanols is the homolytic C-H bond cleavage in the α-position of alcohols $H\text{-}CR^1R^2\text{-}OH$. The dissociation energy of this bond is different [6-8] in dependence of the structure, the highest being in methanol ($H\text{-}CH_2OH$ 400.2, $H\text{-}CH(CH_3)OH$ 393.6, $H\text{-}C(CH_3)_2OH$ 377.2 kJ/mol). The experimentally found reactivity order of alcohols in the addition is in accord with the dissociation energies, as follows from Table 1: methanol proved to be the least reactive.

The yields of the addition of alcohols are connected with the efficiency of the individual initiators. Benzoin methyl ethers proved to be the least effective initiators for all the alcohols tested, and only with 2-propanol, a small amount of the products (3c,5c) was found. Also azo-bis-isobutyronitrile exhibits low efficiency as an initiator, probably due



<u>3a</u>, <u>5a</u>, $R^1 = R^2 = H$

<u>3b</u>, <u>5b</u>, $R^1 = H$, $R^2 = CH_3$

<u>3c</u>, <u>5c</u>, $R^1 = R^2 = CH_3$

Scheme

to its relatively fast decomposition: initiators of this type are effective in thermal initiation [1,2] at higher concentrations of the olefin. On the other hand, dibenzoyl peroxide proved to be a suitable initiator for the addition of all the alcohols studied; in the case of methanol the yields were relatively low but acceptable. The reaction of 2-propanol offers application of a sensitiser. Aromatic ketones are used [9] generally as sensitisers, but in our case they were quite ineffective (see Table 1). Contrary to this observation, the reaction sensitised with acetone gave by far the highest yield of the 1:1 adduct 3c with a small portion of byproduct 5c. The unreacted tetrafluoroethylene was trapped by cooling with liquid nitrogen and re-used in a next run. Therefore, the yields of products 3-5 reached, depending on recovery losses, 73-82 % relatively to the converted tetrafluoroethylene.

An important role in the photoaddition is played by a filter absorbing radiation of wavelengths under 300 nm, moderating in this way the decomposition of initiators. Simax^R technical glass proved to be a suitable filter in our case, its absorption curve being similar to that of Pyrex^R glass.

The NMR spectra of the products 3a-3c and 5a-5c are summarized in Table 2.

EXPERIMENTAL

The temperature data are uncorrected. Gas-liquid chromatographic analyses were performed on a Chrom 41 instrument [Laboratorní přístroje, Prague; FID, columns 380 x 0.3 cm, carrier gas nitrogen, support Chromaton N-AW-DMCS (Lachema, Brno), stationary phases poly(1,4-butanediol succinate) and Carbowax 6000]. The NMR spectra were taken on Varian XL-100-15 (CW, 100 and 94 MHz, respectively) and Bruker AM-400 (FT, 400 and 376 MHz, respectively) instruments (^{19}F NMR spectra with CCl_3F as the standard). UV spectra were measured on a Specord M-40 (Zeiss, Jena) instrument.

TABLE 1

Conditions and results of photoinitiated reactions of alcohols with tetrafluoroethylene

Alcohol		Initiator (Sensitiser)			Filter	Time	Temperature	Products[a]		
								1:1 Adduct		1:2 Telomer
g	mol		g	mol		h	°C	g	mol	% rel.[b]
Methanol										
198	6.18	AIBN[c]	4.1	0.025[d]	Simax[e]	2	-16	trace		-
		DBP[f]	5.5	0.022[g]	Simax	6	-30	12.3	0.093	46
Ethanol										
197	4.28	AIBN	4.1	0.025[d]	Simax	3	-10	1.1	0.01	-
		DBP	5.6	0.023[h]	-	8	-30	4.2	0.03	22
316	6.85	DBP	3.8	0.016[g,h]	Simax	8	-30	26.1	0.18	39
2-Propanol										
196	3.26	BME[i]	5.35	0.25[d]	Simax	1.5	-25	1.0	0.006	trace
		DBP	6.0	0.025[g,h]	Simax	6.3	-30	26	0.16	11
		DBP	2.0	0.008[h]	-	6.5	-30	10	0.06	11
		Benzophenone	0.55	0.003[g]	Simax	2	-25	0.5	0.003	-
		Acetone	15	0.274[g]	-	8	-30	57	0.36	12

[a] Calculated from GLC analysis of the raw product;
[b] wt. % relative to 1:1 adduct;
[c] azo-bis-isobutyronitrile;
[d] UV lamp Tesla, RVK 125 W;
[e] Simax^{R} technical-glass filter;
[f] dibenzoyl peroxide;
[g] UV lamp Tesla, RVK 250 W;
[h] saturated solution with undissolved DBP;
[i] benzoin methyl ether.

TABLE 2

NMR Spectra of the compounds 3a-3c, 5a-5c

Compound	Group, Character of signals
$HCF_2-CF_2-CH_2-OH$ 3a	
A[a]	HO- s 3.04 (29 °C); $-CH_2-$ t 3.92, ^3J(H-F) 15; HCF_2- t 5.85, ^3J(H-F) 53, ^3J(F-F) 4
B[b]	$-CF_2CH_2-$ dt -128.1; HCF_2- qd -139.2, ^3J(F-F) ca. 2
$HCF_2-CF_2-CH(CH_3)OH$ 3b	
A	HO- s 2.92 (25 °C); -CH- m 4.14, ^3J(H-H) 6.6, ^3J(H-F) 15; CH_3- dd 1.36, ^4J(H-F) 0.8
B	$-CF_2CH-$ dt -130.2, ^2J(F-F) 271, ^3J(F-F) 5, ddd -134.2, ^3J(F-F) 7.5; HCF_2- ddd -137.3, ^2J(F-F) 305, ^3J(F-F) 7.5, ddt -141.3, ^3J(F-F) 5
$HCF_2-CF_2-C(CH_3)_2OH$ 3c	
A	HO- s 2.55 (31 °C); CH_3- t 1.38, ^4J(H-F) 1.2; HCF_2- tt 6.03, ^2J(H-F) 53, ^3J(H-F) 5.8
B	$-CF_2C(CH_3)_2-$ dt -130.3, ^3J(F-F) 6; HCF_2- dt -136.2, ^3J(F-F) 6
$H\overset{4}{C}F_2-\overset{3}{C}F_2-\overset{2}{C}F_2-\overset{1}{C}F_2-CH_2OH$ 5a	
A	HO- s 3.57 (25°C); $-CH_2-$ t 4.05, ^3J(H-F) 14.4; HCF_2- tt 6.03, ^2J(H-F) 53, ^3J(H-F) 5.5 ;
B	$-CF_2CH_2-$ m 123.3, ^3J(F-F) 12, ^4J(F-F) 3; $-\overset{3}{C}F_2\overset{4}{C}F_2-$ (4 F) qt -126.3, ^3J(F-F) 12, m -130,8; HCF_2- dm -138.0
$H\overset{4}{C}F_2-\overset{3}{C}F_2-\overset{2}{C}F_2-\overset{1}{C}F_2-CH(CH_3)OH$ 5b	
A	HO- s 3.32 (25 °C); $-CF_2CH-$ m 4.28, ^3J(H-F) 7.6; CH_3- qd 1.38, ^3J(H-H) 6.6; HCF_2- tt 6.08, ^2J(H-F) 52, ^3J(H-F) 5.5

(Continued)

TABLE 2 (cont.)

B	$-CF_2CH-$ dm -122.86 (F_{1a}), dm -127.84 (F_{1b}), $^2J(F-F)$ 280; $-CF_2-$ dq -124.1 (F_{2a}), dq -124.6 (F_{2b}), $^2J(F-F)$ 298, $^3J(F-F)$ 8; $-CF_2-$ dm -130.61 (F_{3a}), dm -131.13 (F_{3b}), $^2J(F-F)$ 290, $^3J(F-F)$ 6; HCF_2- dm -138.0
$HCF_2-CF_2-CF_2-CF_2-C(CH_3)_2OH$ 5c	
A	$HO-$ s 2.58 (25 °C); CH_3- qs 1.44, $^4J(H-F)$ 1.6; HCF_2- tt 6.08, $^2J(H-F)$ 52.2; $^3J(H-F)$ 5.6
B	$-CF_2C(CH_3)_2-$ m -130.8, $^3J(F-F)$ 6; $-C_2F_4-$ (4 F) m -121.8; HCF_2- dm -137.9

[a] ^1H NMR spectrum; [b] ^{19}F NMR spectrum; s - singlet, d - doublet, t - triplet, m - multiplet, q - quasi .

Chemicals used

Methanol, ethanol and 2-propanol were dried as usual and fractionated; the optical purity of the distillate was continuously checked by its UV absorption . 1,2-Dibromotetrafluoroethane (technical grade) was dried over anhydrous calcium chloride and rectified on a packed column (b.p. 45-47 °C). Powdered zinc (technical grade) was dried at 100-120 °C before use. Benzoin methyl ether (BME) was purified on a column with aluminium oxide (diethyl ether/hexane 1:1). Azo-bis-isobutyronitrile (AIBN) was recrystallised from methanol at 28-30 °C. Dibenzoyl peroxide (DBP) was dissolved in chloroform, dried over anhydrous calcium chloride, the solution was kept in darkness and the solvent was evaporated prior to use at 20-25 °C on a rotatory evaporator. Benzophenone was recrystallised from light petroleum.

Preparation of tetrafluoroethylene

The apparatus and liquid chemicals were flushed before reaction with pure nitrogen to remove oxygen. The reaction was performed in a three-necked flask fitted with a by-pass dropping funnel, a stainless-wire stirrer with a gas-tight shaft and with a reflux condenser tandem (a Dimroth condenser with attached dry-ice-cooled condenser). 1,2-Dibromotetrafluoroethane (260 g; 1 mol) and methanol (350 ml) at bath temperature of ca. 50 °C, and the tetrafluoroethylene formed was trapped in a receiver cooled with liquid nitrogen. A slight stream of nitrogen was passed through the apparatus during the reaction (yield 82-91 %).

Photoreaction of tetrafluoroethylene with alcohols

(a) Apparatus

An immersion-well photoreactor cooled from outside to -30 to-10 °C, a UV lamp (Tesla, RVK 125 W) in a water-cooled double jacket (quartz and Simax^R glass); tetrafluoroethylene sintered-glass inlet at the bottom of the reactor; tetrafluoroethylene leaving the reactor passed through a dry-ice cooled spiral cooler and then through a hydraulic seal with ethylene glycol into a liquid nitrogen-cooled trap, connected with the atmosphere by a hydraulic seal with sulphuric acid.

(b) Preparation

Prior to the reaction the whole apparatus was carefully flushed with pure nitrogen. The photoreactor contained a solution (suspension) of an initiator (sensitiser). Tetrafluoroethylene was introduced in a surplus flow during the reaction and the unreacted gas was trapped and re-used in the reaction. The presence of an initiator in the withdrawn samples was checked by UV spectroscopy. After the end of reaction, the mixture was filtered, distilled under reduced pressure and fractionated on packed columns. The boiling points of the products correspond to those in the literature [1], [10] (3a 108-109 °C, Ref. [10] 109 °C; 5a, 140-141 °C, Ref. [10] 141 °C; 3b, 109-110 °C, Ref. [1] 110 °C; 5b, 141-143 °C, Ref. [1]

140 °C; 3c, 119-120 °C, Ref. [1] 120 °C; 5c, 148-150 °C, Ref. [1] 150 °C).

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