

PHOTOCHEMICAL ADDITION OF SECONDARY ALCOHOLS  
TO METHYL TRIFLUOROACRYLATE\*V.P.ŠENDRIK<sup>a</sup>, O.PALETA<sup>b</sup> and V.DĚDEK<sup>b</sup><sup>a</sup> Odessa Polytechnical Institute, Odessa, SSSR, and<sup>b</sup> Department of Organic Chemistry,

Prague Institute of Chemical Technology, 166 28 Prague 6

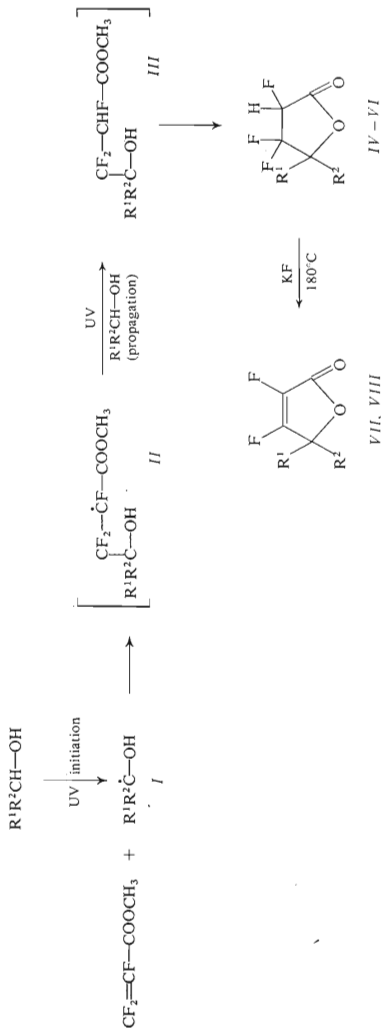
Received October 26th, 1976

Photochemically initiated reaction of 2-propanol, 2-butanol and cyclohexanol with methyl trifluoroacrylate in liquid phase afforded fluorinated butanolides, *i.e.* 4,4-dimethyl-(*IV*), 4-ethyl-4-methyl-2,3,3-trifluoro-4-butanolide (*V*) and 1-oxa-2-oxo-3,4,4-trifluorospiro[4,5]decane (*VI*). Dehydrofluorination of the butanolides *IV* and *V* gave the corresponding difluorobutenolides *VII* and *VIII*.

Photochemically initiated addition of alcohols to olefinic double bonds represents an important preparative reaction<sup>1,2</sup>. The addition usually proceeds with cleavage of the C—H bond on the hydroxyl carbon, leading thus to higher alkanols. In some cases the cleavage takes place at the O—H bond<sup>3-5</sup> and the reaction then affords alkoxy derivatives.  $\alpha,\beta$ -Unsaturated carboxylic acids and their esters give the corresponding hydroxy acids and hydroxy esters which cyclise spontaneously<sup>1,2</sup> to lactones<sup>6-11</sup>. Alcohols enter the photochemically initiated addition to fluorinated olefins<sup>12-15</sup>, affording in all cases fluorinated alkanols. In this context, it was of interest to study the course of the photochemical reaction of methyl trifluoroacrylate with hydroxy compounds.

This paper investigates the photochemically initiated reaction of methyl trifluoroacrylate with secondary alcohols, particularly with 2-propanol, 2-butanol and cyclohexanol (see also ref.<sup>16</sup>). The reactions were carried out in a quartz reactor at 20 to 22°C. Using 1 : 60 ratio of acrylate to alcohol, we were able to achieve preferred formation of the 1 : 1 adduct. In the photoaddition the C—H bond on the hydroxyl carbon was cleaved and the species  $R^1R^2\dot{C}$ —OH and H<sup>•</sup> added to the olefinic bond of methyl trifluoroacrylate (Scheme 1). Addition of these species should afford hydroxy esters of the type *III* which, however, were not detected in the reaction mixture. The only isolated products were butanolides *IV*—*VI* (according to the alcohol used). The reaction mixture contained also unidentified high-boiling compounds (yield 2–3%) which we suppose to be telomers.

\* Part X in the series Haloacrylic Acids; Part IX: Sb. Vys. Šk. Chemicko-technol. Praze, in press.



IV, VII, R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>  
 V, VIII, R<sup>1</sup> = CH<sub>3</sub>, R<sup>2</sup> = C<sub>2</sub>H<sub>5</sub>  
 VI, R<sup>1</sup> = R<sup>2</sup> = -(CH<sub>2</sub>)<sub>5</sub>-

SCHEME 1

The products *IV*–*VI* were isolated by distillation in 31–58% yields; reaction conditions and results are given in Table I.

The addition of 2-propanol afforded 4,4-dimethyl-2,3,3-trifluoro-4-butanolide (*IV*), 2-butanol reacted under formation of 4-ethyl-4-methyl-2,3,3-trifluoro-4-butanolide (*V*) and the reaction of cyclohexanol led to 1-oxa-2-oxo-3,4,4-trifluorospiro[4,5]decane (*VI*).

We tried to transform the lactones *IV* and *V* into the fluorinated butenolides which could be potentially biologically active compounds. Since both the products and the starting material in this elimination are not stable in the presence of strong

TABLE I

Conditions and Products of the Reaction of Secondary Alcohols with Methyl Trifluoroacrylate

Alcohol <sup>a</sup>	g	mol	Time, h	Product	g	%
2-Propanol	181	3	6	<i>IV</i>	4.71	56.4
2-Butanol	222	3	2	<i>V</i>	3.09	31.8
Cyclohexanol <sup>b</sup>	60.0	0.6	2	<i>VI</i>	1.22	58.1

<sup>a</sup> Amount of methyl trifluoroacrylate used: 7.01 g (50 mmol); <sup>b</sup> 1.40 g (10 mmol).

TABLE II

Properties of the Isolated Products

Compound	Formula (M.wt.)	Calculated/Found			B.p., °C/Torr (kPa) (Purity, % rel.)
		% C	% H	% F	
<i>IV</i>	C <sub>6</sub> H <sub>7</sub> F <sub>3</sub> O <sub>2</sub> (168.1)	42.89	4.16	33.91	80–84/12 (1.60) (98)
		42.78	4.25	34.02	
<i>V</i>	C <sub>7</sub> H <sub>9</sub> F <sub>3</sub> O <sub>2</sub> (182.1)	46.19	4.94	31.30	76–80/10 (1.33) (95)
		45.78	4.84	30.62	
<i>VI</i>	C <sub>9</sub> H <sub>11</sub> F <sub>3</sub> O <sub>2</sub> (208.1)	51.95	5.28	27.39	115–120/11 (1.47) (95)
		52.37	5.62	26.43	
<i>VII</i>	C <sub>6</sub> H <sub>6</sub> F <sub>2</sub> O <sub>2</sub> (148.1)	48.65	4.08	25.65	103–105/130 (17.33) (98)
		48.01	4.27	25.46	
<i>VIII</i>	C <sub>7</sub> H <sub>8</sub> F <sub>2</sub> O <sub>2</sub> (162.1)	51.88	4.93	23.45	110–115/170 (22.66) (98)
		51.40	5.08	23.59	

bases (such as *e.g.* nitrogen bases<sup>17</sup>), it was necessary to choose the appropriate experimental conditions. Dehydrofluorination by anhydrous potassium fluoride appeared to be the method of choice. We prepared thus 4,4-dimethyl-2,3-difluoro-2-buten-4-olide (VII) from the lactone IV and 4-ethyl-4-methyl-2,3-difluoro-2-buten-4-olide (VIII) from the lactone V.

The molecule of the lactone V contains two asymmetric carbon atoms. Since the diastereoisomers, present in the reaction mixture, differed sufficiently in their physico-chemical properties, they were separated by gas-liquid chromatography on packed columns. Both the diastereoisomers exhibit identical mass spectra; similar behaviour was described in the literature<sup>14,18</sup>. The structure of the compounds IV–VIII was proved by their elemental analyses (Table II), NMR spectra (Table III), mass spectra (Table IV) and IR spectra (Table V).

Mechanism of the addition of alcohols to esters of  $\alpha,\beta$ -unsaturated acids has not been hitherto unequivocally elucidated<sup>11</sup>. The uninvestigated step is the formation of the "solvent-radical" I. If the reaction is carried out in the absence of photosensibilisators we can assume that the splitting of the hydrogen from the alcohol is caused

TABLE III

## NMR Spectra of the Compounds IV–VIII

Chemical shift in ppm (number of protons); s singlet, d doublet, t triplet; coupling constants J in Hz.

Compound	Spectrum <sup>a</sup>	Character of the signals
IV	A	ddd 5.34 (1), $^2J_{\text{HF}} = 48.2$ , $^3J_{\text{HF}} = 8.5-12.2$ , $-\text{HFC}-\text{CF}_2$ ; ds 1.55 (6), $-\text{CH}_3$
V	A	ddd 5.33 (1), $^2J_{\text{HF}} = 48.1$ , $^3J_{\text{HF}} = 9.0-10.2$ , $-\text{HFC}-\text{CF}_2$ ; t 1.92 (2), $^3J_{\text{HH}} = 9.1$ , $-\text{CH}_2$ ; s 1.54 (3), $-\text{CH}_3$ ; t 1.10 (3), $^3J_{\text{HH}} = 8.1$ , $-\text{CH}_2\text{CH}_3$
VI	A	ddd 5.30 (1), $^2J_{\text{HF}} = 49$ , $^3J_{\text{HF}} = 12.2-15.4$ , $-\text{HFC}-\text{CF}_2$ ; s 1.74 (10), $-(\text{CH}_2)_5-$
VII	A	ds 1.61 (6), $-\text{CH}_3$
	B	d 164.0 (1), $^3J_{\text{FF}} = 8.0$ , $\text{OCOCF}$ , d 166.0 (1), $^3J_{\text{FF}} = 8.0$ , $=\text{CF}-\text{C}(\text{CH}_3)_2\text{O}$
VIII	A	t 1.86 (2), $^3J_{\text{HH}} = 12.2$ , $-\text{CH}_2-$ ; s 1.60 (3), $-\text{CH}_3$ ; t 0.94 (3), $^3J_{\text{HH}} = 7.8$ , $-\text{CH}_2\text{CH}_3$

<sup>a</sup> A <sup>1</sup>H-NMR spectrum; B <sup>19</sup>F-NMR spectrum (relative to  $\text{CFCl}_3$ ) with noise <sup>1</sup>H decoupling.

by the photochemically excited ester. The second, more probable, alternative is a chain mechanism, in which the radical *I* arises in the vibrationally excited ground state

TABLE IV

Mass Spectra of the Butanolides *IV*–*VI*  
Ionic species *m/e*, relative intensity %.

Compound (mol.wt.)	Principal ionic species
<i>IV</i> (168)	153/6.6 (M – CH <sub>3</sub> ) <sup>+</sup> ; 140/2.83 (M – CO) <sup>+</sup> ; 125/11.3 (M – C <sub>2</sub> H <sub>3</sub> O) <sup>+</sup> ; 109/50.9 (C <sub>3</sub> H <sub>3</sub> F <sub>2</sub> O <sub>2</sub> ) <sup>+</sup> ; 82/13.2 (C <sub>2</sub> HF <sub>3</sub> ) <sup>+</sup> ; 74/11.3 (C <sub>3</sub> H <sub>3</sub> FO) <sup>+</sup> ; 59/20.7 (C <sub>2</sub> H <sub>3</sub> O <sub>2</sub> ) <sup>+</sup> ; 58/23.6 (C <sub>2</sub> H <sub>2</sub> O <sub>2</sub> ) <sup>+</sup> ; 43/100 (C <sub>2</sub> H <sub>3</sub> O) <sup>+</sup>
<i>V</i> (182)	167/2.56 (M – CH <sub>3</sub> ) <sup>+</sup> ; 153/3.33 (M – C <sub>2</sub> H <sub>5</sub> ) <sup>+</sup> ; 109/15.3 (C <sub>3</sub> H <sub>3</sub> F <sub>2</sub> O <sub>2</sub> ) <sup>+</sup> ; 91/15.2 (C <sub>3</sub> H <sub>4</sub> FO <sub>2</sub> ) <sup>+</sup> ; 82/12.8 (C <sub>2</sub> HF <sub>3</sub> ) <sup>+</sup> ; 72/29.9 (C <sub>3</sub> H <sub>4</sub> O <sub>2</sub> ) <sup>+</sup> ; 56/83.7, 43/100 (C <sub>2</sub> H <sub>3</sub> O) <sup>+</sup>
<i>VI</i> (208)	209/0.001 (M + 1) <sup>+</sup> ; 208/0.002 (M) <sup>+</sup> ; 207/0.001 (M – 1) <sup>+</sup> ; 98/87.2 (C <sub>6</sub> H <sub>10</sub> O) <sup>+</sup> ; 82/93.6 (C <sub>2</sub> HF <sub>3</sub> ) <sup>+</sup> ; 81/100 (C <sub>6</sub> H <sub>9</sub> ) <sup>+</sup> ; 69/32.3 (C <sub>5</sub> H <sub>9</sub> ) <sup>+</sup> ; 55/75 (C <sub>3</sub> H <sub>3</sub> O) <sup>+</sup>

TABLE V

Absorption Maxima (cm<sup>-1</sup>) in the IR Spectra of the Compounds *IV*–*VIII* (tetrachloromethane)

Compound	$\nu(\text{C}=\text{O})$	Other bands
<i>IV</i>	1 800 s	827 m, 878 m, 970 m, 1 053 m, 1 100 s, 1 126 s, 1 195 s, 1 127 m, 1 257 m, 1 278 m, 1 297 m, 1 375 m, 1 390 m, 1 430 w, 1 460 m, 2 850 w, 2 950 w, 2 990 w
<i>V</i>	1 800 s	820 m, 897 m, 952 m, 992 m, 1 022 m, 1 084 s, 1 098 s, 1 123 s, 1 185 m, 1 212 m, 1 244 m, 1 290 m, 1 350 w, 1 370 w, 1 380 w, 1 430 w, 1 450 w, 2 885 w, 2 947 w, 2 980 w
<i>VI</i>	1 808 s	855 m, 912 m, 969 s, 1 015 m, 1 040 m, 1 108 s, 1 128 s, 1 180 s, 1 210 m, 1 230 m, 1 269 m, 1 299 m, 1 374 m, 1 446 m, 2 855 m, 2 940 s
<i>VII</i>	1 795 s	938 m, 1 015 m, 1 105 s, 1 153 s, 1 204 m, 1 344 s, 1 386 w, 1 460 m, 1 745 s $\nu(\text{C}=\text{C})$ , 2 870 w, 2 933 w, 2 990 w
<i>VIII</i>	1 788 s	823 m, 930 m, 1 030 m, 1 103 s, 1 150 s, 1 197 m, 1 365 m, 1 450 m, 1 740 s $\nu(\text{C}=\text{C})$ , 2 880 w, 2 935 w, 2 980 w

of the alcohol. Then the species *I* in the ground state adds to the double bond of methyl trifluoroacrylate under formation of the "adduct-radical" *II* whose reaction with solvent regenerates the solvent-radical *I*.

## EXPERIMENTAL

The temperature data are uncorrected. Gas-liquid chromatography was carried out on a Chrom 3 chromatograph (Laboratorní přístroje, Prague; flame ionisation detector, column diameter 0.6 cm, carrier gas nitrogen, poly(1,4-butanediol succinate) on Chromaton N—AW-DMCS, Lachema, Brno). The IR spectra were taken on a Perkin-Elmer 325 (Bodenseewerk) spectrometer, NMR spectra were taken in deuteriochloroform on a Varian XL-100-15 (Palo Alto) instrument. The mass spectra were measured on a Gas Chromatograph — Mass Spectrometer LKB 9000 (Stockholm; one focus, electron energy 70 eV, chromatographic inlet poly(ethylene glycol adipate), carrier gas helium).

### Butanolides *IV*—*VI*

A mixture of the corresponding alcohol and methyl trifluoroacrylate<sup>19,20</sup> (Table I) in a quartz reactor<sup>12-14</sup> was irradiated with a UV lamp (Tesla, 125 W) in a stream of argon at 15–18°C. The starting compounds were distilled off and the 1:1 adduct was obtained by distillation in vacuo. Boiling points, yields and elemental analyses are given in Table II.

### Butenolides *VII* and *VIII*

The butanolide *IV* or *V* (0.84 g of *IV* or 0.91 g of *V*; 5 mmol) was heated with anhydrous potassium fluoride (5.8 g; 0.1 mol) to about 180°C and the obtained butenolide *VII* or *VIII* was isolated by distillation. The boiling points, yields and elemental analyses are given in Table I.

*Spectral measurements were performed in the Department of NMR Spectroscopy (Head Dr P. Trška), Department of IR Spectroscopy (Head Dr A. Muck) and Department of Mass Spectrometry (Head Dr V. Kubelka) the elemental analyses were carried out in the Department of Organic Analysis (Head Dr L. Helešic), Prague Institute of Chemical Technology, Prague. To all of them we are indebted for the kind help.*

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Translated by M. Tichý.