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HALOACRYLIC ACIDS

XI* . PHOTOCHEMICAL REACTIONS OF ALIPHATIC ALDEHYDES WITH METHYL TRIFLUOROACRYLATE

V.P. SHENDRIK

Odessa Polytechnical Institute, Odessa (U.S.S.R.)

J. SVOBODA, O. PALETA and V. DĚDEK

Institute of Chemical Technology, 16628 Prague 6 (Czechoslovakia)

SUMMARY

Photochemically initiated reactions of aliphatic aldehydes, namely acetaldehyde, propionaldehyde and butyraldehyde, with methyl trifluoroacrylate afforded γ -ketoesters of the type $R-CO-CF_2CHF-COOCCH_3$ in the liquid phase. In the gas phase reaction further products were formed by addition of the aldehyde fragments to the olefinic bond of the methyl trifluoroacrylate.

INTRODUCTION

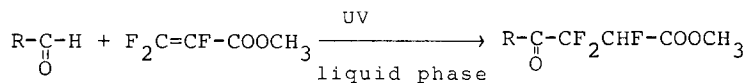
Fluoroolefins are known to be reactive components in radical reactions [1-3]. The olefinic bond in methyl trifluoroacrylate exhibits some characteristic chemical properties of fluoroolefins, as we demonstrated in the nucleophilic addition of alcohols [4] and amines [5], and in the photochemical addition of ethers [6]. Following these experiments one would suppose the reaction of aldehydes with methyl trifluoroacrylate induced photochemically to be successful.

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Radical reactions of aldehydes with fluoroolefins have previously been performed both in the liquid phase [7-13] and in the gas phase [8, 10, 14] using peroxides [7-10], ultraviolet light [9, 14], and γ -irradiation [7, 11-13, 15] as initiators. In some photochemically induced reactions both oxetanes and linear adducts were formed [14], but sometimes oxetanes were the only products [9].

RESULTS AND DISCUSSION

In this paper we describe the reaction of methyl trifluoroacrylate initiated by ultraviolet light with acetaldehyde, propionaldehyde and butyraldehyde. The reaction with the above aldehydes was carried out in the liquid phase, and with propionaldehyde and butyraldehyde in the gas phase also. In the liquid phase we obtained γ -ketoesters (I-III) in yields of 49-73% together with high boiling point telomer products. The reactions were carried out with a large excess of aldehyde (Table 1) to lower the relative amounts of the telomers obtained.



I-III

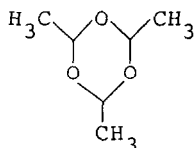
- I, R = CH₃
 II, R = CH₂CH₃
 III, R = CH₂CH₂CH₃

Scheme 1

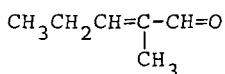
From the structure of the products (I-III) it is obvious that in the course of the reaction fission of the C-H bond on the carbonyl atom of the aldehyde took place, as well as addition of both fragments to the olefinic bond of the methyl trifluoroacrylate (scheme 1). In contrast to former observations [9, 14] we did not detect oxetanes as products of 1,2-cycloaddition in the reaction mixtures.

Acetaldehyde afforded 2,3,3-trifluoro-4-oxopentanoate (I), propionaldehyde gave methyl 2,3,3-trifluoro-4-oxohexanoate (II),

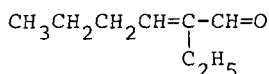
and butyraldehyde yielded, by the above reaction, methyl 2,3,3-trifluoro-4-oxoheptanoate (III). These main reactions were accompanied by the formation of non-fluorinated by-products as the result of aldehyde reactions, i.e. a trimerization by-product (IV), or aldol condensation by-products (V and VI) catalyzed probably by hydrogen fluoride arising in the reaction mixture.



IV

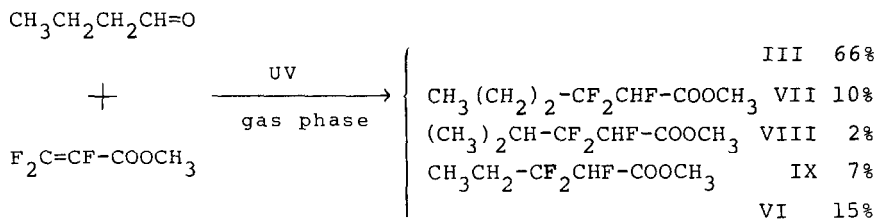


V



VI

A different course was observed in the reactions of propionaldehyde and butyraldehyde in the gas phase. Butyraldehyde afforded the known product (III) in addition to further products (VII-IX), while propionaldehyde yielded compound (IX) as the principal product (Table 1). We did not find a compound with the oxetane ring among the products although the gas phase reaction is usually suitable for a cycloaddition [14].



The formation of compounds (VII-IX) may be explained by the addition of aldehyde fragments to methyl trifluoroacrylate. As given in the literature [17], the cleavage of C-C bonds in aldehydes by the action of UV light follows the Norrish type I and II mechanisms and the resulting radicals may undergo further transformations, such as isomerization, fragmentation, and recombination. From the structures of compounds (VII-IX) it emerges

that, in the gas phase, the decarbonylation of the acyl radical is an important reaction. Fragmentations take place usually in a vibrationally excited ground state and they are effectively quenched in the liquid phase as a consequence of fast vibrational equilibration [17]. For that reason the reaction in the liquid phase takes a simple course and can be employed to prepare γ -ketoesters.

To obtain more detailed information about the relative reaction rates, we measured the decrease of methyl trifluoroacrylate concentration during the gas and liquid phase reactions with butyraldehyde (Fig. 1). The concentration dependences in Fig. 1 show that the gas phase reaction is faster in excess of butyraldehyde than in excess of methyl trifluoroacrylate (curve A), but for aldehyde excesses 2:1 (curve B) and 5:1 (curve C) the rates are almost the same. The liquid phase reaction place much faster in excess of butyraldehyde (curve D)..

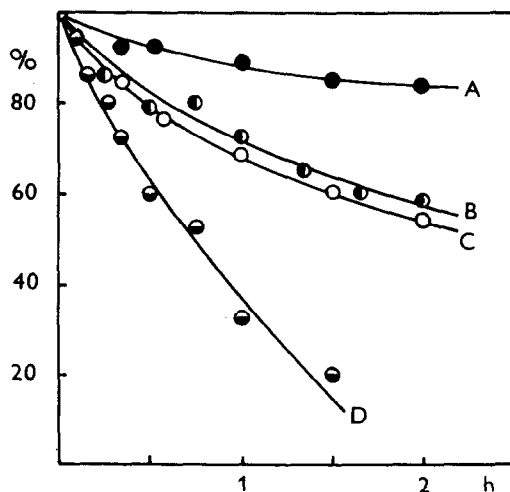


Fig. 1. Decrease of methyl trifluoroacrylate concentration with time during its photoinitiated reaction with butyraldehyde. Trifluoroacrylate butyraldehyde ratio: curve A, 3:1 (gas phase reaction); curve B, 1:2 (gas phase reaction); curve C, 1:5 (gas phase reaction); curve D, 1:10 (liquid phase reaction).

EXPERIMENTAL

Apparatus

Gas chromatography

Chromatographic analyses were performed on a Chrom 3 (Laboratorní přístroje, Prague) instrument (FID, analytical column diameter 0.6 cm; preparative column diameter 1 cm, length 500 cm; carrier gas nitrogen, support Chromaton N-AW-DMCS, Lachema, Brno).

NMR spectroscopy

The NMR spectra were taken in deuteriochloroform on a Varian XL-100/15 instrument.

IR spectroscopy

The IR spectra were measured on a Perkin-Elmer 325 (Bodenseewerk) instrument.

Mass spectra

The mass spectra were measured on a gas chromatograph - mass spectrometer LKB 9000 (Stockholm); single focus, 70 eV, chromatographic inlet: poly(ethylene glycol adipate) on Chromaton N-AW, 250 cm x 0.23 cm glass column, carrier gas helium

Chemicals used

Methyl trifluoroacrylate was prepared according to our own method [18-20] starting from Ledon 11 (trichlorofluoromethane) and 1,2-dichlorodifluoroethylene.

Photochemically induced reaction of aldehydes with methyl trifluoroacrylate

Reaction mixtures were irradiated at 12-15°C with a high pressure UV lamp (Tesla, 125 W) placed in a water-cooled quartz

double-jacket. During the reaction of acetaldehyde the reaction vessel was fitted with a dry-ice-cooled condenser.

(a) In the liquid phase

A mixture of aldehyde and methyl trifluoroacrylate was irradiated in a slow stream of nitrogen. After reaction, the mixture was washed with water and dried with anhydrous magnesium sulphate. The products were isolated by distillation. Reaction conditions and results are shown in Table 1. Boiling point and elemental analyses of products (I-III) are given in Table 2, and their NMR and IR spectra are shown in Tables 3 and 4, respectively. Gas chromatography: 15% Carbowax 6000, column length 240 cm, 120-180°C.

(b) In the gas phase

A mixture of reactants with different molar ratios (Table 1) was irradiated in the reaction flask (6000 ml) for 3 hours at 90°C (propionaldehyde), or at 100°C (butyraldehyde). At the bottom of the flask was a layer of glass rings. After the reaction of butyraldehyde (9.70 g, 0.134 mol), the reaction

TABLE 1
CONDITIONS AND RESULTS OF THE REACTION OF ALDEHYDES WITH METHYL TRIFLUOROACRYLATE

Aldehyde			F ₂ C=CF-CO ₂ CH ₃		Time (h)	Products	
	(g)	(mol)	(g)	(mmol)		Comp.	Yield (%)
AA	26.4	0.60	1.40	10	0.3	I	49
PA	34.8	0.60	1.40	10	0.5	II	63.2
PA	34.8	0.60	1.40	10	2	II	73.3
PA ^a	8.7	0.15	42	300	11	IX	31.1
BA	30.2	0.419	2.70	19.2	0.5	III	67.8

AA, acetaldehyde; PA, propionaldehyde; BA, butyraldehyde.

^a Gas phase reaction.

vessel was cooled to 0°C, the reaction products were mixed with diethyl ether (200 ml), and the ether solution was washed with aqueous potassium bicarbonate, then with water, and dried over anhydrous magnesium sulphate. During distillation, a fraction 65-85°C/1.33 kPa was collected (2.31 g) containing a mixture of compounds (III, VI-IX); the distillation residue (2.13 g) contained mostly telomerization products (gas chromatography: 15% poly(1,4-butanediol)succinate, column length 240 cm). Products (III, VII-IX) were separated by preparative gas chromatography on the same stationary phase. For elemental analyses and spectral data see Tables 2-5.

(c) Rate of the butyraldehyde reaction

The reaction was performed at 100°C in a 1000 ml glass vessel with inner UV lamp. The composition of the reaction mixture was analyzed by gas chromatography using the inner standard method (benzene). The course of the runs is shown in Fig. 1 (gas chromatography: 15% Carbowax 6000, column length 360 cm).

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TABLE 2
ELEMENTAL ANALYSES AND PROPERTIES OF COMPOUNDS (I-III, VII, IX)

Compound*	Formula (mol. wt.)	Calc. (Exper.)		Boiling point (°C/torr (kPa))	Purity (%rel.)
		%C	%H %F		
I	C ₆ H ₇ F ₃ O ₃ (184.0)	39.2 (40.1)	3.8 (3.9) 31.0 (29.9)	55-60/13 (1.73)	93
II	C ₇ H ₉ F ₃ O ₃ (198.0)	42.5 (43.1)	4.5 (4.9) 28.8 (28.2)	86-90/11 (1.46)	94
III	C ₈ H ₁₁ F ₃ O ₃ (212.1)	45.3 (44.7)	5.2 (5.4) 26.9 (26.2)	80-84/10 (1.33)	95
VII	C ₇ H ₁₁ F ₃ O ₂ (184.1)	45.6 (45.2)	6.0 (5.8) 31.0 (30.7)		97
IX	C ₆ H ₉ F ₃ O ₂ (170.0)	- -	- - 33.5 (33.2)	65-70/31 (4.12)	95

*All new compounds.

TABLE 3

NMR SPECTRA OF THE COMPOUNDS (I-III, VII, IX)

Compound	Spectrum ^a	Character of signals ^b
I	A	dt 5.26 (1), ² J(H-F) 46, ³ J(H-F) 11.6 [CF ₂ CHF]; s 3.84 (3) [OCH ₃]; s 2.36 (3) [CO-CH ₃]
II	A	dt 5.44 (1), ² J(H-F) 46.1, ³ J(H-F) 9.8-12.2 [CF ₂ CHF]; s 3.86 (3) [OCH ₃]; q 2.76 (2), ³ J(H-H) 7.1 [CH ₃ CH ₂ CO]; t 1.12 (3) [CH ₃ CH ₂ CO]
III	A	dt 5.37 (1), ² J(H-F) 46, ³ J(H-F) 10 [CF ₂ CHF]; s 3.89 (3) [OCH ₃]; t 2.75 (2) [CH ₂ CO]; m 1.68 (2) [CH ₂ CH ₃]; t 1.00 (3) [CH ₃ CH ₂]
VII	A	dt 4.97 (1), ² J(H-F) 46, ³ J(H-F) 10 [CF ₂ CHF]; s 3.89 (3) [OCH ₃]; m 2.33 [CF ₂ CH ₂]; m 1.68 (2) [CH ₂ CH ₃]; t 1.00 (3) [CH ₃ CH ₂]
	B	m -108.5 (2) [CF ₂]; dt -202.5 (1), ² J(H-F) 46, ³ J(F-F) 12 [CHF]
IX	A	dt 5.00 (1), ² J(H-F) 46.2, ³ J(H-F) 10.6 [CF ₂ CHF]; s 3.91 (3) [OCH ₃]; m 1.96 (2) [CH ₂ CF ₂]; t 1.12 (3) [CH ₃ CH ₂]
	B ^c	dd -106.6 (2), ² J(F-F) 23, ³ J(F-F) 11 [CF ₂]; t -202.5 (1), ³ J(F-F) 10.5 [CHF]

a A ¹H NMR spectrum, B ¹⁹F NMR spectrum (internal standard (CFCl₃)).

b Chemical shifts ppm (number of protons or fluorine atoms); s singlet, d doublet, t triplet, q quartet, m multiplet; coupling constants J in Hz.

c Noise decoupling of protons.

TABLE 4
 ABSORPTION MAXIMA (cm^{-1}) IN THE INFRARED SPECTRA OF THE COMPOUNDS (I-III and IX)
 IN TETRACHLOROMETHANE AND CARBON DISULFIDE

Compound	Absorption bands
I	1750 s, 1780 s $\nu(\text{C}=\text{O})$; 968 m, 996 m, 1010 m, 1048 m, 1100 s, 1220 m, 1255 m, 1360 m, 1438 m, 2913 w, 2960 w, 3000 w
II	1740 s, 1765 s $\nu(\text{C}=\text{O})$; 820 m, 842 m, 918 m, 1015 m, 1053 m, 1110 s, 1230 s, 1275 m, 1320 s, 1345 s, 1380 m, 1403 m, 1436 s, 1456 m, 2940 m, 2960 m, 2980 m
III	1750 s, 1780 s $\nu(\text{C}=\text{O})$; 963 m, 1013 m, 1066 m, 1106 s, 1140 m, 1215 m, 1233 s, 1278 m, 1325 m, 1344 m, 1402 m, 1458 m, 1466 m, 1713 m, 2884 m, 2940 m, 2970 m
IX	1760 s, 1773 s $\nu(\text{C}=\text{O})$; 845 m, 1113 s, 1145 m, 1210 m, 1230 s, 1285 m, 1320 m, 1358 m, 1370 m, 1440 m, 1470 m, 2960 w, 2990 w

TABLE 5
 MASS SPECTRA OF THE COMPOUNDS (VII-IX) (MASS/RELATIVE INTENSITY, IONIC SPECIES)

Compound formula (mol. wt.)	Principal ionic species ^a
VII C ₇ H ₁₁ F ₃ O ₂ (184)	185/3 (M + 1) ⁺ ; 184/10 (M) ⁺ ; 164/23 (M - HF) ⁺ ; 149/15 (C ₆ H ₇ F ₂ O ₂) ⁺ ; 135/10 (C ₅ H ₅ F ₂ O ₂) ⁺ ; 134/100 (C ₅ H ₄ F ₂ O ₂) ⁺ ; 105/95 (C ₅ H ₇ F ₂) ⁺ ; 73/79; 59/89 (CH ₃ CO ₂) ⁺ ; 45/34; 43/25 (C ₃ H ₇) ⁺ ; 29/21 (C ₂ H ₅) ⁺
VIII C ₇ H ₁₁ F ₃ O ₂ (184)	185/2 (M + 1) ⁺ ; 184/53 (M) ⁺ ; 110/16 (C ₄ H ₅ F ₃) ⁺ ; 109/35 (C ₄ H ₄ F ₃) ⁺ ; 89/10; 76/35; 73/29, 71/42; 59/65 (COOCH ₃) ⁺ ; 55/47; 43/100 (C ₃ H ₇) ⁺ ; 41/51 (C ₃ H ₅) ⁺
IX C ₆ H ₉ F ₃ O ₂ (170)	171/0.08 (M + 1) ⁺ ; 155/0.17 (M - CH ₃) ⁺ ; 150/0.87 (M - HF) ⁺ ; 91/18 (C ₃ H ₄ FO ₂) ⁺ ; 79/29 (C ₃ H ₅ F ₂) ⁺ ; 60/10; 59/100 (COOCH ₃) ⁺ ; 31/6 (CH ₃ O) ⁺ ; 29/4 (C ₂ H ₅) ⁺

^a Assumed structures.

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