

REACTIONS OF METHYL TRIFLUOROACRYLATE WITH HYDROXY COMPOUNDS

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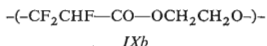
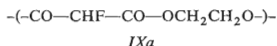
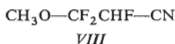
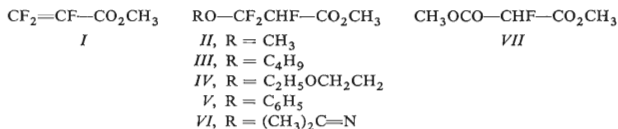
The main reaction of hydroxy compounds with methyl trifluoroacrylate (*I*) is the addition to the olefinic bond. The reactivity decreases in the following order: primary hydroxy compounds > sec-butyl alcohol > phenol > tert-butyl alcohol. The substantially greater relative rate of addition of alcohols to methyl trifluoroacrylate than to methyl acrylate is compared with quantum chemical calculations.

A characteristic property of the olefinic bond in acrylic acid derivatives is the ability to add nucleophilic reagents¹. Among these reactions the base-catalysed addition of alcohols to methyl acrylate has been studied²⁻⁶, for example. The nucleophilic addition is especially characteristic of the reaction of olefins of the type $\text{CF}_2=\text{CF}-\text{X}$; this property is not substantially affected by the substituent⁷⁻⁹ X. On the basis of the facts mentioned it may be assumed that the functional derivatives of trifluoroacrylic acid will also react very easily in the nucleophilic addition reactions. These inferences were already confirmed experimentally^{10,11} in the case of trifluoroacrylonitrile.

In this paper we directed our attention to the reactions of some hydroxy compounds as for example primary, secondary, and tertiary alcohols, phenol, and acetone oxime, with methyl trifluoroacrylate (*I*). Further we intended to compare the reactivity of trifluoroacrylate *I* with methyl acrylate (*X*).

The hydroxy compounds react with trifluoroacrylate *I* giving different results. Generally it may be said that the main reaction is the addition under formation of alkoxypropionates *II-VI*. At an elevated temperature and in an excess of the hydroxy compound, nucleophilic substitution of the fluorine atoms neighbouring the alkoxy group takes place as a subsequent reaction, under formation of fluoro-malonic acid derivative *VII*. Another side-reaction is the re-esterification of the original ester function. The addition of primary alcohols takes place most easily. For example, methanol or n-butanol are added in the absence of a catalyst (products *II* and *III*). The addition of primary alcohols in the presence of catalysts, as for example sodium alkoxide or anhydrous alkali fluoride (CsF) is very rapid, and accompanied by heat evolution. The disadvantage of alkoxides as catalysts consists in their reactivity with the addition products; if only a small amount of the catalysts is used it is consumed by this side-reaction and then the addition takes place uncatalysed

far more slowly (see the reactions with *n*-butanol). The catalysed addition of acetone oxime took place with a high yield (92%). *Sec*-butanol reacts substantially slower than *n*-butanol even in the presence of a catalyst, and it affords a series of products¹². *Tert*-butanol could be added even at elevated temperature in the presence of catalyst. Phenol also adds reluctantly and only at elevated temperatures in the presence of a catalyst (yield 29%).



When acrylate *I* is heated with ethylene glycol an intermolecular addition and re-esterification takes place in the second reaction step, under formation of a polymer. From the elemental analysis and the spectra it followed that a substantial part of the polymer units has the structure *IXa*, which was created by the transformation of the $-\text{CF}_2-$ group in the *IXb* units to the $\text{C}=\text{O}$ group.

For the checking of further data^{10,11} we carried out the reaction of methanol with trifluoroacrylonitrile in the presence of cesium fluoride. The reaction took place smoothly with complete conversion of the starting nitrile, and gave the addition product *VIII* in good yield (72%).

The structure of the main products of the reactions of hydroxy compounds with trifluoroacrylate *I* was determined on the basis of their NMR and IR spectra (Table I), and elemental analyses (Table II). In the infrared spectra the double maximum of the carbonyl group is remarkable. It is found in all 3-alkoxypropionates *II*–*VI*, fluoromalonate *VII*, and polymer *IX*. The double absorption maximum of the carbonyl was observed earlier in the spectra of trifluoroacrylates¹³ and fluorochloropropionates¹⁴, and it is also present in the spectra of other halogen esters¹⁵.

From the qualitative results the following sequence of the reactivity of hydroxy compounds with trifluoroacrylate *I* emerges: primary hydroxy derivatives > *sec*-butyl alcohol > phenol > *tert*-butyl alcohol. We tried to compare the reaction rate semiquantitatively in dependence on the structure of alcohols, represented by isomeric butyl alcohols. The course of the reactions is given in Fig. 1. During this non-catalysed reaction neither *tert*-butyl alcohol nor phenol reacted. We intended to compare the reactivity of trifluoroacrylate *I* and methyl acrylate (*X*) during a competi-

TABLE I
Identified Absorption Maxima (cm^{-1}) in the IR Spectra of Compounds II–VIII (tetrachloromethane, carbon disulfide)

Compound	$\nu(\text{C—F})$	$\nu(\text{C—O})$	$\delta(\text{CH}_3)$ as	$\nu(\text{C=O})$	$\nu(\text{CH}_3)$	$\nu(\text{C—H})$	Further maxima
II	1 078 s, 1 105 s 1 131 s, 1 155 ms	1 230 s 1 302 s	1 442 m 1 458 m	1 768 s 1 784 s	2 866 w 2 962 mw	3 009 w	—
III	1 068 s, 1 125 s	1 204 s 1 292 s	1 437 m	1 759 s 1 777 s	2 963 mw	3 007 w	1 015 ms
IV	1 071 s, 1 114 s	1 205 s 1 292 s	1 437 m	1 760 s 1 778 s	2 964 w 2 982 mw	3 012 w	1 016 m
V	1 088 s, 1 127 s	1 192 s 1 266 s	1 440 m	1 764 s 1 783 s	2 959 w	2 990 to 3 100 w(band)	753 m $\nu(\text{C—H})$ ar, 1 018 m; 1 494 s, 1 590 m $\nu(\text{C—C})$ ar
VI	1 106–1 118 s, 1 162 s	1 218 s 1 279 s	1 438 s	1 761 s 1 778 s	2 850 w 2 957 w	3 002 w	1 019 ms, 1 250 s, 1 293 s 1 318 s, 1 657 w $\nu(\text{C=N})$
VII	1 118 m	1 206 s	1 440 m	1 766 s 1 785 s	2 849 w 2 957 mw	3 005 w	1 022 s 1 291 s, 2 259 w $\nu(\text{C}\equiv\text{N})$
VIII	1 082 vs, 1 115 ms, 1 156 s	1 230 s	1 451 m	—	2 860 w 2 963 mw	3 007 w	1 025 m, 1 251 s 1 300 s, 1 349 s

tive reaction with methanol in an analogous manner. Because of the very differing reaction rate of the two acrylates these substances may be evaluated only qualita-

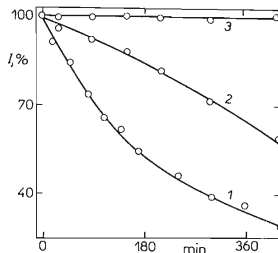


FIG. 1

Concentration Decrease of Methyl Trifluoroacrylate (*I*) in Time during its Reaction with Hydroxy Compounds

1 Reaction with *n*-butanol; 2 reaction with sec-butyl alcohol; 3 reaction with tert-butyl alcohol. Average of two measurements.

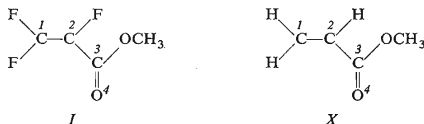
TABLE II
Elemental Analyses of Compounds II—VIII

Compound	Formula (m. w.)	Calculated/Found		
		% C	% H	% F
II	C ₅ H ₇ F ₃ O ₃ (172.1)	34.87	4.10	33.14
		35.16	4.20	32.78
III	C ₈ H ₁₃ F ₃ O ₃ (214.1)	44.85	6.08	26.65
		44.57	5.65	26.62
IV	C ₈ H ₁₃ F ₃ O ₄ (231.1)	41.58	5.67	24.66
		40.89	5.40	23.96
V	C ₁₀ H ₉ F ₃ O ₃ (234.1)	51.27	3.86	24.32
		53.69	3.93	23.89
VI ^a	C ₇ H ₁₀ F ₃ NO ₃ (218.2)	40.49	4.61	26.27
		40.08	4.93	26.69
VII	C ₅ H ₇ FO ₄ (150.1)	40.04	4.69	12.66
		40.42	4.83	12.20
VIII ^b	C ₄ H ₄ F ₃ NO (139.1)	34.53	2.91	40.99
		33.79	2.84	39.48

^aCalculated: 6.52% N; found: 6.34% N; ^bcalculated: 10.07% N; found: 9.62% N.

tively. During the competitive reaction in the presence of a catalyst (sodium methylate) trifluoroacrylate reacted very rapidly, the catalyst was consumed by the reaction with the product *II*, and methyl acrylate did not undergo a measurable conversion. In a non-catalysed reaction only trifluoroacrylate reacted; methyl acrylate reacted independently only in the presence of a catalyst^{2,3}. Hence, we may state that the nucleophilic reactivities of acrylates *I* and *X* differ by one order of magnitude in favour of trifluoroacrylate *I*.

A high nucleophilic reactivity of the olefinic bond in trifluoroacrylate *I*, in comparison with methyl acrylate, may be predicted by quantum chemical calculations. For nucleophilic reactions the total electron densities (charges) were found suitable as qualitative criteria of the reactivity, which from this point of view were checked in a series of fluorinated benzenes¹⁶ and fluorinated methanes¹². Total electron densities or total charges τ were obtained by the summation of the π -electron charges computed by the simple Hückel method of molecular orbitals¹⁷ (HMO), and σ -electron charges which were computed by the Del Re¹⁸ method based on bicentric localized orbitals.



When comparing the total charges π on the central No 1, it is evident that the electron gap on the carbon atom of the fluorinated acrylate is approximately ten times larger and it also predicts similarly large differences in nucleophilic reactivity. A negligible difference may be observed in total charges on the carbon of the carbonyl group of both substances, from which it follows that in both acrylates we may expect approximately the same reesterification rate, which is in agreement with the observations¹⁹. Finally, it may be said that the total charges τ are satisfactory as a criterion for qualitative evaluation of the nucleophilic reactivity of methyl trifluoroacrylate and methyl acrylate.

TABLE III
 π -, σ - and Total Charges τ (in units 10^{-3} of the electron charge) in Compounds *I* and *X*

Compound	<i>I</i>				<i>X</i>			
	1	2	3	4	1	2	3	4
π	+202	-110	+319	-663	+166	-34	+343	-603
σ	+376	+227	+182	-60	-109	-39	+168	-64
τ	+578	+117	+501	-693	+57	-73	+511	-667

EXPERIMENTAL

Temperature data were not corrected. Gas chromatography was carried out on a Chrom 3 (Laboratory apparatus, Prague; TC and FI detector, column diameter 0.6 cm, Celite 545 as the carrier of the stationary phase 20% poly(propylene sebacate)). The IR spectra were measured on a Perkin-Elmer 325 (Bodenseewerk) apparatus, the NMR spectra on a BSS 477 (60 Mc/s; Tesla Brno; s singlet, d doublet, t triplet, q quartet, m multiplet, dt doublet of triplets, qs quasi; chemical shifts τ , coupling constants Hz).

Calculations: HMO models of substances *I* and *X* were computed on a digital computer NE 803 B using a program elaborated by Dr V. Kvasnička (Computation Center of this Institute), using the following computation parameters¹⁷: h_F 3.0; k_{CF} 0.7; $k_{C=C}$ 1.0; $k_{C=O}$ 1.0; h_O 1.7; k_{C-O} 0.8. σ -Electron charges were calculated by the Del Re method using parameters as in¹⁸.

Chemicals: Methyl trifluoroacrylate and trifluoroacrylonitrile were prepared according to the procedures^{13,20,21} described earlier. Methyl 3-methoxypropionate was prepared by a base-catalysed addition of methanol to methyl acrylate^{2,3}.

Measurement of the Reaction Rate of Hydroxy Compounds with Trifluoroacrylate *I*

A mixture of hydroxy compound (0.015 mol), acrylate *I* (2.10 g; 15 mmol), and benzene (0.585 g; 7.5 mmol; internal standard) was shaken at 85°C and samples were withdrawn periodically and analysed gas chromatographically (90–180°C, nitrogen, ionisation detection). The "zero sample" was withdrawn at 20°C immediately after the mixing of the reaction mixture. Molar proportions of single components of the mixture were calculated from the areas of corresponding peaks and calibration graphs (Fig. 1).

Methyl 3-Methoxy-2,3,3-trifluoropropionate (*II*) and Methyl Fluoromalonate (*VII*)

A. A mixture of acrylate *I* (4.05 g; 28.9 mmol) and methanol (3.95 g; 124 mmol) was stirred for 5 h at 25°C and for 3 h under reflux. During distillation 3 fractions were collected in the 65–95°C/14 Torr range. The yield, calculated from gas chromatography was: 35.4% of compound *II* and 37.1% of compound *VII*. Redistillation gave compound *II* of b.p. 70–71°C/14 Torr, purity 97%. The malonate *VII* was isolated by preparative gas chromatography in a 98% purity.
B. To a solution of sodium (0.53 g; 23.1 mmol) in methanol (50 ml; 1.24 mol) acrylate *I* (4.21 g; 29.3 mmol) was added at 30–35°C over 15 minutes. The mixture was stirred for 0.5 h and mixed with 1,1,2-trifluoroethane (50 ml), then washed with ether and dried over magnesium sulfate. The calculated yield of compound *II* was 69%, of compound *VII* 18%.
C. A mixture of acrylate *I* (2.1 g; 15 mmol), methanol (0.96 g; 30 mmol), and dioxane (1.32 g; 15 mmol; internal standard) was shaken at 65°C and the reaction course controlled by gas chromatography. After 7 h the conversion of acrylate *I* was 81%, the yield of compound *II* was 68%. The NMR spectrum of compound *II* (deuteriochloroform): dt 5.16, $^2J_{HF}$ = 48.2, $^3J_{HF}$ = 5.7 (–CF₂CHF–); s 6.17 (–CH₃O–C=O–); s 6.36 (CH₃O–CF₂); Compound *VII*: d 4.81, $^2J_{HF}$ = 46.9 (–CHF–); s 6.18 (CH₃O–C=O).

Methyl 3-Butoxy-2,3,3-trifluoropropionate (*III*)

Acrylate *I* (4.01 g; 28.8 mmol) was added to a solution of sodium (0.062 g; 2.7 mmol) in *n*-butanol (4.12 g; 57.9 mmol) at 22°C over 0.5 h and the mixture was stirred for 12 h and worked up as compound *II* (procedure *B*). During distillation fraction 46–47°C/0.3 Torr was collected (1.73 g), containing 95% of compound *III*, and fraction 47–71°C/0.3 Torr (1.32 g), containing 45% of higher boiling substances which were not isolated. The calculated yield of substance *III* made

2.19 g (35.2%). NMR spectrum: dt 5.03, $^2J_{\text{HF}} = 46.8$, $^3J_{\text{HF}} = 5.4$ ($-\text{CF}_2\text{CHF}-$); m 5.92–6.22, $^3J_{\text{HH}} = 6.3$ ($-\text{CH}_2\text{O}-$); m 8.08–8.87, ($-\text{CH}_2\text{CH}_2-\text{CH}_3$); m 8.87–9.33 ($\text{CH}_3-\text{CH}_2\text{CH}_2-$).

Methyl 3-(2-Ethoxy-ethoxy)-2,3,3-trifluoropropionate (IV)

Acrylate *I* (1.32 g; 9.42 mmol) was added at 15–20°C over 15 min to a mixture of 2-ethoxyethanol (0.63 g; 8.29 mmol), anhydrous cesium fluoride (approx. 0.05 g), and ether (5 ml), and the mixture was stirred at 20°C for 3 h. After dilution with 10 ml of ether, washing with water (20 ml), and drying over magnesium sulfate, it was distilled and the fraction 57–59°C/0.3 Torr collected. Yield 0.99 g (55.2%) of 91% purity. NMR spectrum: dt 4.98, $^2J_{\text{HF}} = 47.6$, $^3J_{\text{HF}} = 5.9$ ($-\text{CF}_2\text{CHF}-$); q 5.95, $^3J_{\text{HH}} = 5.0$ ($\text{CH}_3-\text{CH}_2-\text{O}-$); s 6.13 ($\text{CH}_3\text{O}-\text{C}=\text{O}$); m 6.38 (max.) ($-\text{OCH}_2\text{CH}_2\text{O}-$); t 8.80, $^3J_{\text{HH}} = 6.6$ ($\text{CH}_3-\text{CH}_2\text{O}-$).

Methyl 3-Phenoxy-2,3,3-trifluoropropionate (V)

A mixture of acrylate *I* (3.31 g; 23.6 mmol) and phenol (1.52 g; 16.1 mmol) was heated at 70°C for 5 h. However, chromatographic analysis did not demonstrate the presence of a product. Sodium was then added (approx. 50 mg) and the mixture was stirred at 20–30°C for another 5 h. During distillation the fraction 43–45°C/0.1 Torr was collected (0.34 g), containing 92% of compound *V*. The total calculated yield of compound *V* was 28.6%. NMR spectrum: a band at 2.50–2.95 ($\text{C}_6\text{H}_5\text{O}-$); dt 4.83, $^2J_{\text{HF}} = 46.4$, $^3J_{\text{HF}} = 5.7$ ($-\text{CF}_2\text{CHF}-$); s 6.11 ($\text{CH}_3-\text{O}-\text{C}=\text{O}$).

Methyl 3-Acetonoximo-2,3,3-trifluoropropionate (VI)

Trifluoroacrylate *I* (4.42 g; 31.6 mmol) was added over 20 min at 30°C to a mixture of acetone oxime (1.03 g; 14.1 mmol), 1,2-dimethoxyethane (20 ml), and dissolved sodium (approx. 30 mg), and stirred at 25–30°C for 2 h. The mixture was worked up as substance *II* (under *B*). Distillation gave product *VI*, b.p. 61–63°C/0.2 Torr (1.94 g; purity 98%). The total calculated yield of compound *VI* was 92.3%. NMR spectrum: dt 4.65, $^2J_{\text{HF}} = 46.5$, $^3J_{\text{HF}} = 6.6$ ($-\text{CF}_2\text{CHF}-$); s 6.05 ($\text{CH}_3\text{O}-\text{C}=\text{O}$); s 7.94 ($(\text{CH}_3)_2\text{C}=\text{N}-$).

3-Methoxy-2,3,3-trifluoropropionitrile (VIII)

A glass ampoule was filled with methanol (6.03 g; 0.208 mol), caesium fluoride (0.03 g; 0.02 mmol), and finally trifluoroacrylonitrile (1.24 g; 11.6 mmol) at dry ice temperature. The cooled mixture was allowed to warm up slowly in a Dewar bottle (12 h). After working up at room temperature (compound *II*, procedure *B*) the product *VIII* was collected at 105–106°C (0.76 g; purity 92%). The total calculated yield of compound *VIII* was 72%, conversion of the nitrile was complete. NMR spectrum: dt 4.85, $^2J_{\text{HF}} = 46.4$, $^3J_{\text{HF}} = 5.1$ ($-\text{CF}_2\text{CHF}-$); s 6.33 ($\text{CH}_3\text{O}-\text{CF}_2-$).

Reaction of Trifluoroacrylate *I* with Ethylene Glycol

A mixture of acrylate *I* (5.02 g; 35.8 mmol) and ethylene glycol (0.74 g; 12 mmol) was refluxed for 5 h. After addition of 5 ml of ether the refluxing was continued for another one hour. After evaporation of the heads (bath 130°C/0.5 Torr) a yellow polymer was obtained (1.91 g). IR spectrum (chloroform): 1025 m, 1126 s $\nu(\text{C}-\text{F})$; 1240 ms and 1296 s $\nu(\text{C}-\text{O})$; 1765–1790 (a double band) $\nu(\text{C}=\text{O})$, 3032 mw $\nu(\text{C}-\text{H})$. NMR spectrum: qsd 4.66, ($^2J_{\text{HF}} = 47.4$), ($-\text{CO}-\text{CHF}-\text{CO}-$)_n–; qss 5.48; qss 6.13, $-\text{OCH}_2\text{CH}_2-\text{OCO}-$)_n–. For *IXa* ($\text{C}_5\text{H}_5\text{FO}_4$)_n

$(148.4)_n$ calculated: 40.63% C, 3.39% H, 12.73% F; for IXb $(C_5H_5F_3O_4)_n$ $(186.4)_n$ calculated: 32.38% C, 2.70% H, 30.54% F; found: 40.86% C, 4.20% H, 18.78% F.

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