

THE REACTION OF GRIGNARD REAGENTS WITH METHYL 2,3,3-TRIFLUOROCARBOXYLATES*

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Reaction of methyl- or ethylmagnesium halide with methyl 2,3,3-trifluoro-3(2-tetrahydrofuryl)propionate (*I*) or with methyl 2,3,3-trifluoro-4-ethoxypentanoate (*II*) afforded at 35°C the corresponding alcohol (*VII—X*) whereas at -35°C the reaction gave a mixture of the corresponding ketone (*III—VI*) and tertiary alcohol. The reaction of isopropylmagnesium bromide with the ester *I* afforded in addition to the tertiary alcohol *XI* also the secondary alcohol *XIII* which arose by reduction. Treatment of the tertiary alcohols *VII*, *IX* and *X* with phosphorus pentoxide afforded the olefins *XVI—XVIII*. The reaction of 3,4,4-trifluoro-2-methyl-4(2-tetrahydrofuryl)-2-butanol (*VII*) with thionyl chloride gave 1,1,2-trifluoro-3-chloro-3-methyl-1(2-tetrahydrofuryl)butane (*XIX*) whereas the analogous reaction of 3,4,4-trifluoro-2-methyl-5-ethoxy-2-hexanol (*IX*) led to 3,4,4-trifluoro-2-methyl-5-ethoxy-1-hexene (*XVII*).

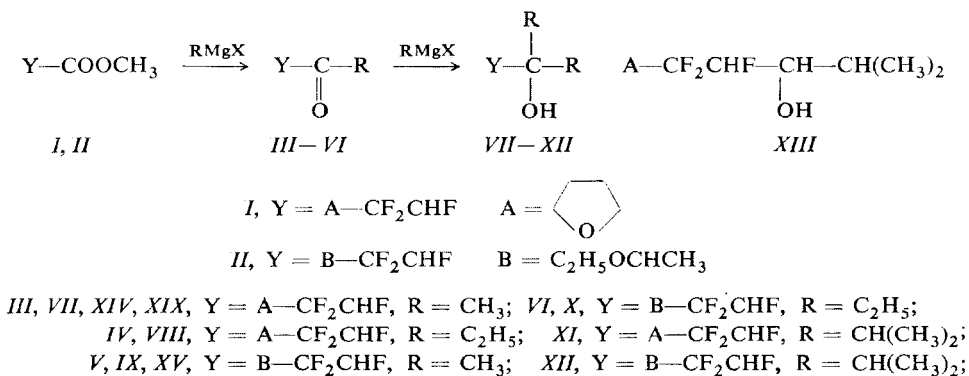
In order to synthesize potentially biologically active fluoroalcohols, we made use of the reaction of substituted methyl 2,3,3-trifluorocarboxylates, namely methyl 2,3,3-trifluoro-3(2-tetrahydrofuryl)propionate (*I*) and methyl 2,3,3-trifluoro-4-ethoxypentanoate (*II*), with Grignard reagents. We prepared both the esters previously¹ by photochemical addition of tetrahydrofuran or diethyl ether to methyl trifluoroacrylate.

In the reaction of Grignard reagents with derivatives of fluorinated carboxylic acids^{2,3}, the "normal" addition reaction of the ester with two molecules of the reagent, leading to a tertiary alcohol, is accompanied to enhanced extent by reduction, leading to a secondary alcohol. The secondary alcohol is formed by reduction of the intermediate ketone^{4,5}, and the relative proportion of both products depends on the structure of the reagent. In the reaction with esters of perfluorinated carboxylic acids, already ethylmagnesium iodide exhibits reductive properties⁴, which depend on the character of the carbon chain of the perfluorinated carboxylic acid. The reductive ability of isopropylmagnesium halides is well known³.

We have chosen such conditions of the reaction of Grignard reagents with the esters *I* and *II* as to obtain, with complete conversion, the tertiary alcohols as the sole reaction product. The reactions were therefore carried out using a great excess

* Part IV in the series Haloacrylic Acids; Part III: This Journal 39, 1336 (1974); Part II, ref. 1; Part I; This Journal 38, 66 (1973).

of the reagent in the presence of magnesium bromide³. The yields of the isolated tertiary alcohols ranged between 76–97%. Reaction of the ester *I* with methylmagnesium iodide and ethylmagnesium bromide afforded 3,4,4-trifluoro-2-methyl-4(2-tetrahydrofuryl)-2-butanol (*VII*) and 1,1,2-trifluoro-3-ethyl-1(2-tetrahydrofuryl)-3-pentanol (*VIII*), respectively. The ester *II* afforded with the same reagents 3,4,4-trifluoro-2-methyl-5-ethoxy-2-hexanol (*IX*) and 4,5,5-trifluoro-3-ethyl-6-ethoxy-3-heptanol (*X*), respectively.

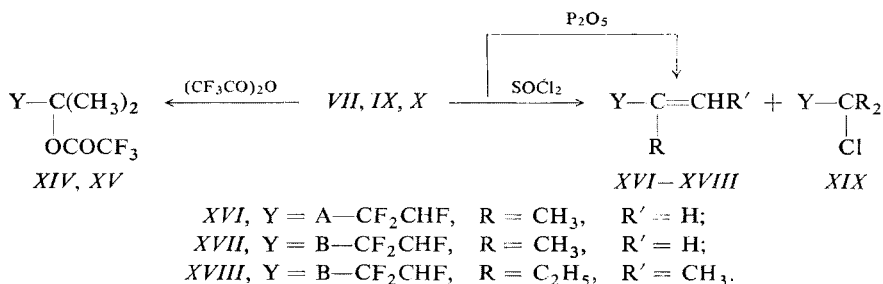


We tried to stop the Grignard reaction at the ketone stage by lowering the reaction temperature and by changing the ratio of the reaction components. Even at low temperatures, however, the tertiary alcohol arised besides the ketone, and at temperatures above 0°C the alcohol is practically the sole product. The outcome of the reaction of the esters *I* and *II*, together with the reaction conditions, is given in Table I. The ketones were identified directly in the mixture by mass spectrometry (Table II). In the reaction products of the ester *I* with methyl- and ethylmagnesium halide we identified 3,4,4-trifluoro-4(2-tetrahydrofuryl)-2-butanone (*III*) which we isolated by preparative gas-liquid chromatography and 1,1,2-trifluoro-1(2-tetrahydrofuryl)-3-pentanone (*IV*), respectively; the reaction of the ester *II* with the same reagents afforded 3,4,4-trifluoro-5-ethoxy-2-hexanone (*V*) and 4,5,5-trifluoro-6-ethoxy-3-heptanone (*VI*).

Reaction with isopropylmagnesium bromide proceeded by a different course: The ester *I* afforded a mixture of four compounds (complete conversion), containing 1,1,2-trifluoro-4-methyl-3-isopropyl-1(2-tetrahydrofuryl)-3-pentanol (*XI*; 26% rel.) and 1,1,2-trifluoro-4-methyl-1(2-tetrahydrofuryl)-3-pentanol (*XIII*; 16% rel.). Similarly, the reaction of *II* resulted in a mixture of three compounds (complete conversion), which contained 4,5,5-trifluoro-2-methyl-6-ethoxy-3-isopropyl-3-heptanol (*XII*; 33% rel.), whereas a secondary alcohol, analogous to the compound *XIII*, was not formed. As evidenced by mass spectrometry, neither of the reaction mixtures contained a ketone of the type *III* or *IV*. The compounds *XI*–*XIII* were identified by their

mass spectra in the product mixtures and therefore the given structure are to be taken as probable.

For the sake of analysis, we transformed the tertiary alcohols *VII* and *IX* by treatment with trifluoroacetic anhydride into the corresponding trifluoroacetates *XIV* and *XV*. For the same reason we dehydrated⁶ the tertiary alcohols *VII*, *IX* and *X* with phosphorus pentoxide to olefins, *i.e.* 3,4,4-trifluoro-2-methyl-4(2-tetrahydrofuryl)-2-butene (*XVI*), 3,4,4-trifluoro-2-methyl-5-ethoxy-1-hexene (*XVII*) and 4,5,5-trifluoro-3-ethyl-6-ethoxy-2-hexene (*XVIII*), respectively. In order to prepare chloro derivatives, we investigated the reaction of some tertiary alcohols with thionyl chloride. The tetrahydrofuryl derivative *VII* afforded 1,2,2-trifluoro-3-chloro-3-methyl-1(2-tetrahydrofuryl)butane (*XIX*), together with the starting compound. On the other hand, the hydroxy derivative *IX* was completely dehydrated to the olefin *XVII*. Analogous dehydration effects of thionyl chloride were observed⁷ already earlier.



The molecules of compounds *I–XII* and *XIV–XIX* contain two asymmetric carbon atoms. Gas liquid chromatography of the tertiary alcohols *VII–X* and of the derivatives *XIV–XVIII* shows the presence of two peaks of diastereoisomers. This isomerism was confirmed by the identity of mass spectra of the two chromatographically separated compounds. Similar separation of diastereoisomers by gas-liquid

TABLE I

Conditions and Results of the Reaction of Esters *I* and *II* with Grignard Reagents (reaction time 1 hour, complete conversion)

No	Reactants	Mol. ratio	Products	Yields of the products, rel. %		
				-35°C	0°C	35°C
1	<i>I</i> /CH ₃ MgI	1 : 4	<i>III</i> / <i>VII</i>	60/40	93.5/6.5	99.5/0.5
2	<i>I</i> /CH ₃ MgI	1 : 2	<i>III</i> / <i>VII</i>	42/58	—	—
3	<i>I</i> /C ₂ H ₅ MgI	1 : 2	<i>IV</i> / <i>VIII</i>	32/68	—	—
4	<i>II</i> /CH ₃ MgI	1 : 4	<i>V</i> / <i>X</i>	92/8	96.5/3.5	99.8/0.2

TABLE II
Mass Spectra of the Compounds III—XIX (ionic species, mass/relative intensity)

Compound Mol.wt.	Principal ionic species ^a
III 196·0	M^+ , 196/2·1, $(M - HF)^+$, 176/2·8, 148/1·4, 133/14, 120/16, 91/8·3, 71/100, $(CH_3CO)^+$, 43/97
IV 210·2	M^+ , 210/1·4, $(M - HF)^+$, 190/12, 162/4·1, 133/25, 120/9·6, 119/6·8, 105/5·5, 91/9·6, 71/100, $(C_2H_5CO)^+$, 57/84, 43/37, 42/26
V 198·2	$(M - CH_3CO)^+$, 155/1·9, $(M - C_2H_5O)^+$, 153/1·9, 135/2·2, 134/2·2, 123/1·9, 122/1·9 $(C_2H_5O - CHCH_3)^+$, 73/26, $(C_2H_5O)^+$, 45/67, $(CH_3CO)^+$, 43/100
VI 212·2	$(M - HF)^+$, 192/25, 173/8·2, 147/23, 145/34, 99/15, $(C_2H_5OCHCH_3)^+$, 73/15, $(C_2H_5CO)^+$, 57/97 $(C_2H_5O)^+$, 45/29, $(CH_3CO)^+$, 43/100
VII 21·2	$(M + 1)^+$, 213/1·0, $(M - CH_3)^+$, 197/3·9, 177/2·9; 157/3·9; 134/9·8; 71/100, $((CH_3)_2COH)^+$, 59/56; 43/80; 41/23
VIII 240·2	M^+ , 240/0·15; $(M - C_2H_5)^+$, 211/11; 191/4·7; 178/3·1; 170/4·7; 134/5·5; $((C_2H_5)_2 \cdot COH)^+$, 87/44; 71/100; 57/41; 45/22; 43/34; 41/20
IX 214·0	$(M + 1)^+$, 215/0·3; $(M - CH_3)^+$, 199/3·7; 177/1·0; 153/30; 138/7·7; 121/10·3; $(C_2H_5OCHCH_3)^+$, 73/100; $((CH_3)_2COH)^+$, 59/93; $(C_2H_5O)^+$, 45/17; 43/15
X 242·2	$(M - C_2H_5)^+$, 213/17; 167/78; 136/4·6; 121/6·4; 99/5·5; $((C_2H_5)_2COH)^+$, 87/72; 77/11; $(C_2H_5OCH - CH_3)^+$, 73/100; 57/23; $(C_2H_5O)^+$, 45/23; 43/18; 41/16
XI 268·3	$(M - HF_2)^+$, 229/1·1; $(M - C_3H_7 - HF)^+$, 205/24; 187/20; 185/16; 141/5·6; 139/4·5; 71/33; 57/9; 55/9; 43/100; 41/27
XII	$(M - C_3H_7 - HF)^+$, 207/13; 187/6; 161/9; 139/4; 121/75; 113/6; 91/9; $(C_2H_5 \cdot OCHCH_3)^+$, 73/70; 71/15; 45/67; 43/100
XIII 226·2	$(M)^+$, 226/0·6; $(M - HF)^+$, 206/0·9; $(M - CH(CH_3)_2)^+$, 183/5; 163/1·9; 143/2·5; 134/12; $((CH_3)_2CHOH)^+$, 73/13; 71/100; 57/4·4; 55/8·8; 43/52; 42/26; 26/16
XIV 308·1	$(M - CF_3COO)^+$, 195/1·7; 175/6·1; $(CF_3COOC(CH_3)_2)^+$, 155/11; 91/3·9; 89/3·9; 77/5; 71/100; 43/90
XV 310·1	$(M - CF_3COO)^+$, 197/1; 177/5·4; $(CF_3COOC(CH_3)_2)^+$, 155/17; 131/5·9; 129/4·8; 109/4·8; 91/3·8; $(C_2H_5OCHCH_3)^+$, 73/100; $(CF_3)^+$, 69/37; $(C_2H_5O)^+$, 45/89
XVI 194·1	M^+ , 194/0·35; $(M - CH_3)^+$, 179/3·5; $(M - HF)^+$, 174/3·1; 120/6·9; 104/3·5; 89/6·9; 71/100; 43/41
XVII 196·1	$(M - CH_3)^+$, 181/0·7; $(M - HF)^+$, 176/5; 161/5; 153/11; 135/23; 122/14; 104/32; 91/57; 77/47; $(C_2H_5O - CHCH_3)^+$, 73/100; 51/29; $(C_2H_5O)^+$, 45/95
XVIII 224·3	M^+ , 224/0·2; $(M - HF)^+$, 204/2·5; 189/1·4; 149/2·3; 132/1·8; 131/1·4; 101/6·1; 91·7·3; 77/6·8; $(C_2H_5OCHCH_3)^+$, 73/82; $(C_2H_5O)^+$, 45/100; 43/16
XIX 230·5	M^+ , 230/0·5; $(M - CH_3)^+$, 215/5·3; $(M - Cl)^+$, 195/2·1; 174/0·53; $(M - (CH_3)_2 \cdot CCl)^+$, 153/3·2; 110/7·5; 104/8·5; 90/4·3; 88/5·3; $((CH_3)_2CCl)^+$, 77/7·5; 71/100; 43/51

^a Assumed structures.

chromatography was observed^{8,9} also in the case of other fluorinated aliphatic compounds. The NMR (Table III) and IR spectra (Table IV) of compounds VII–X and XIV–XVII refer to the diastereoisomeric mixtures. The mass spectra of compounds, derived from the ester I (III, IV, VII, VIII, XII, XIV, XVI and XIX) are characterized by the main ionic species m/e 71, corresponding to tetrahydrofuryl ion. Products, derived from the ester II (V, VI, IX, X, XI, XVII and XVIII) are characterized by an intensive, or main, ionic species m/e 73, corresponding probably to the ion $(\text{CH}_3\text{CH}_2\text{OCHCH}_3)^{(\cdot)}$.

EXPERIMENTAL

The temperature data are not corrected. Gas-liquid chromatography was performed on a Chrom 3 (Laboratorní přístroje, Prague) instrument (flame-ionisation detector, analytical columns diameter 0.6 cm, preparative column diameter 1 cm, length 500 cm, carrier gas nitrogen, support Chromaton N-AW-DMCS, Lachema, Brno). IR spectral measurements were performed on a Per-

TABLE III

NMR Spectra of Compounds III, VII–X, XIV–XVII (chemical shift δ , number of protons; s singlet, d doublet, t triplet, qt quadruplet, m multiplet, q quasi; interaction constants J in Hz)

Compound	Charakter of the peaks
III	dm 4.99 (1), —CHF—; dm 4.32 (1), —OCH—CF ₂ ; qt 3.85 (2), ³ J _{HH} 6.1, —OCH ₂ —; s 3.36 and s 3.33 (3), —CH ₃ ; m 2.65–3.25 (4), —CH ₂ CH ₂ —
VII ^a	m 4.04–4.90 (2), —CHF— and —OCH—CF ₂ ; m 3.77–4.03 (2), —OCH ₂ —; d 3.29 (1), —OH; m 2.80–3.25 (4), —CH ₂ CH ₂ —; qs 1.35 (3), CH ₃
VIII ^a	m 4.04–5.06 (2), —CHF— and —OCH—CF ₂ ; m 3.74–6.02 (2), —OCH ₂ —; m 1.86–2.20 (4), —CH ₂ CH ₂ —; m 1.65 (4), CH ₂ —; m 0.74–1.06 (6), —CH ₃
IX ^a	m 4.10–4.96 (1), —CHF—; m 3.39–3.98 (3), —OCH— and —OCH ₂ —; s 6.96 (1), —OH; m 1.15–1.53 (12), —OCH ₃
X ^a	m 4.24–5.08 (1), —CHF—; m 3.40–3.98 (3), —OCH—CF ₂ and —OCH ₂ —; ds 2.32 and 3.00 (1), OH; m 1.50–1.86 (4), —CH ₂ C—CH ₂ —; m 1.06–1.40 (6), —CH ₃ ; qt 0.92 (6), ³ J _{HH} 7.1, C((CH ₂)CH ₃) ₂
XIV ^a	m 4.76–5.56 (1), —CHF—; m 3.98–4.49 (1), —CHCF ₂ —; m 3.68–3.98 (2) OCH ₂ ; m 1.78–2.20 (4), —CH ₂ CH ₂ —; qs 9.28 (6), —CH ₃
XV ^a	m 4.80–5.62 (1), —CHF—; m 3.36–3.99 (3), —OCHCF ₂ and OCH ₂ %; qs 1.73 (6), —C(CH ₃) ₂ ; m 1.20–1.42 (6), CH ₃
XVI ^a	m 4.68–5.48 (1), —CHF—; m 5.02–5.26 (2), =CH ₂ ; m 3.98–4.52 (1), OCH—CF ₂ ; m 3.64–3.98 (2), —OCH ₂ —; m 1.86–2.26 (4), —CH ₂ CH ₂ —; qs 1.83 (3), —CH ₃
XVII ^a	dm 5.17 (1), —CHF—; s 5.19 (2), =CH ₂ ; m 3.28–4.15 (3), —OCH and —OCH ₂ ; s 1.86 (3), —C—CH ₃ ; m 1.04–1.38 (6), —CH ₃

^a Proved mixture of diastereoisomers.

kin-Elmer 325 (Bodenseewerk) spectrometer, NMR spectra were taken in deuteriochloroform on a Varian XL-100-15 (Palo Alto) instrument. Mass spectra were measured on Gas Chromatograph-Mass Spectrometer LKB 9000, Stockholm (one focus, electron energy 70 eV, chromatographic inlet: polyethyleneglycol adipate on Chromaton N-AW, 250 cm glass column of diameter 0.23 cm, carrier gas helium, 10 ml/min).

Material

Trifluoroacetic anhydride was prepared¹⁰ by heating trifluoroacetic acid with phosphorus pentoxide. Magnesium bromide was prepared¹¹ by reaction of bromine with magnesium in diethyl ether. The preparation of methyl 2,3,3-trifluoro-3-(2-tetrahydrofuryl)propionate (*I*) and methyl 2,3,3-trifluoro-4-ethoxypentanoate (*II*) is described in the previous paper¹.

Reaction of Grignard Reagents with Esters *I* and *II*

A) A solution of the ester *I* or *II* (10 mmol) in diethyl ether (20 ml) was added under nitrogen during 15 minutes at 35°C to a stirred mixture of diethyl ether (20 ml), magnesium bromide

TABLE IV

Absorption Maxima (cm^{-1}) in the Infrared Spectra of Compounds *III*, *VII*–*X*, *XIV*–*XVII* in Tetrachloromethane

Compound	Absorption maxima
<i>III</i>	845 m, 934 m, 1085 vs, 1291 mw, 1353 m, 1718 s $\nu(\text{C}=\text{O})$, 2880 m, 2925 m, 2955 m, 2982 m
<i>VII</i> ^a	935 m, 970 m, 1042 s(sh), 1080 s, 1126 m, 1155 m, 1180 m, 1225 m, 1373 m, 1383 m, 2875 ms, 2980 ms, 3470 m $\nu(\text{O}-\text{N})$ assoc.; 3610 w a 3625 w (sh) $\nu(\text{O}-\text{H})$
<i>VIII</i> ^a	891 mw, 935 ms, 1025 s (sh), 1050 s, 1075 s, 1125 m, 1148 m, 1165 m, 1223 m, 1240 m, 1385 m, 1460 ms, 2880 s, 2940 s, 2964 s, 3470 m $\nu(\text{O}-\text{H})$ assoc.; 3609 w and 3623 w $\nu(\text{O}-\text{H})$
<i>IX</i> ^a	823 m, 830 m, 854 m, 926 m, 964 m, 1006 s, 1052 s, 1113 s, 1176 s, 1226 m, 1329 m, 1350 m, 1378 m, 1400 m, 1458 m, 2878 m, 2895 m, 2942 s, 2978 s, 3460 m $\nu(\text{O}-\text{H})$ assoc.; 3610 m, 3625 w $\nu(\text{O}-\text{H})$
<i>X</i> ^a	826 m, 853 m, 936 m, 967 m, 1003 s, 1050 s, 1070 s, 1112 s, 1227 m, 1329 m, 1378 m, 1403 m, 1460 m, 2882 m, 2940 s, 2978 s, 3458 m $\nu(\text{O}-\text{H})$ assoc.; 3607 w and 3614 w $\nu(\text{O}-\text{H})$
<i>XIV</i> ^a	940 mw, 1045 m, 1083 s, 1128 s, 1170 s, 1222 s, 1365 m, 1785 x $\nu(\text{C}=\text{O})$, 2877 w, 2955 w, 2985 w
<i>XV</i> ^a	1009 mw, 1071 m, 1132 s, 1225 s, 1367 m, 1379 m (sh), 1783 s $\nu(\text{C}=\text{O})$, 2980 mw
<i>XVI</i> ^a	892 m, 918 s, 938 m, 974 m, 1011 s, 1035 s, 1082 s, 1177 m, 1201 m, 1224 m, 1379 mw, 1464 s, 1651 w $\nu(\text{C}=\text{C})$, 2874 m, 2925 m, 2979 m, 3084 w
<i>XVII</i> ^a	855 m, 915 s, 937 m, 970 m, 1006 s, 1070 s, 1120 vs, 1200 m, 1225 m, 1329 m, 1379 m, 1404 mw, 1455 m, 1651 w $\nu(\text{C}=\text{C})$, 2897 m, 2923 m, 2941 m, 2990 s, 3084 w

^a Proved mixture of diastereoisomers.

TABLE V
Elemental Analyses and Boiling Points of the Isolated Products

Compound	Formula (mol.wt.)	Calculated/Found			B.p. °C/Torr	Purity % rel.
		% C	% H	% F		
<i>III</i>	C ₈ H ₁₁ F ₃ O ₂ (196.0)	—	—	29.06	—	98
		—	—	29.03		
<i>VII^a</i>	C ₉ H ₁₅ F ₃ O ₂ (212.0)	50.97	7.07	26.86	111—113/14	96
		51.95	7.20	26.70		
<i>VIII^a</i>	C ₁₁ H ₁₉ F ₃ O ₂ (240.2)	55.03	7.91	23.73	123—125/11	90
		57.26	8.05	21.82		
<i>IX^a</i>	C ₉ H ₁₇ F ₃ O ₂ (214.0)	50.49	7.90	26.61	78—80/11	99
		50.85	8.09	26.56		
<i>X^a</i>	C ₁₁ H ₂₁ F ₃ O ₂ (242.2)	54.54	8.73	23.51	96—100/11	97
		55.91	8.98	21.63		
<i>XIV^a</i>	C ₁₁ H ₁₄ F ₆ O ₃ (308.1)	42.87	4.56	37.01	92—95/12	95
		44.21	4.71	37.10		
<i>XV^a</i>	C ₁₁ H ₁₆ F ₆ O ₃ (310.1)	42.57	5.16	36.77	60—62/15	97
		43.14	5.12	36.87		
<i>XVI^a</i>	C ₉ H ₁₃ F ₃ O (194.1)	55.69	6.69	29.36	83—84/14	99
		55.00	6.67	29.28		
<i>XVII^a</i>	C ₉ H ₁₅ F ₃ O (196.1)	55.13	7.65	29.06	55—56/11	99
		55.37	7.84	30.07		

^a Proved mixture of diastereoisomers.

(1.84 g, 10 mmol) and Grignard reagent (40 mmol; methylmagnesium iodide, ethylmagnesium bromide or isopropylmagnesium bromide) and the reaction mixture was stirred for 4 hours at 35°C. The mixture was decomposed with dilute hydrochloric acid, washed with a sodium hydrogen carbonate solution and dried over magnesium sulphate. Distillation *in vacuo* afforded *VII* (79%), *VIII* (76%), *IX* (88%), *X* (97%), *XI* (26% according to chromatographic analysis of the fraction boiling at 80—83°C/0.6 Torr), and *XII* (33%, according to gas-liquid chromatographic analysis of the fraction boiling at 80—110°C/11 Torr). The gas-liquid chromatography was performed on a 360 cm column with silicone elastomer E 301, and on a 120 cm column with polybutanediol succinate.

B) A solution of Grignard reagent (30 mmol) in diethyl ether (15 ml) was added under nitrogen during 15 minutes at 35°C (0°C, —35°C) to a mixture of the ester *I* or *II* (150 mmol) and diethyl ether (30 ml). The mixture was stirred for 2 hours at this temperature and then worked up as described under *A*, yielding a mixture of ketones (*III*—*VI*) and tertiary alcohols (*VII*—*X*). Gas-liquid chromatography was performed under the same conditions as described under *A*, preparative gas-liquid chromatography: 500 cm column with 20% silicone elastomer E 30₁.

Reaction of Alcohols *VII* and *IX* with Trifluoroacetic Anhydride

Trifluoroacetic anhydride (1.68 g, 8 mmol) was added under stirring to the alcohol (4 mmol) and the mixture was stirred for 6 hours at 50°C. Distillation under nitrogen afforded *XIV* (97%) or *XV* (96%). IR spectra of these products are listed in Table IV, NMR spectra in Table III, mass spectra in Table II, and elemental analyses in Table V.

Reaction of Tertiary Alcohols *VII*, *IX* and *X* with Phosphorus Pentoxide

A mixture of the alcohol (4 mmol) and phosphorus pentoxide (3.51 g, 25 mmol) was distilled under nitrogen *in vacuo*, yielding the corresponding olefinic derivatives *XVI* (63%), *XVII* (96%) or *XVIII* (54%, together with *X*, b.p. 80–83°C/14 Torr). Gas-liquid chromatography see preceding experiments. For elemental analyses and boiling points of *XVI* and *XVII* see Table V, for IR spectra see Table IV and for NMR spectra see Table III. Mass spectral data of the compounds *XVI*–*XVIII* are listed in Table II.

Reaction of Alcohols *VII* and *IX* with Thionyl Chloride

Thionyl chloride (1.92 g, 16 mmol) was added at 50°C to a stirred mixture of the alcohol (8 mmol) and pyridine (2.01 g, 25 mmol). The reaction mixture was stirred for 1 hour at 50°C, diluted with ether (50 ml), washed with a sodium hydrogen carbonate solution and dried over magnesium sulphate. Distillation afforded the corresponding products, *i.e.* alcohol *IX* gave the olefin *XVII* (83%) and alcohol *VII* afforded the chloro derivative *XIX* (20%, together with *VII*, fraction boiling at 80–81°C/13 Torr). Gas-liquid chromatography see preceding experiments. The mass spectrum of *XIX* is given in Table II.

Spectral measurements were performed in the Department of Infrared Spectroscopy (Head Dr P. Adámek), in the Department of Mass Spectroscopy (Head Dr V. Kubelka), and in the Department of NMR spectroscopy (Head Dr P. Trška); elemental analyses were carried out in the Department of Organic Analysis (Head Dr L. Helešić), Institute of Chemical Technology. We are indebted also to Dr A. Pošta for the assistance in carrying out the chromatographic analyses.

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