

Substituent Effects in the Reaction of *t*-Butylmagnesium Chloride with Substituted Ethyl Cinnamates. A Correlation with ^{13}C NMR Chemical Shifts

LARS JALANDER

Department of Organic Chemistry, Åbo Academy, SF-20500 Åbo 50, Finland

The reaction of *t*-butylmagnesium chloride with some substituted ethyl (*E*)-cinnamates gave mainly 1,3-, 1,4-, 1,2- and 1,4-addition products and minor amounts of 1,2- and 1,3-addition products. The relative amounts of 1,3-addition products has been shown to correlate with ^{13}C NMR chemical shifts of C- α of the ethyl cinnamates. The correlation indicates that the regio selectivity of the reactions is to a great extent dependent of polar effects and that the *t*-butyl radical has a nucleophilic character.

Some time ago it was reported that ethyl cinnamate and *t*-butylmagnesium chloride react to yield 1,4- and 1,3-addition products.¹ The mechanism of the reaction has later been extensively investigated by Holm and Crossland.² The same reaction products are also formed when ethyl cinnamate is heated in the presence of *t*-butyl radicals generated from 4-*t*-butyl-1,4-dihydrobenzophenone³ or 2,2,4,4-tetramethyl-3-*t*-butylpentan-3-ol.⁴ It has also been found that 1,4- and 1,3-addition products are produced in a ratio of 1:1 when magnesium *t*-butylmethylcuprate(I) is allowed to react with ethyl cinnamate.⁵ This reaction is, however, not supposed to proceed by a radical mechanism.⁶

The purpose of the present study was to examine the polar and steric effects of substituents on the product distribution in the reaction of substituted ethyl cinnamates with *t*-butylmagnesium chloride. Since ^{13}C NMR chemical shift measurements provide information about electron densities⁷ it was of interest also to study if there is a correlation between the ratio of 1,4- and 1,3-addition products and the ^{13}C chemical shifts of the ethyl cinnamates.

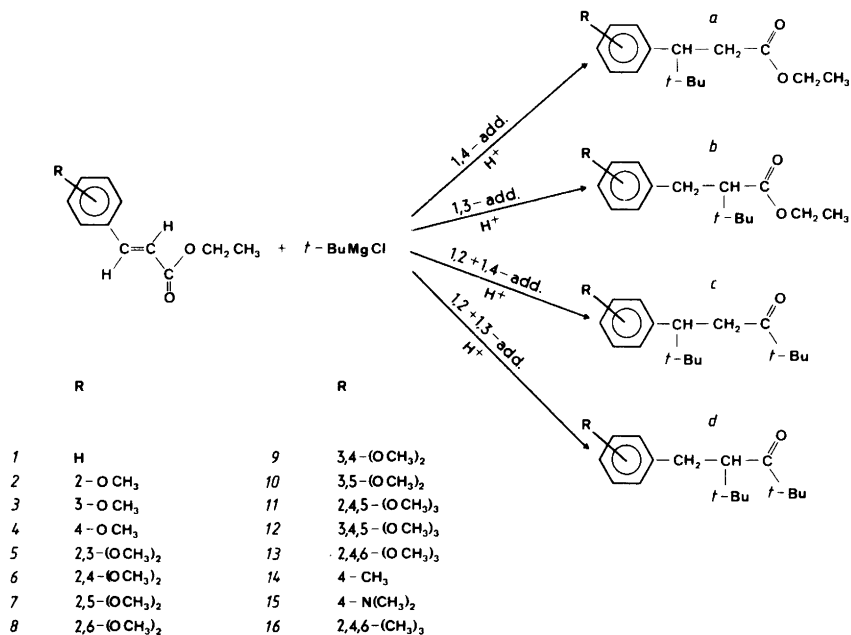
RESULTS AND DISCUSSION

The Grignard reagent (*t*-butylmagnesium chloride in excess 3:1) was allowed to react with sixteen ethyl cinnamates (1–16). The reaction is illustrated in Scheme 1.

The worked-up reaction mixtures were analyzed by capillary GLC. The proportion of 1,4- and 1,3-addition products, which were the main reaction products, are given in Table 1. The ^{13}C NMR chemical shifts of the ethyl cinnamates 1–16 were measured and assigned. The chemical shift values of C- α and C- β are shown in Table 1.

The structures of 1,4- and 1,3-addition products were mainly deduced from different mass spectral fragmentations and in some cases by controlled alkaline hydrolysis.¹ The results in Table 1 show that out of the sum of 1,3- and 1,4-addition products the proportion of 1,3-addition products varied from 10 % in the reaction of 15 to 98 % in the reaction of 16. The chemical shift differences of C- α varied from +4.9 ppm to –5.9 ppm in relation to the C- α chemical shifts of ethyl cinnamate (1). The highest shielding effect was that of the *para*-dimethylamino group and the highest deshielding effect was observed for the methyl substituents in both *ortho* positions. The shift differences indicate that the resonance effect of a methoxy or a dimethylamino group in *para* position will primarily increase the π -electron density at C- α and that the substituents in both *ortho* positions inhibit sterically the coplanarity of the phenyl ring and the olefinic carbons so that the electron releasing effect from the phenyl ring is inhibited.

The fact that the relative amount of 1,3-addition



Scheme 1.

products decreased when the electron releasing substituents in *para* position increased the electron density at C- α shows that the regioselectivity of

the reaction is dependent on polar effects. The results also indicate that the *t*-butyl radical has nucleophilic character. The low yield of the 1,4-

Table 1. a. The ratio of 1,3- and 1,4-addition products formed in the reaction of RPh-CH=CH-COOCH₂CH₃ and *t*-BuMgCl as determined by GLC. b. ¹³C NMR chemical shifts of C- α and C- β of the same esters.

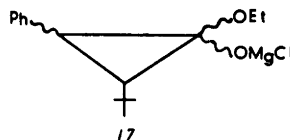
Substrate No.	a Substituent R	Addition		b ¹³ C NMR chemical shifts (δ values)	
		1,3 ratio/%	1,4 ratio/%	C- α	C- β
1	H	52	48	118.4	144.6
2	2-OCH ₃	69	31	118.7	140.0
3	3-OCH ₃	53	47	118.6	144.5
4	4-OCH ₃	24	76	115.8	144.2
5	2,3-(OCH ₃) ₂	58	42	118.9	139.7
6	2,4-(OCH ₃) ₂	33	67	116.2	140.0
7	2,5-(OCH ₃) ₂	64	36	119.5	139.3
8	2,6-(OCH ₃) ₂	76	24	120.7	135.4
9	3,4-(OCH ₃) ₂	39	61	115.9	144.5
10	3,5-(OCH ₃) ₂	56	44	118.8	144.6
11	2,4,5-(OCH ₃) ₃	37	63	115.5	139.3
12	3,4,5-(OCH ₃) ₃	23	77	117.5	144.5
13	2,4,6-(OCH ₃) ₃	56	44	117.7	135.5
14	4-CH ₃	45	55	117.3	144.6
15	4-N(CH ₃) ₂	10	90	112.5	145.1
16	2,4,6-(CH ₃) ₃	98	2	123.3	143.2

addition products in the case of the *ortho*-substituted esters cannot simply be explained by steric hindrance at C- β since the relative amount of 1,4-addition increased when a methoxy group was added in *para* position to *ortho*-substituted esters. The relative amount of 1,4-addition products in the reaction of ethyl 3-(2,4,6-trimethylphenyl)-2-propenoate (16) was, however, almost negligible which seems to be a result of steric hindrance at C- β . But the polar effects have also to be taken into consideration because the electron density at C- α was low for this ester which should activate a reaction in a 1,3-fashion. This may explain why the relative amount of 1,3-addition was high (98%). The steric hindrance at C- β should be almost the same for the 2,4,6-trimethoxy-substituted ester as for the 2,4,6-trimethyl-substituted ester but the relative amount of the 1,4-addition is still 44% in the former case and only 2% in the latter.

A plot of the normalized yield of 1,3-addition products against the chemical shift of C- α is shown in Fig. 1. The correlation coefficient is $r=0.970$ when the point for the reaction of the 3,4,5-trimethoxy-substituted ester (12) is not taken into account. The normalized yields of the 1,3- and 1,4-addition products (Table 1) is a mean value of three experiments. There is only an indication of correlation when the amounts of secondary products and the amounts of unreacted starting material left after a reaction time of 45 min are taken into account in the correlation. Owing to this it is doubtful to draw too extensive conclusions on the basis of the correlation. Nevertheless, the correlation provides

information about the complex nature of the reaction of substituted ethyl cinnamates with *t*-butylmagnesium chloride. No correlation was observed when the relative amount of the 1,4-addition products was plotted against the chemical shifts of C- β . One cannot expect a correlation with the shift of C- β either, since the electron-releasing substituents will mainly influence the π -electron density at C- α . Neither is there a good correlation between the relative amount of the 1,3-addition products and the ^1H NMR chemical shifts of H- α . This can be at least partly due to the large anisotropy term in the ^1H spectra whereas in the case of the ^{13}C chemical shifts the anisotropy term is relatively insignificant.⁸

The 1,3-addition mechanism as suggested by Holm and Crossland^{1,3} is initiated by a single electron transfer (SET) from *t*-butylmagnesium chloride to ethyl cinnamate to form after rearrangement and diffusion a free *t*-butyl radical which reacts with C- α of ethyl cinnamate. The formation of the final 1,3-addition product proceeds *via* a cyclopropanone hemiketal salt (17).



If SET is the rate-controlling step in these reactions then an electron-releasing substituent in *para* position will have a rate-reducing effect because the

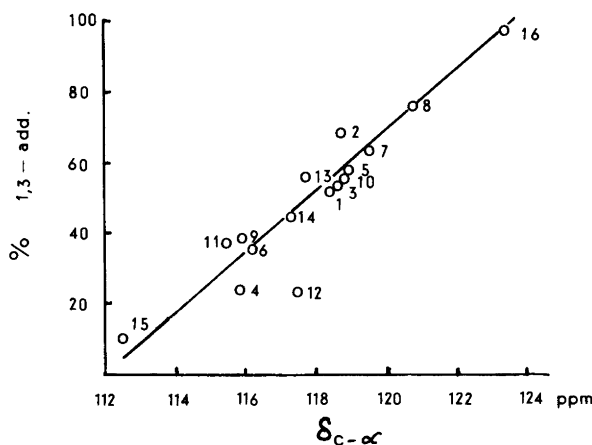


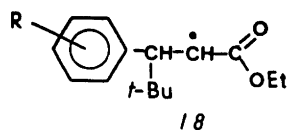
Fig. 1. ^{13}C NMR chemical shifts of C- α against the relative amount of 1,3-addition products formed in the reaction of *t*-butylmagnesium chloride with the substituted ethyl cinnamates listed in Table 1.

electron-accepting capacity of the reaction center is diminished. This effect was observed in the present study where the reaction rate, as estimated from the amount of unreacted ester left after a reaction time of 20 min, was lower in the reaction of *para*-substituted esters than in the reactions of unsubstituted, *meta*-substituted and *ortho*-substituted esters. Similar trends were achieved when the half-wave reduction potentials ($E_{1/2}$) of the same esters were measured by differential pulse polarography,⁹ *i.e.*, electron releasing substituents in *para* position caused more negative reduction potentials. Consequently there should exist a correlation between the rate of the reaction of substituted ethyl cinnamates with *t*-butylmagnesium chloride and the half-wave reduction potentials of the same esters.

The reddish brown colour of the reaction mixture has an obvious connection with some intermediates in the 1,3-addition reaction since the intensity of the colour was stronger in the reactions which yielded higher amounts of 1,3-addition products. The ethyl cinnamate radical anion magnesium salt is supposed to be responsible for this colour.² The reason for the *para*-substituted ethyl cinnamates giving low amounts of 1,3-addition products may be a stronger cage effect due to a delocalization effect of the electron releasing substituents in the *para* position. When the radical is prevented to diffuse out of the cage and form the free radical the possibility to

collapse and form a 1,4-addition adduct is favourable.

The decrease of the 1,3-addition product in the presence of α -methylstyrene is taken as evidence of free *t*-butyl radicals being responsible for the formation of the 1,3-addition product.² The formation of the 1,4-addition product is supposed to take place within the cage because the amount of this product did not change in the presence of α -methylstyrene. The reason why a 1,4-addition adduct cannot easily be formed by the reaction of a free *t*-butyl radical with ethyl cinnamate outside the cage may be the low stability of the intermediate 18.



This intermediate cannot be stabilized by a resonance effect from the substituents in the phenyl ring. The intermediate 19 can, however, be stabilized by a methoxy group in *para* position.

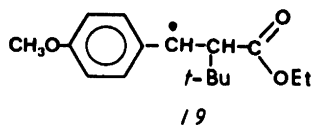
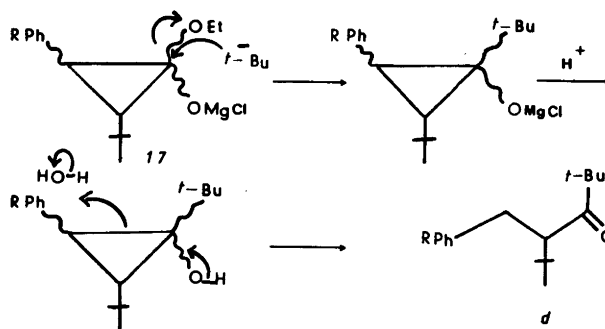


Table 2. Normalized and total yields of products formed in the reactions of $RPh-CH=CH-COOCH_2CH_3$ with *t*-BuMgCl as determined by GLC.

Substrate No.	Substituent R	1,4 yield/%	1,3 yield/%	Addition 1,2+1,4 yield/%	1,2+1,3 yield/%	Unreacted %	Total yield %
1	H	50	46	4		1	71
2	2-OCH ₃	25	56	19		1	65
3	3-OCH ₃	47	53			1	72
4	4-OCH ₃	68	21	11		9	58
5	2,3-(OCH ₃) ₂	32	44	24		2	68
6	2,4-(OCH ₃) ₂	54	26	20		10	55
7	2,5-(OCH ₃) ₂	29	52	19		3	63
8	2,6-(OCH ₃) ₂	20	66	14		8	48
9	3,4-(OCH ₃) ₂	57	37		6	12	56
10	3,5-(OCH ₃) ₂	42	54	4		1	67
11	2,4,5-(OCH ₃) ₃	52	31	7	10	9	56
12	3,4,5-(OCH ₃) ₃	55	17		28	4	61
13	2,4,6-(OCH ₃) ₃	28	35	37		45	33
14	4-CH ₃	55	45			1	67
15	4-N(CH ₃) ₂	87	9	3		10	51
16	2,4,6-(CH ₃) ₃	1	49	50		12	37



Scheme 2.

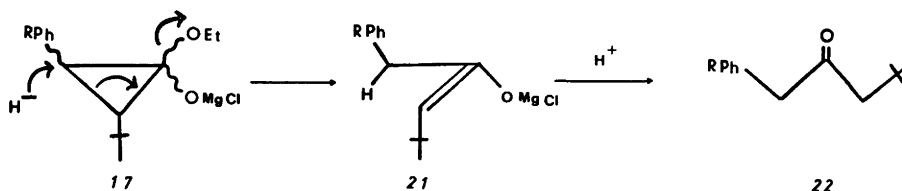
But the amounts of 1,3-addition products are nevertheless lower in the reaction of *para*-substituted esters than in the reaction of *meta*- and *ortho*-substituted esters. An explanation to the lower yields in the former may be the enhanced electron density at C- α , which renders an attack of the nucleophilic *t*-butyl radical at C- α more difficult. This is best demonstrated by ethyl 3-(*N,N*-dimethyl-4-aminophenyl)-2-propenoate (15) which has the highest electron density at C- α and which yielded the lowest amount of the 1,3-addition product (10%).

The amounts of the main reaction products as analyzed by combined GLC and MS are given in Table 2. The main byproducts were the ketones formed by 1,2- and 1,4-addition mechanism. The amounts of 1,2- and 1,4-addition products were higher in the reactions of *ortho*-substituted ethyl cinnamates than in the reaction of *para*- and *meta*-substituted ethyl cinnamates. The substituents in one or both *ortho* positions should sterically prevent the addition of *t*-butylmagnesium chloride in a 1,4-fashion and the reaction may therefore proceed by a 1,2-addition mechanism. The ketone formed by 1,2-addition has higher reactivity than the parent ester and hence the reaction can be continued by a 1,4-addition mechanism despite the steric hindrance at C- β . The initial stage in 1,2-addition can be a

SET from *t*-butylmagnesium chloride in the same fashion as a SET to a ketone.¹⁰

In the reactions of 9, 11, 12 and 13 with *t*-butylmagnesium chloride 1,2- and 1,3-addition products were formed in small amounts. The formation of these reaction products may take place at the expense of 1,3-addition products because the amount of 1,3-addition product was unexpectedly low (10%) and the amount of 1,2- and 1,3-addition product high (28%) in the reaction of ethyl 3-(3,4,5-trimethoxyphenyl)-2-propenoate with *t*-butylmagnesium chloride. These products can be formed by an anionic attack of the *t*-butyl group of the Grignard reagent at C- α of the cyclopropanone hemiketal magnesium salt (17) with a consequent elimination of the ethoxyl group as shown in Scheme 2.

When ethyl 3-(2,4,6-trimethoxyphenyl)-2-propenoate (13) was allowed to react with a large excess of *t*-butylmagnesium chloride (see Experimental) 80% of the main reaction product was accounted for by a ketone formed *via* a 1,2+1,4-addition mechanism. On the other hand when ethyl 3-(2,4,6-trimethylphenyl)-2-propenoate (16) reacted under the same reaction conditions an allene 4,4-dimethyl-1-(2,4,6-trimethylphenyl)-1,2-pentadiene (20) was formed in about 30% yield. The formation of the allene may take place at the



Scheme 3.

expense of the 1,3-addition product since the amount of 1,3-addition product was lowered. The allene may arise from the cyclopropanone hemiketal (17) after reduction and deprotonation.² A ketone 4,4-dimethyl-1-(2,4,6-trimethylphenyl)pentan-2-one (22) was also formed in this reaction. The origin of this reaction product can also be the cyclopropanone hemiketal (17) which reacts with a hydride ion at the benzylic carbon to form the enolate 21 as shown in Scheme 3.

The *Z*-isomers of unsubstituted and *ortho*-methoxy-substituted ethyl cinnamates were also allowed to react with *t*-butylmagnesium chloride. The relative amounts of the reaction products were about the same as in the reactions of the corresponding *E*-isomers. This must be due to the isomerization of the radical anion formed in the single electron transfer.

EXPERIMENTAL

A Varian 1400 gas chromatograph equipped with a 50 m × 0.2 mm glass capillary column (stationary phase SE-30) was used for GLC analyses. Mass spectra were recorded on an LKB 9000 instrument equipped with the same capillary column GLC system. The electron energy was 70 eV. ¹H NMR spectra were recorded on a Perkin-Elmer R 12 A instrument at 60 MHz or on a Jeol FX-60 FT NMR spectrometer at 59.75 MHz and ¹³C NMR on the same instrument operating at 15.03 MHz. The pulse width was 4 μs and the spectral width 4 kHz. CDCl₃ was used as solvent and TMS as an internal standard. The concentration of ethyl cinnamates in CDCl₃ was 0.7 M.

The Grignard reactions were carried out in oven dried glassware under purified nitrogen. Diethyl ether was distilled from a mixture of benzophenone and sodium prior to use. Grignard reagents were made in 1 l reagent bottles and added in different experiments using a multiburette (Metrohm E 485) equipped with a 50 cm³ cylinder. The concentration of Grignard reagents were determined by standard titrations. The magnesium turnings were synthetic grade from Merck.

The substituted benzaldehydes were purchased from Koch-Light or Fluka and used without purification except 2,6-dimethoxybenzaldehyde¹¹ which was synthesized in good yield (78 %) from 2,6-dimethoxyphenyllithium and *N*-methylformanilide.¹²

Substituted ethyl 3-phenyl-2-propenoates. The acids of the ethyl cinnamates 1–5, 7, 10, 14 and 15 were synthesized from the corresponding substituted benzaldehydes and malonic acid in pyridine with

piperidine as catalyst.¹³ After recrystallization the acids were esterified in ethanol with sulfuric acid as catalyst and distilled *in vacuo*. Ethyl 3-(*N,N*-dimethyl-4-aminophenyl)-2-propenoate was prepared by reduction of the corresponding nitro derivative¹⁴ followed by methylation with methyl iodide. The condensation reaction of 2,4,6-trimethoxybenzaldehyde was made with monoethyl malonate instead of malonic acid.¹³

The ethylcinnamates 6, 8, 11 and 12 were prepared by the reaction of the corresponding aldehydes with ethyl acetate and sodium metal.¹⁵ Ethyl (*Z*) zinnamate was prepared by hydrogenation of ethyl phenylpropynoate with hydrogen in the presence of a Lindlar catalyst,¹⁶ and (*Z*) *o*-methoxycinnamic acid¹⁷ by saponification of coumarin with sodium hydroxide followed by methylation of the phenolic hydroxy groups with dimethyl sulfate. The ethyl cinnamates were then subjected to GLC and ¹H NMR analyses, as a check of the purity.

General procedure for the reaction of t-butylmagnesium chloride with ethyl cinnamates. Ethyl cinnamate (10 mmol) in 50 cm³ diethyl ether was added at once with stirring to 23.1 cm³ of a 1.3 N (30 mmol) *t*-butylmagnesium chloride solution at 0 °C. After stirring for 45 min at 20 °C the reaction mixture was poured onto a mixture of ice and diluted hydrochloric acid. The aqueous phase was extracted three times with diethyl ether. The organic phase was treated with a saturated Na₂CO₃ solution and dried over Na₂SO₄ and the diethyl ether evaporated. The residue was subjected to qualitative and quantitative analyses. Ethyl 3-phenylpropanoate was used as internal standard in capillary GLC analyses. The structures of 1,4- and 1,3-addition products were mainly deduced from some characteristic mass spectral fragmentations. A 1,3-ethoxyl migration¹⁸ was typical for 1,4-addition products and the fragment ion RPhCHCHCO⁺ was intense for 1,3-addition products. The molecular ions of the 1,3-addition products were usually stronger than those of the 1,4-addition products. The structures were also checked by alkaline hydrolyses, which is a reliable test because the 1,3-addition products are not easily saponified in an alkaline water–ethanol solution.

The allene 4,4-dimethyl-1-(2,4,6-trimethylphenyl)-1,2-pentadiene was isolated by TLC and 2,2,5,5-tetramethyl-4-(3,4,5-trimethoxyphenylmethyl)hexan-3-one (12d) by alkaline hydrolyses of the 1,3- and 1,4-addition products.

Ethyl 4,4-dimethyl-3-phenylpentanoate (1a). MS *m/e* (% rel. int.): 234 (1, M), 219 (3, M – CH₃), 189 (5, M – OC₂H₅), 178 [58.6, M – CCH₂(CH₃)₂], 177 [7.8, M – C(CH₃)₃], 135 (9, PhCHOC₂H₅), 131 (7, PhCHCHCO), 104 (100, PhCHCH₂), 91 (21, C₇H₇), 57 [42, C(CH₃)₃].

Ethyl 3,3-dimethyl-2-(phenylmethyl)butanoate

(1b). MS *m/e* (% rel. int.): 234 (8, M), 189 (6, M-OC₂H₅), 177 [100, M-C(CH₃)₃], 149 (21, PhCH₂CHCOOH), 131 (48, PhCHCHCO), 91 (60, C₇H₇), 57 [23, C(CH₃)₃].

2,2,6,6-Tetramethyl-5-phenylheptan-3-one (1c). MS *m/e* (% rel. int.): 246 (2, M), 231 (3, M-CH₃), 189 [69, M-C(CH₃)₃], 147 [35, PhCHC(CH₃)₃], 133 (100, PhCH₂CH₂CO), 105 (66, PhCH₂CH₂), 91 (37, C₇H₇), 57 [93, C(CH₃)₃].

Ethyl 4,4-dimethyl-3-(2-methoxyphenyl)pentanoate (2a). MS *m/e* (% rel. int.): 264 (18, M), 219 (6, M-OC₂H₅), 208 (100, M-56), 165 (83, CH₃OPh-OC₂H₅), 161 (18, CH₃OPhCHCHCO), 135 (32, CH₃OPhCH₂CH₂), 134 (67, CH₃OPhCHCH₂), 121 (30, CH₃OC₇H₆), 57 [15, C(CH₃)₃].

Ethyl 3,3-dimethyl-2-(2-methoxyphenylmethyl)butanoate (2b). MS *m/e* (% rel. int.): 264 (9, M), 219 (3, M-OC₂H₅), 207 [26, M-C(CH₃)₃], 165 (3, CH₃OPhCHOC₂H₅), 161 (67, CH₃OPhCHCHCO), 121 (100, CH₃OC₇H₆), 91 (54, C₇H₇), 57 [21, C(CH₃)₃].

2,2,6,6-Tetramethyl-5-(2-methoxyphenyl)heptan-3-one (2c). MS *m/e* (% rel. int.): 276 (2, M), 219 [25, M-C(CH₃)₃], 177 [62, CH₃OPhCHC(CH₃)₃], 135 (54, CH₃OPhCH₂CH₂), 121 (CH₃OC₇H₆), 99 [30, CH₂COC(CH₃)₃], 57 [100, C(CH₃)₃].

Ethyl 4,4-dimethyl-3-(3-methoxyphenyl)pentanoate (3a). MS *m/e* (% rel. int.): 264 (21, M), 219 (10, M-OC₂H₅), 208 (100, M-56), 165 (19, CH₃OPhCHOC₂H₅), 161 (6, CH₃OPhCHCHCO), 135 (42, CH₃OPhCH₂CH₂), 134 (95, CH₃OPhCHCH₂), 121 (13, CH₃OC₇H₆), 91 (11, C₇H₇), 57 [43, C(CH₃)₃].

Ethyl 3,3-dimethyl-2-(3-methoxyphenylmethyl)butanoate (3b). MS *m/e* (% rel. int.): 264 (43, M), 219 (7, M-OC₂H₅), 209 [100, M-C(CH₃)₃], 192 (10, M-COOC₂H₄), 191 (15, M-COOC₂H₅), 161 (99, CH₃OPhCHCHCO), 135 (15, CH₃OPhCH₂CH₂), 134 (14, CH₃OPhCHCH₂), 121 (53, CH₃OC₇H₆), 91 (17, C₇H₇), 57 [23, C(CH₃)₃].

Ethyl 4,4-dimethyl-3-(4-methoxyphenyl)pentanoate (4a). MS *m/e* (% rel. int.): 264 (15, M), 249 (2, M-CH₃), 219 (2, M-OC₂H₅), 207 [100, M-CCH₂(CH₃)₂], 208 [33.4, M-C(CH₃)₃], 177 [15, CH₃OPhCHC(CH₃)₃], 165 (67, CH₃OPhCHOC₂H₅), 161 (6, CH₃OPhCHCHCO), 135 (31, CH₃OPhCH₂CH₂), 134 (33, CH₃OPhCHCH₂), 121 (28, CH₃OC₇H₆), 91 (11, C₇H₇), 57 [7, C(CH₃)₃].

Ethyl 3,3-dimethyl-2-(4-methoxyphenylmethyl)butanoate (4b). MS *m/e* (% rel. int.): 264 (10, M), 219 (2, M-OC₂H₅), 207 [11, M-C(CH₃)₃], 190 (8), 161 (20, CH₃OPhCHCHCO), 121 (100, CH₃OPhC₇H₆), 57 [6, C(CH₃)₃].

2,2,6,6-Tetramethyl-5-(4-methoxyphenyl)heptan-3-one (4c). MS *m/e* (% rel. int.): 276 (3, M), 219 (12, M-OC₂H₅), 207 [5, M-C(CH₃)₃], 177 [100, CH₃OPhCHC(CH₃)₃], 163 (26, CH₃OPhCH₂CH₂CO), 135 (17, CH₃OPhCH₂CH₂), 121 (CH₃OC₇H₆),

99 [13, CH₃OPhCHC(CH₃)₃], 57 [55, C(CH₃)₃].

Ethyl 4,4-dimethyl-3-(2,3-dimethoxyphenyl)pentanoate (5a). MS *m/e* (% rel. int.): 294 (29, M), 249 (6, M-OC₂H₅), 238 [100, M-CCH₂(CH₃)₂], 237 [18.4, M-C(CH₃)₃], 207 (9, M-CH₂COOC₂H₅), 195 [57, (CH₃O)₂PhCHOC₂H₅], 191 [34, (CH₃O)₂PhCHCHCO], 165 [24, (CH₃O)₂PhCH₂CH₂], 164 [38, (CH₃O)₂PhCHCH], 151 [17, (CH₃O)₂C₇H₅], 57 [14, C(CH₃)₃].

Ethyl 3,3-dimethyl-2-(2,3-dimethoxyphenylmethyl)butanoate (5b). MS *m/e* (% rel. int.): 294 (54, M), 249 (6, M-OC₂H₅), 237 [34, M-C(CH₃)₃], 220 (18, M-HCOOC₂H₅), 191 [100, (CH₃O)₂PhCHCHCO], 151 [60, (CH₃O)₂C₇H₅], 136 (38), 91 (C₇H₇), 57 [13, C(CH₃)₃].

2,2,6,6-Tetramethyl-5-(2,3-dimethoxyphenyl)heptan-3-one (5c). MS *m/e* (% rel. int.): 306 (21, M), 250 [46, M-CCH₂(CH₃)₂], 207 [100, M-CH₂COC(CH₃)₃], 165 [54, (CH₃O)₂PhCH₂CH₂], 151 [97, (CH₃O)₂C₇H₅], 99 [33, CH₂COC(CH₃)₃], 57 [70, C(CH₃)₃].

Ethyl 4,4-dimethyl-3-(2,4-dimethoxyphenyl)pentanoate (6a). MS *m/e* (% rel. int.): 294 (11, M), 249 (1, M-OC₂H₅), 238 [16.4, M-CCH₂(CH₃)₂], 237 [100, M-C(CH₃)₃], 207 (11, M-CH₂COOC₂H₅), 195 [37, (CH₃O)₂PhCHOC₂H₅], 191 [16, (CH₃O)₂PhCHCHCO], 165 [15, (CH₃O)₂PhC₇H₄], 164 [11, (CH₃O)₂PhCHCH₂], 151 [12, (CH₃O)₂C₇H₅], 57 [3, C(CH₃)₃].

Ethyl 3,3-dimethyl-2-(2,4-dimethoxyphenylmethyl)butanoate (6b). MS *m/e* (% rel. int.): 294 (5, M), 249 (1, M-OC₂H₅), 237 [1, M-C(CH₃)₃], 191 [5, (CH₃O)₂PhCHCHCO], 151 [100, (CH₃O)₂C₇H₅], 57 [6, C(CH₃)₃].

2,2,6,6-Tetramethyl-5-(2,4-dimethoxyphenyl)pentan-3-one (6c). MS *m/e* (% rel. int.): 306 (3, M), 250 [6, M-CCH₂(CH₃)₂], 249 [3, M-C(CH₃)₃], 207 [100, M-CH₂COC(CH₃)₃], 193 (20), 165 [22, (CH₃O)₂PhC₇H₄], 151 [48, (CH₃O)₂C₇H₅], 121 (13), 57 [46, C(CH₃)₃].

Ethyl 4,4-dimethyl-3-(2,5-dimethoxyphenyl)pentanoate (7a). MS *m/e* (% rel. int.): 294 (33, M), 249 (4, M-OC₂H₅), 238 [100, M-CCH₂(CH₃)₂], 237 [36, M-C(CH₃)₃], 207 (12, M-CH₂COOC₂H₅), 205 (15), 195 [85, (CH₃O)₂PhCHOC₂H₅], 191 [30, (CH₃O)₂PhCHCHCO], 165 [33, (CH₃O)₂PhC₇H₄], 164 [37, (CH₃O)₂PhCHCH₂], 151 [32, (CH₃O)₂C₇H₅], 121 (15), 57 [15, C(CH₃)₃].

Ethyl 3,3-dimethyl-2-(2,5-dimethoxyphenylmethyl)butanoate (7b). MS *m/e* (% rel. int.): 294 (72, M), 249 (4, M-OC₂H₅), 237 [8, M-C(CH₃)₃], 220 (18, M-HCOOC₂H₅), 205 (8), 195 [4, (CH₃O)₂PhCHOC₂H₅], 191 [68, (CH₃O)₂PhCHCHCO], 151 [100, (CH₃O)₂C₇H₅], 138 (10), 121 (30), 57 [14, C(CH₃)₃].

2,2,6,6-Tetramethyl-5-(2,5-dimethoxyphenyl)heptan-3-one (7c). MS *m/e* (% rel. int.): 306 (36, M), 250 [47, M-CCH₂(CH₃)₂], 207 [100, M-

$\text{CH}_2\text{COC}(\text{CH}_3)_3$, 165 [55, $(\text{CH}_3\text{O})_2\text{PhC}_2\text{H}_4$], 151 [85, $(\text{CH}_3\text{O})_2\text{C}_7\text{H}_5$], 121 (21), 57 [50, $\text{C}(\text{CH}_3)_3$].

Ethyl 4,4-dimethyl-3-(2,6-dimethoxyphenyl)pentanoate (8a). MS *m/e* (% rel. int.): 294 (19, M), 249 (7, $\text{M}-\text{OC}_2\text{H}_5$), 238 [45.7, $\text{M}-\text{CCH}_2(\text{CH}_3)_2$], 237 [100, $\text{M}-\text{C}(\text{CH}_3)_3$], 207 [11, $\text{M}-\text{CH}_2\text{COC}(\text{CH}_3)_3$], 205 (14), 195 [60, $(\text{CH}_3\text{O})_2\text{PhCHOC}_2\text{H}_5$], 191 [97, $(\text{CH}_3\text{O})_2\text{PhCHCHCO}$], 165 [27, $(\text{CH}_3\text{O})_2\text{PhC}_2\text{H}_4$], 164 [16, $(\text{CH}_3\text{O})_2\text{PhCHCH}_2$], 151 [45, $(\text{CH}_3\text{O})_2\text{C}_7\text{H}_5$], 91 (21, C_7H_7).

Ethyl 3,3-dimethyl-2-(2,6-dimethoxyphenylmethyl)butanoate (8b). MS *m/e* (% rel. int.): 294 (16, M), 249 (3, $\text{M}-\text{OC}_2\text{H}_5$), 237 [10, $\text{M}-\text{C}(\text{CH}_3)_3$], 220 (7, $\text{M}-\text{HCOOC}_2\text{H}_5$), 191 [28, $(\text{CH}_3\text{O})_2\text{PhCHCHCO}$], 151 [100, $(\text{CH}_3\text{O})_2\text{C}_7\text{H}_5$], 91 (17, C_7H_7).

2,2,6,6-Tetramethyl-5-(2,6-dimethoxyphenyl)heptan-3-one (8c). MS *m/e* (% rel. int.): 306 (4, M), 249 [37, $\text{M}-\text{C}(\text{CH}_3)_3$], 207 [50, $\text{M}-\text{CH}_2\text{COC}(\text{CH}_3)_3$], 165 [50, $(\text{CH}_3\text{O})_2\text{PhC}_2\text{H}_4$], 151 [100, $(\text{CH}_3\text{O})_2\text{C}_7\text{H}_5$], 99 [10, $\text{CH}_2\text{COC}(\text{CH}_3)_3$], 91 (12, C_7H_7), 57 [27, $\text{C}(\text{CH}_3)_3$].

Ethyl 4,4-dimethyl-3-(3,4-dimethoxyphenyl)pentanoate (9a). MS *m/e* (% rel. int.): 294 (24, M), 249 (4, $\text{M}-\text{OC}_2\text{H}_5$), 238 [28.5, $\text{M}-\text{CCH}_2(\text{CH}_3)_2$], 237 [100, $\text{M}-\text{C}(\text{CH}_3)_3$], 207 (10, $\text{M}-\text{CH}_2\text{COOC}_2\text{H}_5$), 195 [58, $(\text{CH}_3\text{O})_2\text{PhCHOC}_2\text{H}_5$], 191 [3, $(\text{CH}_3\text{O})_2\text{PhCHCHCO}$], 165 [17, $(\text{CH}_3\text{O})_2\text{PhC}_2\text{H}_4$], 164 [25.4, $(\text{CH}_3\text{O})_2\text{PhCHCH}_2$], 151 [19, $(\text{CH}_3\text{O})_2\text{C}_7\text{H}_5$], 91 (6, C_7H_7), 57 [6, $\text{C}(\text{CH}_3)_3$].

Ethyl 3,3-dimethyl-2-(3,4-dimethoxyphenylmethyl)butanoate (9b). MS *m/e* (% rel. int.): 294 (59, M), 249 (5, $\text{M}-\text{OC}_2\text{H}_5$), 237 [11, $\text{M}-\text{C}(\text{CH}_3)_3$], 220 (12, $\text{M}-\text{HCOOC}_2\text{H}_5$), 205 (8), 191 [35, $(\text{CH}_3\text{O})_2\text{PhCHCHCO}$], 151 [100, $(\text{CH}_3\text{O})_2\text{C}_7\text{H}_5$], 138 (11), 91 (4, C_7H_7), 57 [8, $\text{C}(\text{CH}_3)_3$].

2,2,5,5-Tetramethyl-4-(3,4-dimethoxyphenylmethyl)hexan-3-one (9d). MS *m/e* (% rel. int.): 306 (9, M), 250 [4, $\text{M}-\text{CCH}_2(\text{CH}_3)_2$], 249 [7, $\text{M}-\text{C}(\text{CH}_3)_3$], 207 [2, $\text{M}-\text{CH}_2\text{COC}(\text{CH}_3)_3$], 165 [14, $(\text{CH}_3\text{O})_2\text{PhC}_2\text{H}_4$], 164 [4, $(\text{CH}_3\text{O})_2\text{PhCHCH}_2$], 151 [7, $(\text{CH}_3\text{O})_2\text{C}_7\text{H}_5$], 85 [28, $\text{COC}(\text{CH}_3)_3$], 57 [100, $\text{C}(\text{CH}_3)_3$].

Ethyl 4,4-dimethyl-3-(3,5-dimethoxyphenyl)pentanoate (10a). MS *m/e* (% rel. int.): 294 (28, M), 249 (13, $\text{M}-\text{OC}_2\text{H}_5$), 238 [100, $\text{M}-\text{CCH}_2(\text{CH}_3)_2$], 237 [1.6, $\text{M}-\text{C}(\text{CH}_3)_3$], 195 [20, $(\text{CH}_3\text{O})_2\text{PhCHOC}_2\text{H}_5$], 191 [5, $(\text{CH}_3\text{O})_2\text{PhCHCHCO}$], 165 [95, $(\text{CH}_3\text{O})_2\text{PhC}_2\text{H}_4$], 164 [33, $(\text{CH}_3\text{O})_2\text{PhCHCH}_2$], 151 [7, $(\text{CH}_3\text{O})_2\text{C}_7\text{H}_5$], 57 [26, $\text{C}(\text{CH}_3)_3$].

Ethyl 3,3-dimethyl-2-(3,5-dimethoxyphenylmethyl)butanoate (10b). MS *m/e* (% rel. int.): 294 (22, M), 249 (8, $\text{M}-\text{OC}_2\text{H}_5$), 238 [17.1, $\text{M}-\text{CCH}_2(\text{CH}_3)_2$], 237 [100, $\text{M}-\text{C}(\text{CH}_3)_3$], 291 [51, $(\text{CH}_3\text{O})_2\text{PhCHCHCO}$], 165 [15, $(\text{CH}_3\text{O})_2\text{PhC}_2\text{H}_4$], 164 [7, $(\text{CH}_3\text{O})_2\text{PhCHCH}_2$], 151 [28, $(\text{CH}_3\text{O})_2\text{C}_7\text{H}_5$], 91 (6, C_7H_7), 57 [12, $\text{C}(\text{CH}_3)_3$].

2,2,6,6-Tetramethyl-5-(3,5-dimethoxyphenyl)heptan-3-one (10c). MS *m/e* (% rel. int.): 306 (13, M), 250 [16, $\text{M}-\text{CCH}_2(\text{CH}_3)_2$], 249 [3, $\text{M}-\text{C}(\text{CH}_3)_3$], 207 [36, $\text{M}-\text{CH}_2\text{COC}(\text{CH}_3)_3$], 165 [21, $(\text{CH}_3\text{O})_2\text{PhC}_2\text{H}_4$], 151 [11, $(\text{CH}_3\text{O})_2\text{C}_7\text{H}_5$], 99 [58, $\text{CH}_2\text{COC}(\text{CH}_3)_3$], 69 (41), 57 [100, $\text{C}(\text{CH}_3)_3$].

Ethyl 4,4-dimethyl-3-(2,4,5-trimethoxyphenyl)pentanoate (11a). MS *m/e* (% rel. int.): 324 (18, M), 268 [17.7, $\text{M}-\text{CCH}_2(\text{CH}_3)_2$], 267 [100, $\text{M}-\text{C}(\text{CH}_3)_3$], 237 (9), 225 [26, $(\text{CH}_3\text{O})_3\text{PhCHOC}_2\text{H}_5$], 221 [15, $(\text{CH}_3\text{O})_3\text{PhCHCHCO}$], 195 [8, $(\text{CH}_3\text{O})_3\text{PhC}_2\text{H}_4$], 194 [17, $(\text{CH}_3\text{O})_3\text{PhCHCH}_2$], 181 [8, $(\text{CH}_3\text{O})_3\text{C}_7\text{H}_4$].

Ethyl 3,3-dimethyl-2-(2,4,5-trimethoxyphenylmethyl)butanoate (11b). MS *m/e* (% rel. int.): 324 (26, M), 279 (0.5, $\text{M}-\text{OC}_2\text{H}_5$), 267 [0.4, $\text{M}-\text{C}(\text{CH}_3)_3$], 225 [0.5, $(\text{CH}_3\text{O})_3\text{PhCHOC}_2\text{H}_5$], 221 [4, $(\text{CH}_3\text{O})_3\text{PhCHCHCO}$], 181 [100, $(\text{CH}_3\text{O})_3\text{C}_7\text{H}_4$], 151 (10).

2,2,6,6-Tetramethyl-5-(2,4,5-trimethoxyphenyl)heptan-3-one (11c). MS *m/e* (% rel. int.): 336 (9, M), 280 [8, $\text{M}-\text{CCH}_2(\text{CH}_3)_2$], 279 [6, $\text{M}-\text{C}(\text{CH}_3)_3$], 237 [100, $\text{M}-\text{CH}_2\text{COC}(\text{CH}_3)_3$], 223 (8), 195 [13, $(\text{CH}_3\text{O})_3\text{PhC}_2\text{H}_4$], 192 (6), 181 [26, $(\text{CH}_3\text{O})_3\text{C}_7\text{H}_4$], 99 [6, $\text{CH}_2\text{COC}(\text{CH}_3)_3$], 57 [32, $\text{C}(\text{CH}_3)_3$].

2,2,5,5-Tetramethyl-4-(2,4,5-trimethoxyphenylmethyl)hexan-3-one (11d). MS *m/e* (% rel. int.): 336 (14, M), 279 [32, $\text{M}-\text{C}(\text{CH}_3)_3$], 251 [6, $\text{M}-\text{COC}(\text{CH}_3)_3$], 237 (3), 195 [32, $(\text{CH}_3\text{O})_3\text{PhC}_2\text{H}_4$], 194 [6, $(\text{CH}_3\text{O})_3\text{PhCHCHCO}$], 181 [7, $(\text{CH}_3\text{O})_3\text{C}_7\text{H}_4$], 180 [13, $(\text{CH}_3\text{O})_3\text{C}_7\text{H}_3$], 151 (5), 85 [34, $\text{COC}(\text{CH}_3)_3$], 57 [100, $\text{C}(\text{CH}_3)_3$].

Ethyl 4,4-dimethyl-3-(3,4,5-trimethoxyphenyl)pentanoate (12a). MS *m/e* (% rel. int.): 324 (26, M), 279 (6, $\text{M}-\text{OC}_2\text{H}_5$), 268 [25.6, $\text{M}-\text{CCH}_2(\text{CH}_3)_2$], 267 [100, $\text{M}-\text{C}(\text{CH}_3)_3$], 237 (5, $\text{M}-\text{CH}_2\text{COOC}_2\text{H}_5$), 225 [45, $(\text{CH}_3\text{O})_3\text{PhCHOC}_2\text{H}_5$], 221 [2, $(\text{CH}_3\text{O})_3\text{PhCHCHCO}$], 195 [10, $(\text{CH}_3\text{O})_3\text{PhC}_2\text{H}_4$], 194 [17, $(\text{CH}_3\text{O})_3\text{PhCHCH}_2$], 181 [11, $(\text{CH}_3\text{O})_3\text{C}_7\text{H}_4$], 180 (12), 179 (12).

Ethyl 3,3-dimethyl-2-(3,4,5-trimethoxyphenylmethyl)butanoate (12b). MS *m/e* (% rel. int.): 324 (30, M), 279 (4, $\text{M}-\text{OC}_2\text{H}_5$), 268 [3.9, $\text{M}-\text{CCH}_2(\text{CH}_3)_2$], 267 [24.5, $\text{M}-\text{C}(\text{CH}_3)_3$], 221 [24, $(\text{CH}_3\text{O})_3\text{PhCHCHCO}$], 181 [100, $(\text{CH}_3\text{O})_3\text{C}_7\text{H}_4$].

2,2,5,5-Tetramethyl-4-(3,4,5-trimethoxyphenylmethyl)hexan-3-one (12d). After normal work-up the reaction mixture (2 g) was hydrolyzed by 1.5 g potassium hydroxide in 10 cm³ methanol for 20 days. The mixture was extracted with water and diethyl ether. The organic phase was dried and the diethyl ether evaporated leaving a residue (350 mg) which contained besides 12d two new substances (ca. 15%) according to capillary GLC. After repeated recrystallizations from a mixture of methanol and light petroleum 12d was almost clean. MS *m/e* (% rel. int.): 336 (8, M), 279 [5, $\text{M}-\text{C}(\text{CH}_3)_3$], 195 [34, $(\text{CH}_3\text{O})_3\text{PhC}_2\text{H}_4$], 180 (9),

85 [37, $\text{COC}(\text{CH}_3)_3$], 57 [100, $\text{C}(\text{CH}_3)_3$]. $^1\text{H NMR}$ (60 MHz, CDCl_3): δ 0.9 (9 H, s), 1.0 (9 H, s), 2.4–3.2 (3 H, ABC-syst.), 3.81 (3 H, s), 3.83 (6 H, s), 6.36 (2 H, s).

Ethyl 4,4-dimethyl-3-(2,4,6-trimethoxyphenyl)pentanoate (13a). MS *m/e* (% rel. int.): 324 (6, M), 279 (2, M– OC_2H_5), 268 [16.4, M– $\text{CCH}_2(\text{CH}_3)_2$], 267 [100, M– $\text{C}(\text{CH}_3)_3$], 237 (18, M– $\text{CH}_2\text{COOC}_2\text{H}_5$), 225 [21, $(\text{CH}_3\text{O})_3\text{PhCHOC}_2\text{H}_5$], 221 [36, $(\text{CH}_3\text{O})_3\text{PhCHCHCO}$], 195 [18, $(\text{CH}_3\text{O})_3\text{PhC}_2\text{H}_4$], 181 [21, $(\text{CH}_3\text{O})_3\text{C}_7\text{H}_4$].

Ethyl 3,3-dimethyl-2-(2,4,6-trimethoxyphenylmethyl)butanoate (13b). MS *m/e* (% rel. int.): 324 (19, M), 267 [3, M– $\text{C}(\text{CH}_3)_3$], 221 [10, $(\text{CH}_3\text{O})_3\text{PhCHCHCO}$], 181 [100, $(\text{CH}_3\text{O})_3\text{C}_7\text{H}_4$].

2,2,6,6-Tetramethyl-5-(2,4,6-trimethoxyphenyl)heptan-3-one (13c). MS *m/e* (% rel. int.): 336 (5, M), 237 [100, $(\text{CH}_3\text{O})_3\text{PhCHC}(\text{CH}_3)_3$], 195 [26, $(\text{CH}_3\text{O})_3\text{PhC}_2\text{H}_4$], 181 [52, $(\text{CH}_3\text{O})_3\text{C}_7\text{H}_4$], 57 [11, $\text{C}(\text{CH}_3)_3$].

2,2,5,5-Tetramethyl-4-(2,4,6-trimethoxyphenylmethyl)hexan-3-one (13d). MS *m/e* (% rel. int.): 336 (9, M), 279 [100, M– $\text{C}(\text{CH}_3)_3$], 195 [76, $(\text{CH}_3\text{O})_3\text{PhC}_2\text{H}_4$], 181 [35, $(\text{CH}_3\text{O})_3\text{C}_7\text{H}_4$], 85 [60, $\text{COC}(\text{CH}_3)_3$], 57 [60, $\text{C}(\text{CH}_3)_3$].

Ethyl 4,4-dimethyl-3-(4-methylphenyl)pentanoate (14a). MS *m/e* (% rel. int.): 248 (5, M), 203 (3, M– OC_2H_5), 192 [63.7, M– $\text{CCH}_2(\text{CH}_3)_2$], 191 [6.2, M– $\text{C}(\text{CH}_3)_3$], 149 (45, $\text{CH}_3\text{PhCHOC}_2\text{H}_5$), 145 (6, $\text{CH}_3\text{PhCHCHCO}$), 121 (17), 119 (37, $\text{CH}_3\text{PhC}_2\text{H}_4$), 118 (100, CH_3PhCHCH), 105 (27, CH_3PhCH_2), 91 (11, C_7H_7), 57 [23, $\text{C}(\text{CH}_3)_3$].

Ethyl 3,3-dimethyl-2-(4-methylphenyl)butanoate (14b). MS *m/e* (% rel. int.): 248 (18, M), 203 (6, M– OC_2H_5), 192 [15.9, M– $\text{CCH}_2(\text{CH}_3)_2$], 191 [100, M– $\text{C}(\text{CH}_3)_3$], 174 (19, M– HCOOC_2H_5), 163 (12), 159 (12), 145 (62, $\text{CH}_3\text{PhCHCHCO}$), 105 (89, CH_3PhCH_2), 92 (12), 57 [16, $\text{C}(\text{CH}_3)_3$].

Ethyl 4,4-dimethyl-3-(N,N-dimethyl-4-aminophenyl)pentanoate (15a). MS *m/e* (% rel. int.): 277 (10, M), 262 (1, M– CH_3), 232 (2, M– OC_2H_5), 221 [15, M– $\text{CCH}_2(\text{CH}_3)_2$], 220 [100, M– $\text{C}(\text{CH}_3)_3$], 190 (6, M– $\text{CH}_2\text{COOC}_2\text{H}_5$), 178 [7, $(\text{CH}_3)_2\text{NPhCHOC}_2\text{H}_5$], 174 [3, $(\text{CH}_3)_2\text{NPhCHCHCO}$], 147 [34, $(\text{CH}_3)_2\text{NPhCHCH}_2$], 134 [5, $(\text{CH}_3)_2\text{NC}_7\text{H}_6$].

Ethyl 3,3-dimethyl-2-(N,N-dimethyl-4-aminophenylmethyl)butanoate (15b). MS *m/e* (% rel. int.): 277 (12, M), 174 [3, $(\text{CH}_3)_2\text{NPhCHCHCO}$], 147 [3, $(\text{CH}_3)_2\text{NPhCHCH}_2$], 146 [3, $(\text{CH}_3)_2\text{NPhCHCH}$], 134 [100, $(\text{CH}_3)_2\text{NC}_7\text{H}_6$].

2,2,6,6-Tetramethyl-5-(N,N-dimethyl-4-aminophenyl)heptan-3-one (15c). MS *m/e* (% rel. int.): 289 (18, M), 232 [25, M– $\text{C}(\text{CH}_3)_3$], 191 [36, M– $\text{CHCOC}(\text{CH}_3)_3$], 190 [100, M– $\text{CH}_2\text{COC}(\text{CH}_3)_3$], 175 [30, $(\text{CH}_3)_2\text{NPhCH}_2\text{CH}_2\text{CO}$], 175 [24, $(\text{CH}_3)_2\text{NPhCHCH}_2\text{CO}$], 148 [12, $(\text{CH}_3)_2\text{NPhCH}_2\text{CH}_2$], 134 [18, $(\text{CH}_3)_2\text{NC}_7\text{H}_6$], 57 [20, $\text{C}(\text{CH}_3)_3$].

Ethyl 4,4-dimethyl-3-(2,4,6-trimethylphenyl)pentanoate (16a). MS *m/e* (% rel. int.): 276 (1, M), 232 (1, M– OC_2H_5), 231 (1, M– OC_2H_5), 219 [1, M– $\text{C}(\text{CH}_3)_3$], 177 [100, $(\text{CH}_3)_3\text{PhCHOC}_2\text{H}_5$], 149 [26, $(\text{CH}_3)_3\text{PhCHOH}$], 133 [5, $(\text{CH}_3)_3\text{PhCH}_2$], 121 (12), 105 (6), 57 [5, $\text{C}(\text{CH}_3)_3$].

Ethyl 3,3-dimethyl-2-(2,4,6-trimethylphenyl)butanoate (16b). MS *m/e* (% rel. int.): 276 (37, M), 231 (5, M– OC_2H_5), 219 [6, M– $\text{C}(\text{CH}_3)_3$], 202 (5, M–74), 173 [26, $(\text{CH}_3)_3\text{PhCHCHCO}$], 133 [100, $(\text{CH}_3)_3\text{PhCH}_2$], 120 [12, $(\text{CH}_3)_3\text{C}_6\text{H}_5$], 57 [6, $\text{C}(\text{CH}_3)_3$].

2,2,6,6-Tetramethyl-5-(2,4,6-trimethylphenyl)heptan-3-one (16c). MS *m/e* (% rel. int.): 288 (6, M), 232 [100, M– $\text{CCH}_2(\text{CH}_3)_2$], 189 [54, $(\text{CH}_3)_3\text{PhCHC}(\text{CH}_3)_3$], 175 [28, $(\text{CH}_3)_3\text{PhCH}_2\text{CH}_2\text{CO}$], 147 [37, $(\text{CH}_3)_3\text{PhCH}_2\text{CH}_2$], 133 [99, $(\text{CH}_3)_3\text{PhCH}_2$], 99 [26, $\text{CH}_2\text{C}(\text{CH}_3)_3$], 57 [51, $\text{C}(\text{CH}_3)_3$].

The reactions of 2,4,6-trimethoxy- and 2,4,6-trimethyl-substituted ethyl cinnamates with a greater excess of *t*-butylmagnesium chloride were performed in the same way as described in the general procedure except that the ratio of ester to reagent was 1:10 and the reaction mixture was refluxed for 1 h. The spectral data of those reaction products which were not formed by the general procedure are presented below.

2,2,5,5-Tetramethyl-4-(2,4,6-trimethylphenylmethyl)hexan-3-one (16d). MS *m/e* (% rel. int.): 288 (5, M), 232 [9, M– $\text{CCH}_2(\text{CH}_3)_2$], 231 [8, M– $\text{C}(\text{CH}_3)_3$], 203 [2, M– $\text{COC}(\text{CH}_3)_3$], 175 [15, $(\text{CH}_3)_3\text{PhCHCHCO}$], 147 [17, $(\text{CH}_3)_3\text{PhCH}_2\text{CH}_2$], 133 [28, $(\text{CH}_3)_3\text{PhCH}_2$], 85 [84, $(\text{CH}_3)_3\text{CCO}$], 57 [100, $\text{C}(\text{CH}_3)_3$].

4,4-Dimethyl-1-(2,4,6-trimethylphenyl)-1,2-pentadien (20). The allene was isolated from the reaction mixture by TLC using light petroleum as solvent. MS *m/e* (% rel. int.): 214 (12, M), 199 (10, M– CH_3), 184 (4, M– C_2H_6), 171 (9, M– C_3H_7), 157 [100, M– $\text{C}(\text{CH}_3)_3$], 144 (17), 143 (17), 142 (30), 141 (18), 57 (25).

$^1\text{H NMR}$ (60 MHz, CDCl_3): δ 1.06 (9 H, s), 2.26 (3 H, s), 2.34 (6 H, s), 5.3 (1 H, d, *J* 6.6 Hz), 6.3 (1 H, d, *J* 6.6 Hz), 6.84 (2 H, s). $^{13}\text{C NMR}$ (60 MHz, CDCl_3): δ 20.9 (CH_3Ph), 21.4 ($(\text{CH}_3)_2\text{Ph}$), 29.9 (*t*-butyl), 91.7 (C-1), 103.7 (C-3), 129.0, 135.9 and 136.4 (aromatic), 203.6 (C-2).

4,4-Dimethyl-1-(2,4,6-trimethylphenyl)pentan-2-one (22). MS *m/e* (% rel. int.): 232 (21, M), 175 [1, M– $\text{C}(\text{CH}_3)_3$], 161 [2, M– $\text{CH}_2\text{C}(\text{CH}_3)_3$], 157 [3, $(\text{CH}_3)_3\text{PhC}_3\text{H}_2$], 133 [100, $(\text{CH}_3)_3\text{PhCH}_2$], 99 [41, $\text{COCH}_2\text{C}(\text{CH}_3)_3$], 71 [10, $(\text{CH}_3)_3\text{CCH}_2$], 57 [47, $\text{C}(\text{CH}_3)_3$].

Acknowledgement. I wish to thank Professor Kalevi Pihlaja for his helpful comments on the manuscript.

REFERENCES

1. Crossland, I. *Acta Chem. Scand. B* 29 (1975) 468.
2. Holm, T., Crossland, I. and Madsen, J. *Acta Chem. Scand. B* 32 (1978) 754.
3. Holm, T. and Crossland, I. *Acta Chem. Scand.* 25 (1971) 59.
4. Lomas, J. S. and Dubois, J.-E. *J. Org. Chem.* 39 (1974) 1776.
5. Jalander, L. *Unpublished results.*
6. House, H. O. *Acc. Chem. Res.* 9 (1976) 60; Berlan, J., Battioni, J.-P. and Koosha, K. *Bull. Soc. Chim. Fr.* (1979) II-183; Smith, R. A. J. and Hannah, D. J. *Tetrahedron* 35 (1979) 1183.
7. Stothers, J. B. *Carbon-13 NMR Spectroscopy*, Academic, New York 1972, 102.
8. Dharni, K. S. and Stothers, J. B. *Can. J. Chem.* 43 (1965) 510.
9. Results presented in part at an NMR-Symposium in Oulu, Finland, 1980. Kulovaara, M. and Jalander, L. University of Oulu, Department of Physics, *Report No. 77* (1980).
10. Ashby, E. C. and Bowers, J. S. *J. Am. Chem. Soc.* 99 (1977) 8504.
11. Lambooy, J. P. *J. Am. Chem. Soc.* 76 (1954) 137.
12. Fieser, L. F. and Jones, J. E. *Org. Synth. Coll. Vol. 3* (1955) 590.
13. Slotta, K. H. and Heller, H. *Ber. Dtsch. Chem. Ges.* 63 (1930) 3029.
14. Knoevenagel, E. *Ber. Dtsch. Chem. Ges.* 31 (1899) 2612.
15. Claisen, L. and Posner, T. *J. Prakt. Chem.* 82 (1910) 435.
16. Blomfield, J. J. and Fuchs, R. *J. Org. Chem.* 26 (1961) 2991.
17. Reimer, M. and Howard, M. *J. Am. Chem. Soc.* 50 (1928) 197.
18. Williams, D. H., Cooks, R. G., Bowie, J. H., Madsen, P., Schroll, G. and Lawesson, S.-O. *Tetrahedron* 23 (1967) 3173.

Received December 8, 1980.