

Stereochemistry of the Reactions of CuI Catalyzed Grignard Reagents with Ethyl (*E*)- and (*Z*)- β -Chlorocinnamates

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Ethyl (*E*)- and (*Z*)-3-chloro-3-phenyl-2-propenoate were prepared and separated. The (*Z*)-isomer gave β -alkylated ethyl cinnamates in good yield when reacted with alkyl Grignard reagents in the presence of 10 % CuI. The (*Z*)-isomer reacted with retention of configuration, whereas the (*E*)-isomer reacted with loss and retention of configuration.

Ever since the observation of Kharasch¹ that Grignard reagents add in the 1,4-manner to conjugated enones in the presence of catalytic amounts of cuprous salt, organocopper chemistry has been a standard synthetic technique. The different types of organocopper complexes useful in synthetic chemistry have been reviewed by Normant² and Posner.³

The stoichiometry and the kinetics of the copper catalyzed reactions between various Grignard reagents and alkyl halides have been examined by Kochi and Tamura.⁴ Normant and co-workers⁵ have reported that vinylic iodides undergo substitution with Grignard reagents in the presence of catalytic amounts of copper salts and that the reactions occur with retention of configuration. Alkyl-, aryl- and alkenylnickel-phosphine complex catalyzed cross-coupling of Grignard reagents with aryl and alkenyl halides have also been reported.⁶ In our studies concerning the stereoselective synthesis of α - β -unsaturated esters it was of interest to examine the regio- and stereoselectivity of copper(I) iodide catalyzed Grignard substitution reactions with ethyl (*Z*)- and (*E*)- β -chlorocinnamates.

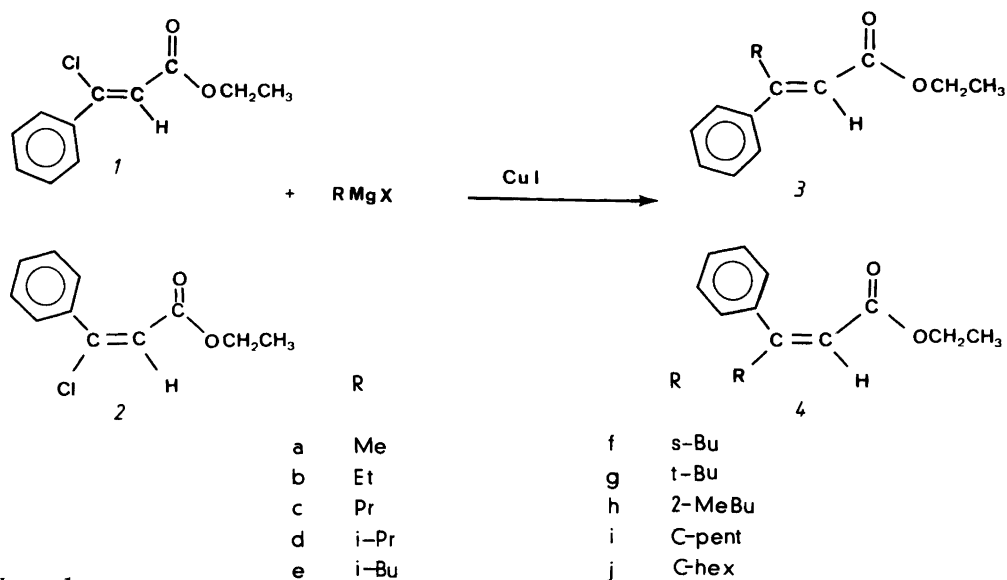
RESULTS AND DISCUSSION

The results from the reactions according to Scheme 1 are presented in Table 1. Primary, secondary and tertiary Grignard reagents reacted with ethyl (*Z*)-3-chloro-3-phenyl-2-propenoate (*I*) by replacement of the β -chloro substituent to produce β -alkyl substituted ethyl cinnamates (*3*)

Table 1. The reactions of CuI catalyzed RMgX with ethyl (*Z*)- and (*E*)-3-chloro-3-phenyl-2-propenoate according to Scheme 1.

Substrate	Reagent R	Product	ratio ^a	Total yield ^a
		<i>E</i> (3) %	<i>Z</i> (4) %	<i>E</i> + <i>Z</i> %
<i>I</i>	Me	100	0	82
<i>I</i>	Et	100	0	72
<i>I</i>	Pr	100	0	76
<i>I</i>	<i>i</i> -Pr	100	0	86
<i>I</i>	<i>i</i> -Bu	100	0	73
<i>I</i>	<i>sec</i> -Bu	100	0	80
<i>I</i>	<i>t</i> -Bu	100	0	70
<i>I</i>	2-MeBu	100	0	71
<i>I</i>	<i>C</i> -pentyl	100	0	86
<i>I</i>	<i>C</i> -hexyl	100	0	91
<i>2</i>	Me	85	15	72
<i>2</i>	Et	82	18	71
<i>2</i>	Pr	83	17	68
<i>2</i>	<i>i</i> -Pr	74	26	82
<i>2</i>	<i>i</i> -Bu	80	20	68
<i>2</i>	<i>sec</i> -Bu	72	28	72
<i>2</i>	<i>t</i> -Bu	62	38	63
<i>2</i>	2-MeBu	81	19	71
<i>2</i>	<i>C</i> -pentyl	72	28	82
<i>2</i>	<i>C</i> -hexyl	70	30	84

^aAs determined by ¹H NMR spectroscopy.



Scheme 1.

in good yield by a copper(I) iodide catalyzed reaction at a temperature above which the corresponding organocopper reagents rapidly decompose. The reactions proceeded by retention of configuration and were successful only if the Grignard reagents were added to the substrate suspended with copper(I) iodide in diethyl ether at 0 °C. The substitution products were not formed if the order of addition was reversed. If the reagent–substrate ratio was 3:1 β,β -dialkylated ketones were formed by conjugate addition and 1,2-addition. The CuI catalyzed reaction with *t*-butylmagnesium chloride was very fast at 0 °C and yielded small amounts of conjugate and 1,2-addition products besides substitution products although the reagent–substrate ratio was 1.2:1.

Ethyl (*E*)-3-chloro-3-phenyl-1-propenoate reacted slower than the corresponding *Z*-isomer and with loss and retention of configuration. The degree of isomerization was somewhat higher with primary than with secondary and tertiary Grignard reagents.

No isomerization of recovered starting material was observed when the reaction was quenched before complete conversion. In a previous study,⁷ concerning the reaction of *t*-butylmagnesium chloride with ethyl (*Z*)-cinnamates, we found that the isomerization of the *Z*-form proceeded faster than conjugate addition since

ethyl (*E*)-cinnamate was recovered. This isomerization was supposed to be the result of a rapid conversion of the less stable *Z*-isomer to the *E*-isomer *via* a radical anion intermediate. If a radical anion is formed in the present study, the alkylation step has to be much faster than the equilibration of the radical anion to the *Z*-isomer. Formation of ethyl cinnamate was not observed, when the reaction was quenched before complete conversion, which indicates that copper–halogen exchange, involving a copper–enoate intermediate, does not occur in these reactions, or that this intermediate is of very short duration. Moreover the concentration of this intermediate, if present, is of course low since the reactions proceed with catalytical amounts of copper. A metal–halogen exchange has, however, been observed in the copper iodide catalyzed reactions of Grignard reagents with vinyl iodides.⁵

The higher reactivity of the *Z*-isomer compared with that of the *E*-isomer can be due to different reaction mechanisms or to the formation of a complex (9) between copper and the *Z*-isomer, which would activate the olefinic double bond and weaken the carbon–chlorine bond.

For comparison it can be mentioned that the corresponding acid of the *Z*-isomer formed a solid complex with barium chloride while the

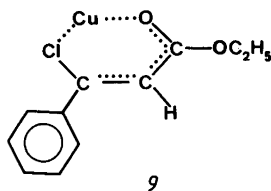


Fig. 1.

E-isomer remained in solution. This difference was used for the separation of *Z*- and *E*-isomers.⁸

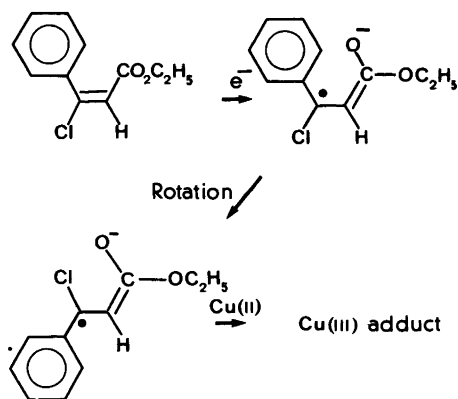
A qualitative order of reactivity of the Grignard reagents, in the reactions with the *E*-isomer (2), as estimated from the amount of starting material left after a reaction time of 10 min at 0 °C, showed the following sequence *t*-Bu > *sec*-Bu, C-hexyl, C-pentyl, *i*-Pr > Pr, Et, *i*-Bu > Me (see Experimental). This observation and the presence of isomerization products, indicate that a direct S_N2 mechanism is unlikely in the reaction with the *E*-isomer.

Chlorine was not substituted by a hydroxyl group when ethyl (*Z*)- and (*E*)- β -chlorocinnamates were reacted with an excess of sodium hydroxide in a mixture of ethanol and water (1:1). Instead, an elimination of hydrogen chloride took place and phenylethyne acid was formed almost quantitatively.

The attempts to substitute chlorine in 1 and 2 by an uncatalyzed Grignard reaction were not successful although we found in a prior study⁹ that the methoxy group in ethyl 1-methoxy-1-inden-2-carboxylate was almost quantitatively exchanged by phenyl and alkyl groups with pure Grignard reagents.

In most substitution reactions to RYC = CXR (Y = activating group, X = leaving group) the outcome has mainly been retention of configuration regardless of whether the precursor has an *E* or a *Z* configuration.¹⁰ These reactions are supposed to proceed by a nucleophilic attack perpendicularly to the plane of the double bond and elimination of the nucleofuge either by a single-step or a multi-step process. The reactions of highly electrophilic olefins YY'C = CXR (Y, Y' = activating groups, X = leaving group) with nucleophiles resulted, however, in complete and partial stereoconversion.¹¹

A single electron transfer to form an intermediary radical anion in the reaction of the *Z*-isomer (1) is hardly likely since the reaction

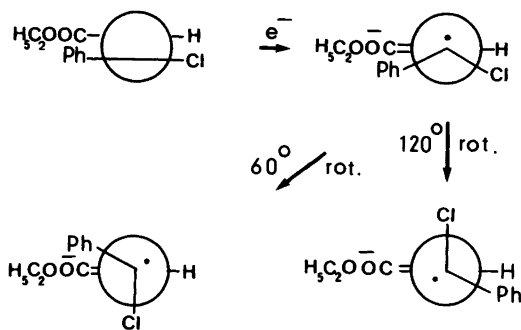


Scheme 2.

proceeded with complete retention of configuration. Retention of configuration suggests rather a nucleophilic substitution to form a Cu(III) adduct with subsequent elimination of chlorine so that the ethylenic bond remains mainly a double bond through the reaction. Even if a direct transfer of the alkyl group from copper, in a process not involving a Cu(III) adduct, cannot be ruled out.

If the barrier to rotation around the C _{α} -C _{β} bond is lowered, due to the formation of a carbonyl metal bond, the steric interactions between the substituents in the transition state should be dominating for the stereochemical outcome.

The reaction of the *E*-isomer (2) which proceeded mainly by isomerization of configuration can be consistent with a single electron transfer mechanism (Scheme 2). Since the *E*-isomer (2) in the present study reacted mainly with isomerization of configuration the assumed electron attack perpendicularly to the plane of the double bond has to be followed by a 120° counterclockwise rotation and elimination of chlorine from a position perpendicularly to the plane of the double bond simultaneously with the formation of the Cu(III) adduct. The latter step has to be fast since no isomerization of recovered starting material was observed. The steric interactions in the transition state of 120° counterclockwise rotation are consistent with the smaller steric interactions (Cl, H) compared with those of 60° rotation (Ph, COOEt) (Scheme 3). If the reaction proceeds by a nucleophilic addition mechanism to form a Cu(III) adduct before rotation the 120° counterclockwise rotation involves a greater steric interaction (Cl, H and Cu-complex,



Scheme 3.

COOEt) compared with the interactions on 60° rotation (Ph, COOEt), which indicates that rotation precedes the formation of a Cu(III) adduct since the dominating outcome is an isomerization product in the reaction of the *E*-isomer.

EXPERIMENTAL

All ^1H NMR spectra were recorded with a Jeol FX-60 FT spectrometer at 59.75 MHz and ^{13}C NMR spectra with the same instrument operating at 15.03 MHz. The spectra were taken in CDCl_3 with TMS as an internal standard. Mass spectra were recorded on an LKB 9000 combined GLC-MS instrument equipped with a (50 m × 0.25 mm ID) capillary column coated with SE-30.

Grignard reagents. Grignard reagents were prepared in an inert atmosphere from the appropriate alkyl halides and synthetic grade magnesium turnings. The concentration in dry diethyl ether varied between 1.2 to 1.8 M as determined by standard titrations.

Ethyl (*Z*)- and (*E*)-3-chloro-3-phenylpropenoate.⁸ The (*Z*)- and (*E*)-3-chloro-3-phenylpropenoic acids were prepared from methyl benzoylacetate. The (*Z*)- and (*E*)-isomers were formed in the proportion 60 to 40%. They were separated as their barium-complexes on the basis of different solubilities in diluted ammonia. The acids were esterified with ethanol and the ethyl esters *1* and *2* distilled at 135–138°C 2 kPa.

Ethyl (*Z*)-3-chloro-3-phenylpropenoate (*1*). ^1H NMR (60 MHz, CDCl_3): δ 1.33 (3H, t, *J* 6.7 Hz), 4.27 (2H, q, *J* 6.7 Hz), 6.54 (1H, s), 7.2–7.7 (Ph).

^{13}C NMR (15.03 MHz, CDCl_3): δ 14.2 (CH_3), 60.6 (CH_2), 116.4 (C-2), 127.2, 128.6, 130.7, 137.2 (Ph), 146.1 (C-3), 164.1 (C-1).

Ethyl (*E*)-3-chloro-3-phenylpropenoate (*2*). ^1H NMR (60 MHz, CDCl_3): δ 1.11 (3H, t, *J* 6.7 Hz), 4.17 (2H, q, *J* 6.7 Hz), 6.35 (1H, s), 7.4 (Ph). ^{13}C NMR (15.03 MHz, CDCl_3): δ 13.8 (CH_3), 60.6 (CH_2), 119.9 (C-2), 127.9, 128.5, 129.9, 136.6 (Ph), 149.7 (C-3), 163.7 (C-1).

General procedure for the reaction of ethyl (*Z*)- and (*E*)-3-chloro-3-phenylpropenoates with CuI catalyzed Grignard reagents. The Grignard reagent (3.0 mmol) was added dropwise using a burette (Metrohm E 485 equipped with a 50 cm³ cylinder) to a suspension of ethyl (*Z*)- β -chlorocinnamate (20 mmol) and CuI (2 mmol) in 50 cm³ anhydrous diethyl ether at 0 °C. After addition the reaction mixture was stirred at 20 °C for 2 h. The suspension was then stirred with a mixture of ice and dilute hydrochloric acid for 30 min and extracted three times with diethyl ether. The organic phase was treated with Na_2CO_3 solution then dried with Na_2SO_4 and the diethyl ether evaporated. The residue was subjected to qualitative and quantitative analyses (Table 1). The reactions of ethyl (*E*)- β -chlorocinnamate were carried out in the same manner as those of the *E*-isomer. The qualitative order of reactivity of the Grignard reagents with the *E*-isomer (*2*) was estimated by withdrawing samples from the reaction mixture held at 0 °C for 10 min. Integration of the ^1H NMR signals of the phenyl protons and the ethylenic protons allowed the determination of ethyl (*E*)-3-chloro-3-phenyl-2-propenoate consumed and the yield of reaction products. The amounts of ethyl (*E*)-3-chloro-3-phenyl-2-propenoate left in the reaction with the Grignard reagents studied were as follows (reagent, %) Me, 32; *i*-Bu, 28; Et, 27; Pr, 25; *i*-Pr, 18; *C*-pentyl, *C*-hexyl, 16; *sec*-Bu 14; *t*-Bu, 11. The order of reactivity of the Grignard reagents with the *Z*-isomer (*1*) was not determined since the reactions were completed during the course of addition of the Grignard reagents. The ^1H , ^{13}C NMR and MS data of the identified reaction products are presented below.

Ethyl (*E*)-3-phenyl-2-butenoate (*3a*). MS [IP 70 eV; *m/e* (% rel. int.)]: 190 (59, M), 175 (4), 161 (38), 145 (100, M-OC₂H₅), 144 (45), 118 (19), 117 (40), 116 (27), 115 (47), 105 (4), 103 (4), 102 (4), 91 (16).

^1H NMR (59.75 MHz, CDCl_3): 1.1 (3H, t, *J* 6.2 Hz), 2.5 (3H, d, *J* 1.3 Hz), 4.1 (2H, q, 6.2 Hz), 6.17 (1H, q, *J* 1.3 Hz), 7.2–7.5 (5H).

^{13}C NMR (15.03 MHz, CDCl_3): δ 14.4 (CH_3), 17.8 (C-4), 59.7 (CH_2), 117.2 (C-2), 126.3, 128.6, 129.0, 142.4 (Ph), 155.4 (C-3), 166.6 (C-1); *J* (C-2, H-4) 4.6 Hz, *J* (C-4, H-2) 7.8 Hz.

Ethyl (*E*)-3-phenyl-2-pentenoate (*3b*). MS [IP 70 eV; *m/e* (% rel. int.)]: 204 (100, M), 176 (11), 175 (13), 159 (70), 158 (99), 131 (22), 129 (35),

115 (23), 91 (31).

^1H NMR (59.75 MHz, CDCl_3): δ 1.0 (3H, t, J 7.0 Hz), 1.3 (3H, t, J 6.5 Hz), 3.1 (2H, q, d, J 7.0 and 0.6), 4.2 (2H, q, J 6.5 Hz), 6.0 (1H, t, J 0.6 Hz), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 13.4 (C-5), 14.3 (CH_3), 24.4 (C-4), 59.7 (CH_2), 116.9 (C-2), 126.7, 128.5, 128.8, 141.3 (Ph), 161.9 (C-3), 166.4 (C-1); J (C-2, H-4) 4.4 Hz.

Ethyl (E)-3-phenyl-2-hexenoate (3c). MS [IP 70 eV; m/e (% rel. int.)]: 218 (100, M), 203 (13), 190 (13), 189 (16), 173 (64), 157 (38), 131 (35), 129 (40), 115 (31), 91 (31).

^1H NMR (59.75 MHz, CDCl_3): δ 0.9 (3H, t, J 7.0 Hz), 1.1 (3H, t, J 6.5 Hz), 1.4 (2H, m), 3.1 (2H, t, d, J 7.0 and 0.6 Hz), 4.2 (2H, q, J 6.5 Hz), 6.1 (1H, t, J 0.6 Hz), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 14.0 (C-6), 14.2 (CH_3), 22.3 (C-5), 32.9 (C-4), 59.6 (CH_2), 116.9 (C-2), 126.7, 128.6, 129.2, 141.3 (Ph), 163.5 (C-3), 166.4 (C-1), J (C-2, H-4) 4.4 Hz.

Ethyl (E)-4-methyl-3-phenyl-2-pentenoate (3d). MS [IP 70 eV; m/e (% rel. int.)]: 218 (100, M), 190 (8), 189 (11), 175 (5), 173 (43), 172 (53), 145 (73), 143 (37), 131 (20), 129 (34), 128 (22), 91 (25), 77 (20), 43 (15).

^1H NMR (59.75 MHz, CDCl_3): 1.09 (6H, d, J 7.1 Hz), 1.29 (3H, t, J 7.1 Hz), 4.15 (1H, sept, J 7.1 Hz), 4.19 (2H, q, J 7.1 Hz), 5.7 (1H, d, J 0.6 Hz), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 14.3 (CH_3), 21.4 (C-5), 29.6 (C-4), 59.6 (CH_2), 118.6 (C-2), 127.3, 127.5, 127.7, 141.0 (Ph), 166.1 (C-3), 166.4 (C-1); J (C-2, H-4) 3.9 Hz.

Ethyl (E)-5-methyl-3-phenyl-2-hexenoate (3e). MS [IP 70 eV; m/e (% rel. int.)]: 232 (62, M), 217 (30), 203 (8), 190 (33), 189 (43), 187 (63), 171 (64), 161 (33), 145 (100), 144 (62), 143 (62), 131 (33), 129 (39), 128 (28), 118 (59), 117 (43), 116 (37), 115 (79), 91 (40).

^1H NMR (59.75 MHz, CDCl_3): δ 0.87 (6H, d, J 6.5 Hz), 1.3 (3H, t, J 7.1 Hz), 1.67 (1H, sept), 3.1 (2H, dd, J 7.1 and 0.5 Hz), 4.2 (2H, q, J 6.5 Hz), 6.1 (1H, t, J 0.5 Hz), 6.9–7.2 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 14.4 (CH_3), 22.4 (C-6), 27.9 (C-5), 38.9 (C-4), 59.8 (CH_2), 118.6 (C-2), 126.8, 128.5, 128.7, 141.8 (Ph), 160.1 (C-3), 166.6 (C-1), J (C-2, H-4) 4.4 Hz.

Ethyl (E)-4-methyl-3-phenyl-2-hexenoate (3f). MS [IP 70 eV; m/e (% rel. int.)]: 232 (85, M), 217 (18), 187 (50), 171 (58), 159 (51), 157 (50), 145 (42), 144 (51), 143 (58), 131 (53), 129 (100), 117 (64), 115 (57), 105 (51), 91 (85).

^1H NMR (59.75 MHz, CDCl_3): δ 1.0 (3H, t, J 7.1 Hz), 1.2 (3H, d, J 7.2 Hz), 1.3 (3H, t, J 6.5 Hz), 1.5 (2H, m), 3.8 (1H, m) 4.2 (2H, q, J 6.5 Hz), 5.75 (1H, d, J 0.5 Hz), 7.3 (5H), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 12.3 (C-6), 14.3 (CH_3), 19.2 (CH_3), 28.2 (C-5), 36.6 (C-4), 59.8 (CH_2), 119.7 (C-2), 127.7, 141.0 (Ph), 166.0 (C-3), 166.3 (C-1), J (C-2, H-4) 3.9 Hz.

Ethyl (E)-4,4-dimethyl-3-phenyl-2-pentenoate (3g). MS [IP 70 eV; m/e (% rel. int.)]: 232 (55, M), 217 (85), 203 (5), 187 (40), 175 (6), 159 (100), 102 (28).

^1H NMR (59.75 MHz, CDCl_3): δ 1.2 (9H, s), 1.3 (3H, t, J 7.1 Hz), 4.2 (2H, q, J 7.1 Hz), 5.65 (1H, s), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 14.0 (CH_3), 30.2 (C-5), 36.4 (C-4), 60.1 (CH_2), 120.4 (C-2), 126.7, 127.4, 127.5, 144.0 (Ph), 163.3 (C-3), 167.1 (C-1).

Ethyl (E)-5-methyl-3-phenyl-2-heptenoate (3h). MS [IP 70 eV; m/e (% rel. int.)]: 246 (14), 231 (4), 217 (25), 201 (20), 190 (100), 171 (25), 161 (20), 145 (29), 144 (30), 143 (23), 118 (84), 115 (32), 91 (23).

^1H NMR (59.75 MHz, CDCl_3): δ 1.3 (3H, t, J 7.1 Hz), 0.76–1.5 (9H, m), 3.2 (2H, d, J 7.4 disturbed), 4.2 (2H, q, J 7.1 Hz), 6.05 (1H, d, J 0.6 Hz), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 11.4 (C-7), 14.4 (CH_3), 18.7 (CH_3), 29.6 (C-6), 34.0 (C-5), 36.9 (C-4), 59.8 (CH_2), 118.8 (C-2), 126.8, 128.5, 141.9 (Ph), 160.2 (C-3), 166.7 (C-1), J (C-2, H-4) 4.4 Hz.

Ethyl (E)-3-cyclopentyl-3-phenyl-2-propenoate (3i). MS [IP 70 eV; m/e (% rel. int.)]: 244 (100, M), 227 (4), 216 (9), 215 (9), 199 (35), 198 (21), 197 (23), 171 (35), 170 (39), 157 (18), 141 (20), 129 (39), 115 (18), 91 (52).

^1H NMR (59.75 MHz, CDCl_3): δ 1.3 (3H, t, J 7.0 Hz), 1.5–1.9 (9H, broad), 4.2 (2H, q, J 7.0 Hz), 5.7 (1H, d, J 0.7 Hz), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 14.35 (CH_3), 25.3, 31.5 (C-pent.), 41.8 (C-4), 59.8 (CH_2), 119.4 (C-2), 127.5, 127.7, 141.2 (Ph), 164.96 (C-3), 166.4 (C-1), J (C-2, H-4) 3.9 Hz.

Ethyl (E)-3-cyclohexyl-3-phenyl-2-propenoate (3j). MS [IP 70 eV; m/e (% rel. int.)]: 258 (100, M), 213 (13), 211 (16), 185 (29), 183 (25), 170 (25), 167 (15), 141 (21), 131 (23), 129 (25), 117 (25), 115 (16), 91 (46).

^1H NMR (59.75 MHz, CDCl_3): δ 1.3 (3H, t, J 7.0 Hz), 1.2–1.4 (11H, broad), 4.2 (2H, q, J 7.0 Hz), 5.7 (1H, d, J 0.6 Hz), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): 14.2 (CH_3), 25.9, 26.4, 31.6 (CH_2 C-hexyl), 40.5 (C-4), 59.6 (CH_2), 118.6 (C-2), 127.2, 127.5, 127.6, 141.4 (Ph), 166.1 (C-3), 166.8 (C-2), J (C-2, H-4) 4.4 Hz.

The corresponding *Z*-isomers were not isolated. Their ^1H and ^{13}C NMR spectra were deduced from the spectra of both isomers by comparison with the spectra of the pure *E*-

isomers. The mass spectra of the *Z*-isomers are not presented here because they did not differ to any greater extent from those of the *E*-isomers.

Ethyl (Z)-3-phenyl-2-butenolate (4a). ^1H NMR (59.75 MHz, CDCl_3): δ 1.1 (3H, t, J 6.2 Hz), 2.1 (3H, d, J 1.34 Hz), 3.8 (2H, d, J 6.2 Hz), 5.8 (1H, q, J 1.34 Hz), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 13.9 (CH_3), 27.0 (C-4), 59.7 (CH_2), 117.8 (C-2), 126.2, 128.5, 128.9, 140.9 (Ph). 155.2 (C-3), 165.7 (C-1), J (C-2, H-4) 6.3 Hz, J (C-4, H-2) 6.8 Hz.

Ethyl (Z)-3-phenyl-2-pentenoate (4b). ^1H NMR (59.75 MHz, CDCl_3): δ 1.0 (3H, t, J 7.1 Hz), 1.3 (3H, t, J 7.0 Hz), 2.4 (2H, q, d, J 7.0 and 1.3 Hz), 4.2 (2H, q, J 7.0 Hz), 5.85 (1H, t, J 1.3 Hz), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 12.1 (CH_3), 13.9 (C-5), 24.7 (C-4), 59.8 (CH_2), 116.5 (C-2), 127.1, 127.5, 128.8, 140.5 (Ph), 162.0 (C-3), 166.4 (C-1).

Ethyl (Z)-4-methyl-3-phenyl-2-pentenoate (4d). ^1H NMR (59.75 MHz, CDCl_3): δ 1.0 (3H, t, J 7.1 Hz), 1.1 (6H, d, J 7.1 Hz), 2.76 (1H, sep, J 7.1 Hz), 3.95 (2H, q, J 7.1 Hz), 5.85 (1H, d, J 1.1 Hz), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 13.9 (CH_3), 21.1 (C-5), 37.3 (C-4), 59.6 (CH_2), 115.9 (C-2), 127.3, 127.5, 127.7, 140.3 (Ph), 164.9 (C-3), 167.1 (C-1), J (C-2, H-4) 3.4 Hz.

Ethyl (Z)-5-methyl-3-phenyl-2-hexenoate (4e). ^1H NMR (59.75 MHz, CDCl_3): δ 0.87 (6H, d, J 7.0 Hz), 1.3 (3H, t, J 6.5 Hz), 1.7 (1H, m), 2.3 (2H, d, J 6.5 Hz), 4.0 (2H, q, J 6.5 Hz), 5.85 (1H, t, J 1.1 Hz), 7.2–7.5 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 14.4 (CH_3), 22.4 (C-6), 27.8 (C-5), 50.0 (C-4), 59.8 (CH_2), 118.4 (C-2), 127.2, 127.6, 127.8, 140.0 (Ph), 158.6 (C-3), 166.0 (C-1), J (C-2, H-4) 5.8 Hz.

Ethyl (Z)-4-methyl-3-phenyl-2-hexenoate (4f). ^1H NMR (59.75 MHz, CDCl_3): δ 0.9–1.6 (8H, m), 2.8 (1H, sex, J 7.1 Hz), 4.2 (2H, q, J 7.0 Hz), 5.85 (1H, d, J 1.1), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 11.6 (C-6), 13.9 (CH_3) 18.6 (CH_3), 27.5 (C-5), 44.5 (C-4), 59.7 (CH_2), 117.0 (C-2), 127.3, 127.6, 127.7, 140.1 (Ph), 163.9 (C-3), 166.4 (C-1), J (C-1, H-4) 5.4 Hz.

Ethyl (Z)-4,4-dimethyl-3-phenyl-2-pentenoate (4g). ^1H NMR (59.75 MHz, CDCl_3): δ 0.99 (3H, t, J 7.1 Hz), 1.13 (9H, s), 3.9 (2H, q, J 7.1 Hz), 6.01 (1H, s), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 13.8 (CH_3), 29.0 (C-5), 37.2 (C-4), 59.4 (CH_2), 116.3 (C-2), 127.1, 127.4, 128.3, 139.3 (Ph), 163.7 (C-3), 166.1 (C-1).

Ethyl (Z)-5-methyl-3-phenyl-2-heptenoate (4h). ^1H NMR (59.75 MHz, CDCl_3): δ 0.85–1.4 (12H, broad), 2.2–2.4 (2H, m), 4.1 (2H, q, J 7.0 Hz),

5.85 (1H, t, J 1.0 Hz), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 11.4 (C-7), 14.0 (CH_3), 18.9 (CH_3), 29.7 (C-6), 34.8 (C-5), 47.5 (C-4), 59.8 (CH_2), 118.5 (C-2), 126.8, 128.5, 140.1 (Ph), 158.2 (C-3), 166.5 (C-1).

Ethyl (Z)-3-cyclopentyl-3-phenyl-2-propenoate (4i). ^1H NMR (59.75 MHz, CDCl_3): δ 1.1 (3H, t, J 7.0 Hz), 1.4–1.9 (9H, broad), 4.1 (2H, q, J 7.0 Hz), 5.9 (1H, d, J 1.3 Hz), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 14.0 (CH_3), 24.6, 31.8 (CH_2 C-pentyl), 46.3 (C-4), 59.8 (CH_2), 115.9 (C-2), 127.1, 127.5, 127.7, 140.7 (Ph), 162.8 (C-3), 166.4 (C-2), J (C-2, H-4) 5.4 Hz.

Ethyl (Z)-3-cyclohexyl-3-phenyl-2-propenoate (4j). ^1H NMR (59.75 MHz, CDCl_3): δ 1.1 (3H, t, J 7.0 Hz), 1.2–1.4 (11H, broad), 3.9 (2H, q, J 7.0 Hz), 5.83 (1H, d, J 1.1 Hz), 7.2–7.4 (5H, broad).

^{13}C NMR (15.03 MHz, CDCl_3): δ 13.9 (CH_3), 26.0, 26.9, 30.24, 47.4 (C-hexyl), 59.6 (CH_2), 116.1 (C-2), 127.5, 127.7, 128.3, 140.6 (Ph), 164.4 (C-3), 166.8 (C-1), J (C-2, H-4) 4.4 Hz.

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