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# Stereochemistry of the Reaction of Diorganocuprate(I) Complexes Derived from Grignard Reagents with α,β-Acetylenic Esters

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Diorganocuprate(I) complexes $RCH_3CuMgX$, prepared from methylcopper and Grignard reagents (i-PrMgBr and *t*-BuMgCl) gave mainly *cis*-1,4-addition of the alkyl group originally present in the Grignard reagents and small amounts of *cis*- and *trans*-1,4-addition of the methyl group introduced by methylcopper, when they were allowed to react with ethyl propiolate and ethyl phenylpropiolate. The proportion of *cis*-1,4-addition products did not change when the reaction temperature was raised from -78 °C to room temperature. The configurations of the main reaction products from the reaction with ethyl phenylpropiolate, ethyl (*Z*)-β-isopropylcinnamate and ethyl (*Z*)-β-*t*-butylcinnamate, were established by conversion of the corresponding acids to β-isopropylindenone and β-*t*-butylindenone.

Alkylcopper, lithium diorganocuprates, organocopper-organoborane complexes and copper-catalyzed Grignard reactions have been used for conjugate addition to α,β-acetylenic acids and derivatives. The stereoselectivity of 1,4-addition has proved to be dependent on reaction temperature, the nature of the solvent and the ligands used.[1]

Ouannes and coworkers[2] have shown that the lithium ion acts as an electrophilic aid in 1,4-addition reactions of lithium dimethylcuprate in conjugated systems. The reaction was inhibited when the lithium ion in the reagent was made into a complex by a lithium selective 12-crown-ether-4. The conjugate addition was again activated when lithium iodide was added to the reaction mixture. Methylcopper has been added to phenylpropiolic acid in a stereoselective *cis* manner. Addition of methyllithium to this reaction mixture caused an isomerization of the enolate and (*E*)-β-methylcinnamic acid was obtained on protonation.[3] If the structure of lithium dimethylcuprates is a ringshaped dimer,[4] it seems natural to assume that magnesium diorganocuprates will have somewhat different properties than lithium diorganocuprates. The stereochemistry of conjugate addition to α,β-acetylenic esters has not been fully studied. The role of different metals in stabilizing the anionic intermediate has been particularly neglected.

In our studies of conjugate addition of magnesium diorganociprate(I) complexes prepared from methylcopper and alkyl or aryl Grignard reagents, we were also encouraged to examine the synthetic use of these reagents for the preparation of stereospecific α,β-unsaturated esters. Methylcopper was chosen as copper carrier since it reacts equally well with primary, secondary, tertiary and aryl Grignard reagents to form magnesium diorganocuprate(I) complexes in good yield. These reagents mainly transfer the alkyl or aryl group originally present in the Grignard reagent by conjugate addition and transfer to a lesser degree the methyl group originally present in methylcopper.[5] The same selectivity has been observed in alkylation reactions of alkyl halides [6] and of acyl chlorides.[7]

## RESULTS AND DISCUSSION

Grignard reagent derived diorganocuprate(I) complexes were made according to eqns. 1–3.

$$CH_3I + 2Li \xrightarrow{\text{diethyl ether}} CH_3Li + LiI \qquad (1)$$

$$CH_3Li + CuI \xrightarrow[0\,^\circ C]{\text{diethyl ether + THF}} CH_3Cu + LiI \qquad (2)$$

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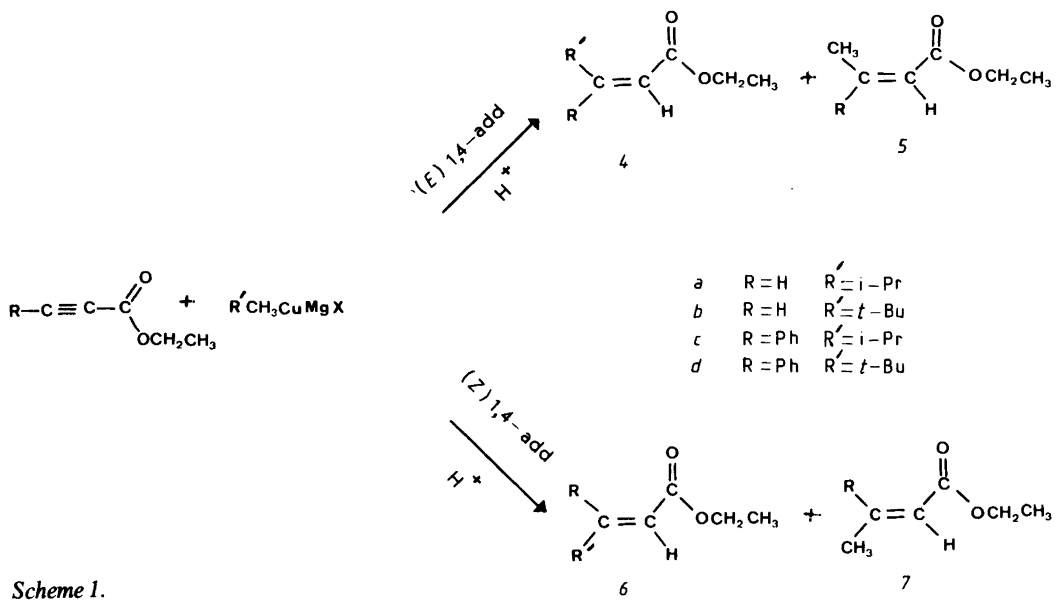


*Scheme 1.*

$$CH_3Cu + RMgX \xrightarrow[-78\,^\circ C]{\text{diethyl ether}} CH_3RCuMgX \qquad (3)$$

R'MgX = *t*-BuMgCl and i-PrMgBr

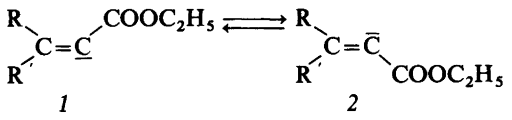
The magnesium diorganocuprate(I) complexes were prepared at −78 °C because the reaction mixture turned black on warming already at −30 °C. The formation of the final orange coloured complexes took about 3 h. After a negative Gilman test[8] they were reacted in 10 % excess with ethyl propiolate or ethyl phenylpropiolate at −78 °C. The reaction temperature was allowed ro reach room temperature after which the reaction mixture was worked up and analyzed by GLC and the reaction products identified by combined GLC−MS and, after separation, by $^1H$ and $^{13}C$ NMR spectroscopy.

The reaction is described in Scheme 1. The configuration of some of the reaction products was determined, in addition to spectroscopic methods, by stereospecific synthesis also. Samples were taken at different temperatures and worked up for GLC-analysis to check when the reactions started and if there was an isomerization when the reaction temperature was raised. The reactions with ethyl phenylpropiolate did not start at −78 °C. All original material was still unchanged after 10 h at that temperature. The reaction started at a temperature above −50 °C, while the reactions with ethyl propiolate were complete after 1 h at −78 °C. The ratio of *cis*- and *trans*-addition products did not change in any of the reactions when the temperature was allowed to rise to room temperature. The results presented in Table 1 show that 1,4-addition is the only reaction

*Table 1.* Yields of the reaction products formed in the reactions between R'$CH_3$CuMgX and R−C≡C−$COOCH_2CH_3$ as determined by GLC.

| Reagent R'$CH_3$CuMgX R' | Substrate R−C≡C−$COOCH_2CH_3$ R | Addition of R' | | Addition of $CH_3$ | | Total yield/ % |
|---|---|---|---|---|---|---|
| | | (*Z*)−1,4 Yield/ % | (*E*)−1,4 Yield/ % | (*Z*)−1,4 Yield/ % | (*E*)−1,4 Yield/ % | |
| *t*-Bu | Ph | 65 | – | 12 | 23 | 73 |
| i-Pr | Ph | 85 | 2 | 5 | 8 | 76 |
| *t*-Bu | H | 94 | 1 | 5 | – | 70 |
| i-Pr | H | 96 | 1 | 3 | – | 69 |

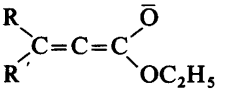
taking place and that the alkyl groups which originate from the Grignard reagents are added in a stereoselective *cis* manner. The methyl group originally present in methylcopper did not react in the same stereospecific manner as the bulky alkyl groups which originated from the Grignard reagents. This can be due to different reaction mechanisms.[9,10] The cuprate reagent can also be composed of several species which react with different stereoselectivity.[11,12] In a previous study we reacted the same esters with i-PrMgBr and *t*-BuMgCl without and in the presence of copper(I) iodide and found that the amount of 1,4-addition was small with pure Grignard reagents.[13] Copper(I) iodide increased the proportion of 1,4-addition, but the stereoselectivity was low. Moreover, *trans*-addition was the main reaction. The results indicate that different anionic intermediates may be present in the reactions with copper(I) iodide catalyzed Grignard reagents and with Grignard reagent derived diorganocuprates(I). In the reactions with the latter reagents anions *1* and *2* may be present.



*1* *2*

The anionic intermediate *1* can be in equilibrium with *2*. The equilibration of these anions has proved to be fast already at −20 °C when acetylenic esters react with lithium diorganocuprates.[14]

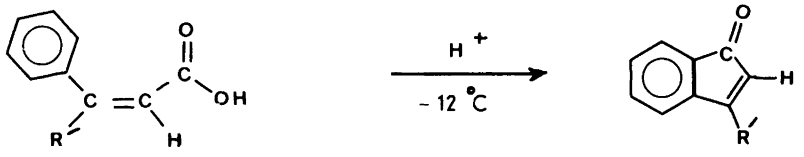
The stereochemical purity of the reactions in the present investigation did not change even at room temperature which indicates that anion *1* may be the dominating intermediate, and that the stability of that intermediate can be due to a partially covalent bond between carbon and a copper-magnesium complex. In the reactions with copper(I) iodide catalyzed Grignard reagents anion *3* may be present and the course of the reaction is then dependent on sterical factors in the protonation step.



*3*

The configurations of the main reaction products in the reaction with ethyl propiolate, ethyl (*E*)-4,4-dimethyl-2-pentenoate (*6b*) and ethyl (*E*)-4-methyl-2-pentenoate (*6a*), were determined primarily from the $^1$H NMR chemical shift values of their olefinic protons. The configurations of ethyl (*Z*)-*β*-isopropylcinnamate (*6c*) and ethyl (*Z*)-*β*-*t*-butylcinnamate (*6d*) could, however, not be determined by $^1$H NMR spectroscopy. These reaction products were hence synthesized by an alternative reaction to get both *Z*- and the *E*-isomers. A mixture of ethyl (*E*)- and (*Z*)-3-chloro-3-phenylpropenoate (1:5) was reacted with i-PrMgBr and *t*-BuMgCl, respectively, in diethyl ether at 0 °C in the presence of copper(I) iodide. This reaction gave almost quantitatively a 1:10 mixture of the corresponding ethyl (*Z*)- and (*E*)-*β*-alkylcinnamates. The *Z*-isomer, which has the ethoxycarbonyl group and chlorine on the same side of the double bond reacted faster than the *E*-isomer. The *Z*- and *E*-isomers were then identified by converting the *Z*-isomers to the corresponding indenone derivatives according to Scheme *2*.

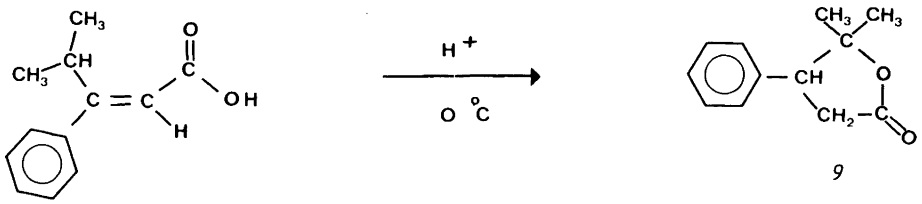
A mixture of the acids from (*4d*) and (*6d*) gave 3-*t*-butylindenone when they were treated with concentrated sulfuric acid for 5 min at −12 °C. There was no isomerization in these reactions. This was controlled by using 2-methoxybenzoic acid as an internal standard in the reaction. The configurations were thus unambiguously determined. The $^1$H NMR absorption of the olefinic proton of the *E*-isomer was upfield (*δ* 5.66) compared to the corresponding values of the *Z*-isomer (*δ* 6.01). However, according to calculated values[15] the *E*-isomer should resonate at lower field (*δ* 6.13) compared with the *Z*-isomer (*δ* 5.76). The calculated



*8*

*a* R′ = i-Pr
*b* R′ = *t*-Bu

*Scheme 2.*




9

*Scheme 3.*

values could here lead to the wrong stereochemical assignment. When the same indenone reaction was carried out with the corresponding isopropyl derivatives (acids from *4c* and *6c*) 3-isopropylindenone was formed. The $^1$H NMR signal of the olefinic proton of the *E*-isomer was at higher field ($\delta$ 5.69) compared to the corresponding values of the *Z*-isomer ($\delta$ 5.85) and again contrary to calculated values.

It is of interest that a lactone (4,4-dimethyl-3-phenyltetranolide *9*) was formed in almost quantitative yield when the pure *E*-isomer was treated with concentrated sulfuric acid for 5 h at 0 °C.

## EXPERIMENTAL

All reactions of air and water sensitive organometallics were carried out in dry glassware under purified nitrogen. The solvents were distilled from a mixture of benzophenone and sodium prior to use. Grignard reagents and methyllithium were made in 1 l reagent bottles and added in different experiments using a multi-burette (Metrohm E 485) equipped with a 50 cm$^3$ cylinder. The concentration of lithium and Grignard reagents were determined by standard titrations. The magnesium turnings were synthetical grade from Merck. Copper(I) iodide was synthesized according to Kauffman[16] or purchased from Fluka and recrystallized before use. The reaction mixtures were worked up by a saturated ammonium chloride solution and dried over sodium sulfate. A Varian 1400 gas chromatograph equipped with a 0.2 mm × 50 m glass capillary column (stationary phase SE-30) was used for GLC analyses. $^1$H NMR spectra were recorded on a Perkin Elmer R 12 A or on a Jeol FX-60 spectrometer, $^{13}$C NMR spectra on a Jeol FX-60 spectrometer and mass spectra on an LKB 9000 spectrometer equipped with a capillary column GLC system. The main reaction products were distilled on a spinning band distillation system (Perkin Elmer, Auto annular still). *Ethyl phenylpropynoate* was synthesized according to Abbot.[17]

*General procedure for the preparation of magnesium alkylmethylcuprates(I) as illustrated by the preparation of $CH_3$-t-BuCuMgCl.* The Grignard reagent was prepared from *t*-butyl chloride and magnesium turnings in diethyl ether. Methylcopper was prepared separately in all experiments in a 250 cm$^3$, four-necked flask equipped with an overhead stirrer and lowtemperature thermometer by the reaction of a suspension of 5.25 g (27.5 mmol) of copper(I) iodide in 30 cm$^3$ THF and 29.6 cm$^3$ of a 0.93 N (27.5 mmol) ether solution of methyllithium at −78 °C. When the reaction mixture showed a negative Gilman test,[8] 13.4 cm$^3$ of a 2.02 N (27.5 mmol) Grignard reagent was added. The reaction mixture was then kept at −78 °C through stirring until the Gilman test was again negative which usually took about 3 h.

*General procedure for the reaction of ethyl phenylpropynoate with magnesium alkylmethylcuprates (I).* A solution of 2.65 g (15.2 mmol) ethyl phenylpropynoate in 50 cm$^3$ ether was added to the copper (I) complex (16.7 mmol). The reaction mixture was kept at −78 °C for several hours. Samples were taken at one hour intervals with a syringe. The samples were worked up by standard methods and then analyzed by GLC. There was no reaction at −78 °C. The reaction mixture was allowed to heat up. The reaction was very slow below −50 °C and complete at −10 °C. In order to check if any isomerization occured at higher temperatures the reaction mixture was allowed to reach room temperature. There was no isomerization. The main reaction products *6d* and *6c* were isolated in almost pure form by distillation. The methyl 1,4-addition products *5c* and *7c* could not be separated, but they were easily identified from their $^1$H NMR and mass spectra.

*Ethyl (Z)-4,4-dimethyl-3-phenyl-2-pentenoate (6d).* $^1$H NMR (60 MHz, $CDCl_3$): 0.99 ($CH_3CH_2-$, t, *J* 7.1 Hz), 1.13 [$(CH_3)_3C-$, s], 3.9 ($CH_3CH_2-$, q, *J* 7.1 Hz), 6.01 [(C=CH, α) s]. MS [IP 70 eV; *m/e* (% rel. int.)]: 232 (55, M), 217 (80, M−$CH_3$), 203 (9, M−$CH_2CH_3$), 287 (43, M−$OCH_2CH_3$), 175 [9, M−$(CH_3)_3C$], 159 (100, M−$COOCH_2CH_3$), 102 [35, M−$COOCH_2CH_3$ and $(CH_3)_3C$].

*Ethyl (Z)-3-phenyl-2-butenoate (7c).* $^1$H NMR (60 MHz, $CDCl_3$): 1.0 ($CH_3CH_2-$, t, *J* 6.2 Hz), 2.1 ($CH_3-C=CH-$, d, *J* 1.5 Hz), 3.8 ($CH_3CH_2-$, q, *J* 6.2 Hz), 5.8 [(C=CH,α), q, *J* 1.5 Hz].

*Ethyl (E)-3-phenyl-2-butenoate (5c).* $^1$H NMR (60 MHz, $CDCl_3$): 1.1 ($CH_3-$, t, $J$ 6.2 Hz), 2.5 ($CH_3-$, d, $J$ 1.5 Hz), 4.1 ($CH_3CH_2-$, q $J$ 6.2 Hz), 6.1 [(C=C*H*, α), q, $J$ 1.5 Hz)].

Ethyl *(Z)-4-methyl-3-phenyl-2-pentenoate (6c).* $^1$H NMR (60 MHz, $CDCl_3$): 1.0 ($CH_3CH_2-$, t, $J$ 7.1 Hz), 1.1 [$(CH_3)_2CH-$, d, $J$ 7.1 Hz], 2.76 [$(CH_3)_2CH-$, sept. $J$ 7.1 Hz], 3.95 ($CH_3CH_2-$, q, $J$ 7.1 Hz), 5.85 [(C=C*H*, α), d, $J$ 1.2 Hz)]. MS [IP 70 eV; *m/e* (% rel. int.)]: 218 (100, M), 190 (8, M−28), 189 (8, M−$CH_2CH_3$), 175 [4, M−$(CH_3)_2CH$], 173 (39, M−$OCH_2CH_3$), 172 (52), 145 (68, M−$COOCH_2CH_3$), 143 (37), 131 (19), 129 (34), 128 (21), 91 (25), 77 (17), 43 (11).

The corresponding *E*-isomer (*4c*) was not isolated. It was identified by comparing its mass spectrum with the spectrum of the same substance isolated from the reaction between i-PrMgBr and ethyl β-chlorocinnamate.

*General procedure for the reaction of ethyl propiolate with magnesium alkylmethylcuprates(I).* The reactions were carried out in the same manner as the corresponding reactions with ethyl phenylpropynoate. The reactions with ethyl propiolate were, however, much faster and were complete after 2 h at −78 °C. No isomerisation took place when the temperature of the reaction mixtures was allowed to reach room temperature. The main reaction products *6b* and *6a* were isolated by distillation and the methyl 1,4-addition products were identified from their mass spectra.

*Ethyl (E)-4,4-dimethyl-2-pentenoate (6b).* $^1$H NMR (60 MHz, $CDCl_3$): 1.0 [$(CH_3)_3C-$, s], 1,2 ($CH_3CH_2-$, t, $J$ 6.6 Hz), 4.1 ($CH_3CH_2-$, q, $J$ 6.6 Hz), 6.9 [(β, C*H*=CH), d, $J$ 1.5 Hz], 5.6 [(CH=C*H*, α), d, $J$ 1.5 Hz]. MS [IP 70 eV; *m/e* (% rel. int.)]: 155 (61, M−H), 154 (81, M−$H_2$), 141 (71, M−$CH_3$), 140 (84, M−H and $CH_3$), 127 (78, M−$CH_2CH_3$), 111 (100, M−$OCH_2CH_3$), 99 [99, M−$(CH_3)_3C$], 95 (87), 83 (99, M−$COOCH_2CH_3$), 57 [76, $(CH_3)_3C$].

*Ethyl (E)-4-methyl-2-pentenoate (6a).* $^1$HMR (60 MHz, $CDCl_3$): 1.05 [$(CH_3)_2CH-$, d, $J$ 6.2 Hz], 1.25 ($CH_3CH_2-$, t, $J$ 6.6 Hz), 4.2 ($CH_3CH_2-$, q, $J$ 6.6 Hz), 2.4 [$(CH_3)_2CH-$, m], 5.7 [(CH=C*H*, α), q, $J$ 15.7 Hz], 6.8 [(β, C*H*=CH), q, $J$ 15.7 Hz]. MS [IP 70 eV; *m/e* (% rel. int.)]: 142 (84, M), 128 (31, M−$CH_2$), 115 (84), 114 (78, M−$CH_2CH_2$), 99 [82, M−$(CH_3)_2CH$], 97 (100, M−$OCH_2CH_3$), 69 (83, M−$COOCH_2CH_3$).

*Ethyl (E)-2-butenoate (7a).* MS [IP 70 eV; *m/e* (% rel. int.)]: 114 (28, M), 99 (79, M−$CH_3$), 86 (65, M−$CH_2CH_2$), 69 (100, M−$OCH_2CH_3$), 41 (65, M−$COOCH_2CH_3$).

*General procedure for the reaction of ethyl (Z)- and (E)-3-chloro-3-phenylpropenoate with copper (I) iodide catalyzed Grignard reagents as illustrated by the reaction of* t-*BuMgCl.* Copper(I) iodide 0.381 g (2 mmol) was added to 4.22 g (20 mmol) of a mixture of 22 % (*E*) and 78 % (*Z*) ethyl 3-chloro-3-phenyl-2-propenoate in 50 cm$^3$ diethyl ether. The suspension was stirred for half an hour at 0 °C, after which 17 cm$^3$ of a 1.3 N (22 mmol) *t*-BuMgCl solution in diethyl ether was added gradually during half an hour. The reaction mixture was then stirred without cooling for 3 h. After hydrolysis of the reaction mixture with a saturated ammonium chloride solution, the organic phase was extracted with diethyl ether and dried with sodium sulfate. The total yield of ethyl (*Z*)- and (*E*)-4,4-dimethyl-3-phenyl-2-pentenoate was almost quantitative. The *E*-isomer was isolated by distillation on a spinning band distillation system but the *Z*-isomer which was formed in lower yield (12 %) could not be completely separated from the *E*-isomer.

*Ethyl (E)-4,4-dimethyl3-phenyl-2-pentenoate (4d).* $^1$H NMR (60 MHz, $CDCl_3$): 1.23 [$(CH_3)_3C-$, s], 1.3 ($CH_3CH_2-$, t, $J$ 7.1 Hz), 4.18 ($CH_3CH_2-$, q, $J$ 7.1 Hz), 5.65 [(C=C*H*, α), s]. MS [IP 70 eV; *m/e* (% rel. int.)]: 232 (58, M), 217 (85, M−$CH_3$), 203 (5, M−$CH_2CH_3$), 287 (40, M−$OCH_2CH_3$), 175 [6, M−$(CH_3)_3C$], 159 (100, M−$COOCH_2CH_3$), 102 [28, M−$COOH_2CH_3$ and $(CH_3)_3C$].

*Ethyl (E)-4-methyl-3-phenyl-2-pentenoate (4c).* $^1$H NMR (60 MHz, $CDCl_3$): 1.09 [$(CH_3)_2CH-$, d, $J$ 7.1 Hz], 1.29 ($CH_3CH_2-$, t, $J$ 7.1 Hz) 4.15 [$(CH_3)_2CH-$, sept, $J$ 7.1], 4.19 ($CH_3CH_2-$, q, $J$ 7.1 Hz), 5.7 [(C=C*H*, α), d, $J$ 0.6 Hz]. MS [IP 70 eV; *m/e* (% rel.int.)]: 218 (100, M), 190 (8, M−$CH_2CH_2$), 189 (11, M−$CH_2CH_3$), 175 [5, M−$(CH_3)_2CH$], 173 (43, M−$OCH_2CH_3$), 172 (53), 145 (73, M−$COOCH_2CH_3$), 143 (37), 131 (20), 129 (34), 128 (22), 91 (25), 77 (20), 43 (15).

*General procedure for the saponification of ethyl (Z)- and (E)-t-butyl- and isopropylcinnamates.* The esters (2.5 g) in a mixture of water (1 cm$^3$), ethanol (5 cm$^3$) and NaOH (1 g) were refluxed for 2 h. After acidification the crude acids crystallized. The acids were purified by recrystallization from hexan.

*(E)-4,4-dimethyl-3-phenyl-2-pentenoic acid (4d acid).* $^1$H NMR (60 MHz, $CDCl_3$): 1.23 [$(CH_3)_3C-$, s], 5.66 [(C=C*H*, α), s], 11.4 (OH−, s).

*(Z)-4,4-dimethyl-3-phenyl-2-pentenoic acid (6d acid).* $^1$H NMR (60 MHz, $CDCl_3$): 1.19 [$(CH_3)_3C-$, s], 6.01 [(C=C*H*, α), s], 11.4 (OH−, s).

*(E)-4-methyl-3-phenyl-2-pentenoic acid (4c acid).* $^1$H NMR (60 MHz, $CDCl_3$): 1.07 [$(CH_3)_2CH-$, d, $J$ 7.1 Hz], 4.16 [$(CH_3)_2CH-$, sept, $J$ 7.1 Hz], 5.69 [(C=C*H*, α), d, $J$ 0.6 Hz], 11.4 (OH−, s).

*(Z)-4-methyl-3-phenyl-2-pentenoic acid (6c acid).* $^1$H NMR (60 MHz, $CDCl_3$): 1.07 [$(CH_3)_2CH-$, d, $J$ 7.1 Hz], 2.67 [$(CH_3)_2CH-$, sept, $J$ 7.1 Hz], 5.85 [(C=C*H*, α), d, $J$ 1.1 Hz], 11.5 (OH−, s).

*General procedure for determination of the stereo-*

*chemical structures of 3-alkyl-3-phenyl-2-pentenoic acids as illustrated for (Z)- and (E)-4,4-dimethyl-3-phenyl-2-pentenoic acids.* A mixture of (*Z*)- and (*E*)-4,4-dimethyl-3-phenyl-2-pentenoic acids (100 mg) and 2-methoxybenzoic acid (80 mg, as internal standard) was treated with 4 $cm^3$ concentrated sulfuric acid for 5 min at −12 °C. The reaction mixture was poured into ice and extracted with diethyl ether. The organic phase was dried over sodium sulfate and the diethyl ether evaporated. The residue was subjected to $^1H$ NMR analysis. The intensity of the olefinic proton signal of (*Z* or *E*) 4,4-dimethyl-3-phenyl-2-pentenoic acid at $\delta$ 6.01 decreased in comparison with the intensity of the corresponding signal of the original acid mixture while the intensity of the signal at $\delta$ 5.66 was unchanged. A new signal was found at $\delta$ 5.58 and shown to belong to 3-*t*-butylindenone which can only be formed from the *Z*-isomer where the phenyl and the carboxy group are on the same side of the double bond. Thus the signal at lower field ($\delta$ 6.01) belongs to the *Z*-isomer and the absorption at higher field ($\delta$ 5.66) to the *E*-isomer. The reaction product 3-*t*-butylindenone was separated from the acids by extracting it with diethyl ether from an alkaline solution.

*3-t-Butylindenone (8b).* $^1H$ NMR (60 MHz, $CDCl_3$): 1.31 [$(CH_3)_3C-$, s], 5.58 ($C=CH$, $\alpha$). MS [IP 70 eV; *m/e* (% rel. int.)]: 186 (89, M), 171 (100, $M-CH_3$), 143 (45), 128 [43, M−CO and $(CH_3)_2$], 115 (16).

*3-Isopropylindenone (8a).* $^1H$ NMR (60 MHz, $CDCl_3$): 1.29 [$(CH_3)_2CH-$, d, *J* 6.7 Hz], 5.66 [($C=CH$, $\alpha$), d, *J* 1.3 Hz]. MS [IP 70 eV; *m/e* (% rel. int.)]: 172 (100, M), 157 (36, $M-CH_3$), 144, (40, M−CO), 129 [58, $M-(CH_3)_2CH$], 128 (36), 127 (15), 115 (15), 102 (9), 77 (9).

When pure (*E*)-4-methyl-3-phenyl-2-pentenoic acid (100 mg) was treated with 5 $cm^3$ concentrated sulfuric acid for 5 h at 0 °C compound *9* was formed in almost quantitative yield.

*4,4-Dimethyl-3-phenyltetranolide (9).* $^1H$ NMR (60 MHz, $CDCl_3$): 1.04 ($CH_3C-$, s), 1.55 ($CH_3C-$, s), 2.93 ($CHCH_2-$, q, *J* 9.3 Hz), 3.55 ($CHCH_2-$, q, *J* 9.3 Hz). MS [IP 70 eV; *m/e* (% rel. int.)]: 190 (16, M), 175 (20, $M-CH_3$), 162 (46, M−CO), 132 (10), 131 (11), 104 (100, $Ph-CH=CH_2$), 91 (10), 78 (19), 77 (18), 43 (16).

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