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A Facile Method for Synthesis of Three Carbon-Homologated Carboxylic Acid by Regioselective Ring-opening of β-Propiolactones with Organocopper Reagents[†]

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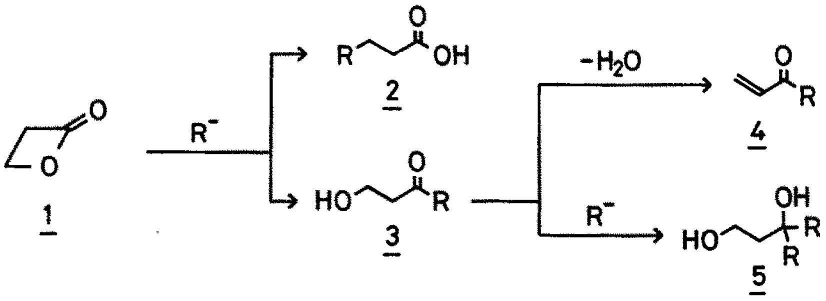
Abstract: Organocopper reagents, such as diorganocuprates, organocopper-tributylphosphine, and Grignard reagents in the presence of a copper (I) salt, reacted with β-propiolactones by regioselective β-carbon-oxygen fission to give 3-substituted propionic acids. Among these three kinds of organocopper reagents, diorganocuprate, especially halomagnesium cuprate gave the highest yields of the acids, which was remarkably observed in the ring-opening of sterically hindered β-propiolactones such as β-methyl- and α,β -dimethyl- β -propiolactones and also in the reactions using the organocopper reagents with vinyl and allyl substituents. The ring-opening of β-propiolactone was confirmed to proceed by S_N2 pathway with predominant inversion of configuration of the β-carbon by using the reaction of cis-α,β-dimethyl- β -propiolactone with di-tert-butylcuprate to afford syn-2,3,4,4-tetramethylpentanoic acid.

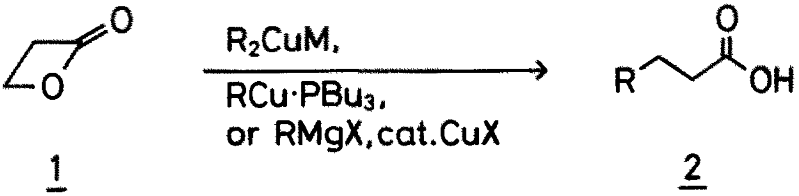
β-Lactones are strained four-membered heterocyclic compounds. Because of their high reactivity, there are many reports on reactions such as polymerization to polyester,[1] pyrolysis to alkenes,[2] and nucleophilic ring-opening.[3] Among the reactions, ring-opening of β-propiolactone (1) using organometallics has been received much attention as three carbon homologation reaction, however, the reactions give different products by the kinds of organometallic reagents. Nucleophilic attack of the organometallics to β-carbon and to carbonyl carbon of the lactone gives 3-substituted propionic acid 2 and β-hydroxycarbonyl compound 3, respectively. Moreover in the latter case, generally it is followed by spontaneous dehydration to the product 4 or further addition of the nucleophile leading to dihydroxy compound 5, although selective synthetic method of β-hydroxyketone using reaction with dilithio sulfone was reported.[4] For example, phenyllithium reacts with the lactone to afford phenyl vinyl ketone and 1,1-diphenyl-1,3-propanediol.[5] Phenylmagnesium bromide gives phenyl vinyl ketone.[6] On the contrary, diphenylzinc and diphenylcadmium give 3-phenylpropionic acid as a major product.[5] These reactions indicate also possibility of the use of a "soft" organometallic compound to afford 3-substituted propionic acid. In fact, ring-opening of 1 with organotin compound has been explained by the HSAB principle.[7] Therefore as the "soft" organometallics,[8] organocopper reagents,[9] which are well known as



[†] Dedicated to Professor E. J. Corey on the occasion of his 60th birthday.

effective reagents for conjugate addition and nucleophilic substitution, are noticed to examine the reaction with β-propiolactone. The present paper shows details on the regioselective ring-opening of β-propiolactones with organocopper reagents, such as diorganocuprates, organocopper-tributylphosphine, and Grignard reagents in the presence of a catalytic amount of copper (I) salt, to afford various kinds of 3-substituted propionic acids[10] which can not be easily obtained by conjugate addition of organocopper reagents to acrylic acid derivatives.[11]

When β-propiolactone (1) was treated with Bu_2CuLi, prepared from 2 equivalents of butyllithium and 1 equivalent of copper (I) iodide, in THF at -30 - 0 °C, heptanoic acid (2b) was obtained in 83% yield without any accompanying product attributed to acyl carbon-oxygen fission. The reaction was carried out also in Et_2O to afford 2b in the same yield. On the other hand, Bu_2CuMgX, prepared from 2 equivalents of butylmagnesium bromide and 1 equivalent of copper (I) iodide, gave 2b in higher yield (90%) than Bu_2CuLi in THF solvent, although the reaction in Et_2O gave only a trace amount of 2b. In the case of cyanocuprates, prepared from butyllithium and copper (I) cyanide, higher-order cuprate, $R_2Cu(CN)Li_2$ gave 2b in much higher yield (89%) than the case of low-order cuprate, BuCu(CN)Li (28%).[12] Moreover as the optimum conditions, it was found that Bu_2CuMgX in THF-Me_2S gave 2b in the highest yield (92%) since dimethyl sulfide makes a formation of halomagnesium cuprate easy by dissolving copper (I) iodide. Other halomagnesium diorganocuprates attacked also regioselectively β-carbon of 1 to afford the corresponding carboxylic acids in better yields than lithium diorganocuprates. Especially, Ph_2CuMgX gave 3-phenylpropionic acid (2d) in a high yield of 80% compared with the yield of only 20% given by the case of Ph_2CuLi. These results of superiority of halomagnesium cuprate seem to be a "softness" of the reagent and this assumption is supported by the report that halomagnesium cuprate prefers γ-alkylation than lithium cuprate in the reaction with an allylic ester.[13] In the case of thermally unstable diallyl cuprate, however, the yield of 5-hexenoic acid (2f), was decreased a little (65% yield) even in THF-Me_2S at -50 °C compared with other halomagnesium diorganocuprates. These effects toward the yields of products by the kinds of substituents on diorganocuprates have appeared also in the ring-opening of ω-alkenyllactones leading to alkenoic acids.[14] These results are summarized in Table 1.



Although, as described above, the reactions of β-propiolactone (1) with diorganocuprates afford 3-substituted propionic acids (2) in good yields, one organic group moiety in the cuprate is wasted. If monoorganocopper reagents react with lactone 1 in a manner similar to diorganocuprates, it would be a more convenient method. Actually monoorganocopper reagents such as organocopper-Lewis acid[15] and organocopper-phosphine complexes[16] have been used for conjugate addition and allylic substitution. Therefore a variety of organocopper-ligand complexes were examined for the reaction with 1. Trifluoroborane, dimethyl sulfide, and trimethyl phosphite complexes afforded a product by β-carbon-oxygen fission, 2b in poor yields, whereas $BuCu.Bu_3P$, prepared from 1 equivalent of butyllithium, 1 equivalent of copper (I) iodide, and 3 equivalents of tributylphosphine, gave 2b in a high yield of 92% in similar to the case of Bu_2CuMgX. Other molar ratios of BuCu to Bu_3P such as 1:2 and 1:4 decreased the yield of 2b. The phosphine complex was more effective in ether than in polar solvent of THF. When $BuCu.Bu_3P$ prepared from butylmagnesium bromide instead of butyllithium was used for reaction with 1, the yield of 2b was decreased to 48% yield. Eventually, it is concluded that monoorganocopper reagent with strong Lewis base ligand possesses high reactivity toward β-carbon of 1, however, reactivity is disturbed by the other ligand such as MgX_2. These results were summarized in Table 2. Table 3 shows results of reactions of organocopper-tributylphosphine complexes with 1. Organocopper-phosphine complexes with primary, secondary, tertiary alkyl, and phenyl groups gave the corresponding acids in good yields. In reactions of vinyl and allylcopper-phosphine complexes, however, the desired acids 2e,f were

Table 1. Reactions of β-Propiolactone (1) with Organocuprates[a]

R_2CuM	Solvent	Temp.,Time	Product	Yield(%)
Me_2CuLi	THF	-30 °C, 1 h → 0 °C	$CH_3(CH_2)_2CO_2H$ 2a	70
Me_2CuMgX	THF-Me_2S	-30 °C, 1 h → 0 °C	2a	86
Bu_2CuLi	THF	-30 °C, 1 h → 0 °C	$CH_3(CH_2)_5CO_2H$ 2b	83
Bu_2CuLi	Et_2O	-30 °C, 1 h → 0 °C	2b	83
Bu_2CuMgX	THF-Me_2S	-30 °C, 1 h → 0 °C	2b	92
Bu_2CuMgX	THF	-30 °C, 1 h → 0 °C	2b	90
Bu_2CuMgX	Et_2O	-30 °C, 1 h → 0 °C	2b	trace
$Bu_2Cu(CN)Li_2$	THF	-30 °C, 1 h → 0 °C	2b	89
$BuCu(CN)Li$	THF	-30 °C, 1 h → 0 °C	2b	28
t-Bu_2CuMgX	THF-Me_2S	-30 °C, 1 h → 0 °C	$(CH_3)_3C(CH_2)_2CO_2H$ 2c	88
Ph_2CuLi	THF	-30 °C, 1 h → 0 °C	$C_6H_5(CH_2)_2CO_2H$ 2d	20
Ph_2CuMgX	THF-Me_2S	-30 °C, 1 h → 0 °C	2d	80
$(CH_2=CH)_2CuMgX$	THF-Me_2S	-30 °C, 1 h → 0 °C	$CH_2=CH(CH_2)_2CO_2H$ 2e	87
$(CH_2=CHCH_2)_2CuMgX$	THF-Me_2S	-50 °C, 1 h → -20 °C	$CH_2=CH(CH_2)_3CO_2H$ 2f	65

[a] All reactions were performed on 2 mmol scales. The molar ratio of R_2CuM and 1 is 1.1:1.0. The yields were based on 1.

obtained only in low yields in contrast to the case of divinyl and diallylcuprates.

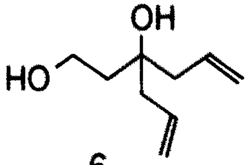
As a further convenient method, copper-catalyzed Grignard reagents, which have been used in conjugate addition and nucleophilic substitution in similar to other organocopper reagents,[17] was applied to the ring-opening of 1. Butylmagnesium bromide reacted with 1 in the presence of 2 mol% of copper (I) chloride in THF at 0 °C to give 2b in a high yield of 90%. Diethyl ether, instead of THF, decreased the yield of 2b to 50%, since an intermediate of active organocopper species is reported[18] to be halomagnesium diorganocuprates which are unstable in ether. Reactions using other copper salts such as copper (I) bromide, iodide, and cyanide all gave 2b in almost the same yields. Although homogeneous reaction was promoted by adding dimethyl sulfide, which was effective as a co-solvent of THF in the case of halomagnesium diorganocuprate, the yield of carboxylic acid was not affected in the reaction of butylmagnesium bromide in the presence of copper (I) iodide with 1. Other copper-catalyzed Grignard reagents with primary, secondary, tertiary alkyl, and phenyl groups also regioselectively attacked the lactone to give the corresponding acids in good yields similar to the reaction of halomagnesium diorganocuprates. Vinylmagnesium bromide gave 2e in a moderate yield. Although allylmagnesium bromide gave a product by acyl carbon-oxygen fission, 3-(2-

Table 2. Reactions of β-Propiolactone (1) with Butylcopper-Ligand Complexes[a]

Ligand	Molar Ratio BuCu : Ligand	Solvent	Temp.(°C)	Time(h)	Yield(%) of Heptanoic acid
BF_3	1 : 1	Et_2O	-78 → 0	1.5	44
Me_2S	1 : 7	Et_2O	-78 → 0	1.5	56
$P(OMe)_3$	1 : 2	Et_2O	-78 → 0	1.5	14
Bu_3P	1 : 2	Et_2O	-78 → 0	1.5	86
Bu_3P	1 : 2	THF	-78 → 0	1.5	73
Bu_3P	1 : 3	Et_2O	-78 → 0	1.5	92
Bu_3P	1 : 4	Et_2O	-78 → 0	1.5	34

[a] All reactions were performed on 2 mmol scales. The molar ratio of BuCu.Ligand and 1 is 1.0 : 1.0. The yields were based on 1.

propenyl)-5-hexene-1,3-diol (6) mainly without any formation of 2f, most ring-openings of 1 using copper-catalyzed reactions of Grignard reagents have some advantages, such as simplicity, short reaction times (only 15 min), and moderate reaction temperatures (0 °C) in comparison with reactions of diorganocuprates and organocopper-tributylphosphine complexes. The reactions of various Grignard reagents in the presence of copper (I) chloride with 1 were summarized in Table 3.



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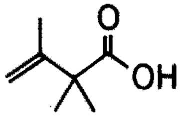

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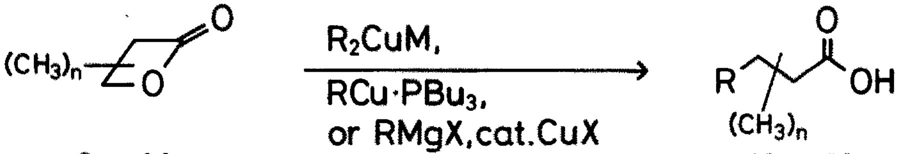
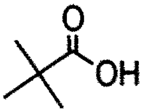
In order to find the scope and limitations of the ring-opening reactions of β-propiolactone with organocopper reagents described above, methyl-substituted β-propiolactones such as α-methyl-, β-methyl-, α,α-dimethyl-, cis-α,β-dimethyl-, and α,α,β,β-tetramethyl-β-propiolactones (8,9,10,11, and 12) were used as the substrates as shown in Table 3. The ring-opening of substituted lactones



8 ~ 11 **13 ~ 16**

using organocopper reagents with methyl and butyl groups afforded the corresponding acids generally in good yields, although the yields of the corresponding acids 14,16 were decreased into the moderate range in the cases where the lactone 9,11 was sterically hindered by β-methyl or α,β-dimethyl substituents. Using organocopper reagents containing phenyl, vinyl, or allyl groups, not only β-methyl-β-propiolactones 9,11 but also α,α-dimethyl-β-propiolactone (10) gave the corresponding acids 14,16, and 15 in poor yields. The reaction of α,α,β,β-tetramethyl-β-propiolactone (12) with halomagnesium dibutylcuprate gave 2,2,3-trimethyl-3-butenoic acid (7), which was formed by an abstraction of hydrogen atom on β-methyl group of the lactone by cuprate, in 52% yield without accompanying even a trace amount of carbon-homologated carboxylic acid. These steric and substituent effects were predominant in reactions of organocopper-phosphine complexes and copper-catalyzed Grignard reagents. In the reaction of α,α-dimethyl- and α,β-dimethyl-β-propiolactones (10,11) with di-tert-butylcuprate, reductive ring-opening products such as pivalic acid (17) and α-methylbutyric acid (18) were obtained in 70% and 35% yields, respectively. On the other hand, reaction of diallylcuprate with β-methyl-β-propiolactone (9) gave 4-(2-propenyl)-6-heptene-2,4-diol (19) in 63% yield, produced by an attack to carbonyl carbon of the lactone. Moreover reaction of 9 with copper-catalyzed vinylmagnesium bromide gave 2-hydroxy-7-octene-4-one (20), which seems to be formed by the Michael addition of Grignard reagent to initial ring-opening product, 5-hydroxy-1-hexen-3-one, and the reaction has been utilized to stereoselective synthesis of (1R,3R,5S)-1,3-dimethyl-2,9-dioxabicyclo[3.3.1]nonane.[19]



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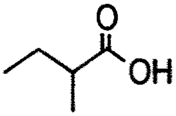

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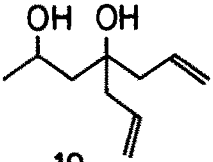

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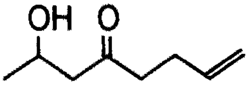

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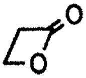
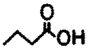
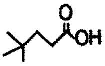
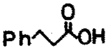
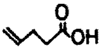
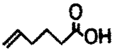
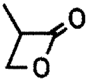
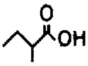
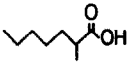
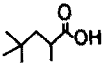
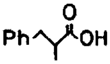
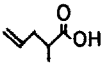
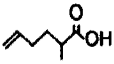
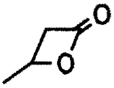
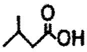
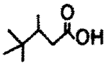
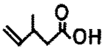
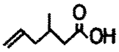
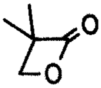
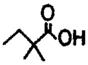
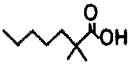
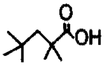
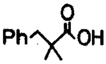
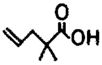
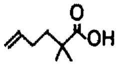
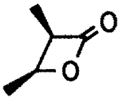
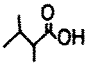
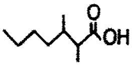
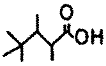
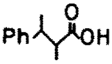
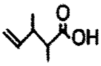
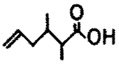
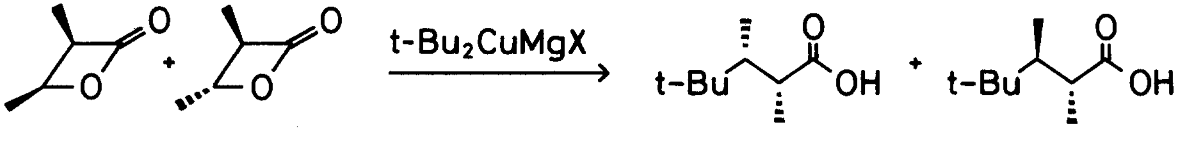
In general, substitution reactions using organocopper reagents proceed in S_N2 type. To confirm S_N2 mechanism of the ring-opening of propiolactones, reaction of a mixture of cis- and trans-α,β-dimethyl-β-propiolactone (11) (89 : 11) with t-Bu_2CuMgX was carried out under the same conditions employed for the reaction of cis-11 with t-Bu_2CuMgX described above. Methyl esters of

Table 3. Reactions of Methyl-substituted β-Propiolactones with Organocopper Reagents[a]

Lactone	Method	R = Me	Bu	t-Bu	Ph	CH_2=CH	CH_2=$CHCH_2$
	Product						
		2a	2b	2c	2d	2e	2f
	R_2CuMgX^b	86	92	88	80	87	65^c
1	$RCu.Bu_3P^d$	80	92	76	69	37	8
	RMgX,cat.CuCl^e	87	90	85	77	59	—
	Product						
		13a	13b	13c	13d	13e	13f
	R_2CuMgX^b	85	85	90	52	72	62^c
8	$RCu.Bu_3P^d$	85	92	61	67	11	8
	RMgX,cat.CuCl^e	83	88	89	52	60	—
	Product						
		14a	14b	14c	14d	14e	14f
	R_2CuMgX^b	80	89	95	11	27	0^c
9	$RCu.Bu_3P^d$	67	70	67	13	2	0
	RMgX,cat.CuCl^e	52	81	84	13	trace	—
	Product						
		15a	15b	15c	15d	15e	15f
	R_2CuMgX^b	91	82	5	3	48	17^c
10	$RCu.Bu_3P^d$	90	94	3	4	12	7
	RMgX,cat.CuCl^e	80	89	24	8	trace	—
	Product						
		16a	16b	16c	16d	16e	16f
	R_2CuMgX^b	81	82	55	6	17	0^c
11	$RCu.Bu_3P^d$	56	75	40	6	4	0
	RMgX,cat.CuCl^e	44	79	38	8	trace	—

[a] The yields were based on β-propiolactone. [b] The reactions were performed in THF-Me_2S (12:1) at -30 °C (1h) and then 0 °C (1h) unless otherwise noted. The molar ratio of R_2CuM and β-propiolactone is 1.1 : 1.0. [c] The reaction was carried out at -50 °C (1h) and then -20 °C (1h). [d] The reactions were performed in ether at -78 °C and raised to 0 °C over 1.5 h. The molar ratio of $RCu.Bu_3P$ and β-propiolactone is 1.0 : 1.0. [e] The reactions were performed in THF at 0 °C for 15 min. The molar ratio of RMgX, β-propiolactone, and CuCl is 1.2 : 1.0 : 0.02.

two diastereomers of 2,3,4,4-tetramethylpentanoic acid (16c) were compared by glpc analysis to reveal that the ester obtained from a diastereomeric mixture of 11 showed two peaks and another ester obtained from diastereomerically pure lactone showed a single peak. This result suggests that the ring-opening of lactone proceeds by a S_N2 pathway with predominant inversion of configuration. S_N2 mechanism of β-propiolactone has been also confirmed by ring-opening of an optically active lactone, (R)-9.[20] The high stereoselectivity was comparable to that of the reaction of alkyl bromide with higher-order mixed cuprate.[21] Thus, the reaction of β-propiolactones provides an effective method for the stereoselective synthesis of carboxylic acids possessing two chiral centers.



cis-11 trans-11 syn-16c anti-16c

The present ring-opening reaction of β-propiolactone by organocopper reagents involves several characteristic features including: (1) Highly regioselective reactions leading to β-substituted propionic acids in high yields along with a simplicity in operating conditions; An equimolar amount of organocopper reagents to β-propiolactones is sufficient for the completion of the reaction. The products are easily isolated by extraction of the acids with an alkaline solution followed by acidification. (2) The products are synthetic equivalent to that of conjugate addition to an α,β-unsaturated acid.[22] However, the conjugate addition to acrylic acid has not been reported yet. The reaction of α,α-disubstituted β-propiolactone can afford α,α-disubstituted carboxylic acid which can not be synthesized by the conjugate addition. Further, although 5-hexenoic acid could not be obtained by the conjugate addition of any allylcopper reagents to acrylic ester, allylation of β-propiolactone by diallylcuprate occurs readily. (3) The utility for a wide range of β-propiolactones and organocopper reagents enables the syntheses of various types of homologated carboxylic acids.

Thus, β-propiolactones can be effectively used as a synthetic route to three carbon-homologated carboxylic acids. Since the terminal carboxylic function can be easily transformed to various functional groups, the present reaction is widely applicable for natural product synthesis. For example, the copper-catalyzed reaction of 1 with a Grignard reagent containing an oxygen functionality has been applied as a key step for the synthesis of exaltolide.[23] (Z)-4-Alkenoic acids[24] and jasmonoids[25] has been synthesized by the use of reaction of di-(Z)-alkenylcuprate with 1. Both 8 and 9 has been used as a building block for terpene synthesis,[26] and optically active terpenes has been synthesized using ring-opening of (R)-9.[20] Recently the reaction of optically active α-nitrogen substituted β-propiolactones with organocopper reagents were reported for the synthesis of α-amino acids.[12]

Experimental Section

General. Boiling points were measured at the pressure indicated and are uncorrected. Infrared spectra were recorded on a Hitachi EPI-G2 spectrometer or on a Jasco A-202 spectrometer. ^1H NMR spectra were recorded on a Varian A-60 spectrometer or on a Jeol JNM-PMX60si spectrometer and are reported in parts per million (δ) from TMS. Samples were dissolved in CCl_4 containing TMS as an internal standard. All reactions were run under a positive pressure of dry argon. Reactions requiring anhydrous conditions were performed in a flame-dried glassware that was cooled under argon. Anhydrous solvents were transferred by an oven-dried syringe. Solvents were distilled before use: diethyl ether from lithium aluminium hydride; tetrahydrofuran (THF) from sodium benzophenone ketyl. Dimethyl sulfide (Me_2S) was used without purification. Tributylphosphine was purified by distillation. Grignard reagents and organolithiums were standardized by titration with 2-butanol using o-phenanthroline as an indicator.[27] Copper (I) iodide was purified by a known method.[28] Copper (I) chloride, bromide, and cyanide was used without any purification. General procedures for the ring-opening of β-propiolactones were representated by the synthesis of heptanoic acid.

Preparation of β-Propiolactones. β-Propiolactone (1) and β-methyl-β-propiolactone (9) are commercially available (Aldrich). α-Methyl-β-propiolactone (8)[5] and α,β-dimethyl-β-propiolactone (11),[29] were prepared according to the reported method for the preparation of 9.[30] Diastereomeric pure cis-11 was obtained from a diastereomeric mixture (cis:trans = 89 : 11) by preparative glpc (SE-30 3 mm x 2 m). α,α-Dimethyl-β-propiolactone (10)[31] and α,α,β,β-tetramethyl-β-propiolactone[32] (12) were prepared according to the reported procedures.

Reaction of Diorganocuprate with β-Propiolactone. In a typical experiment a flask equipped with a magnetic stirring bar and septum was charged 420 mg (2.20 mmol) of CuI. After flushing with dry argon, 10 ml of anhydrous THF and 1 ml of Me_2S were added and the solution was chilled to -30 °C. Butylmagnesium bromide (1.00 M in THF, 4.4 mmol) was slowly added to this solution and the mixture was stirred for 30 min at this temperature. Then, a solution of β-propiolactone (1) 144 mg (2.00 mmol) in 2 ml of THF was added dropwise to the flask. The mixture was stirred at the same temperature for 1 h and allowed to warm to 0 °C for 1 h. The reaction was quenched by addition of 2 ml of 3 M HCl and then heptanoic acid was extracted with three 5 ml portions of 3 M NaOH from the organic layer. The alkaline solution was acidified with 3 ml of 6 M HCl and then extracted with ether. The ethereal extracts were washed with brine and dried ($MgSO_4$). Concentration gave pure heptanoic acid (2b). An analytical sample was obtained by bulb to bulb distillation.

Reaction of Organocopper-Tributylphosphine with β-Propiolactone. In a typical experiment a flask equipped with a magnetic stirring bar and septum was charged 381 mg (2.00 mmol) of CuI. After flushing with dry argon, an ethereal solution (6 ml) of 1214 mg (6.00 mmol) of tributylphosphine was added. To this solution, butyllithium (1.00 M in hexane, 2.00 mmol) was slowly added at -78 °C and the mixture was stirred for 5 min at this temperature. Then a solution of 1 144 mg (2.00 mmol) in ether (2 ml) was added dropwise. The mixture was allowed to warm to 0 °C for 1.5 h with stirring and quenched by adding 2 ml of 6 M HCl solution. 2b was isolated in the same manner described above.

Reaction of Grignard Reagents with β-Propiolactone in the Presence of 2 mol% of CuCl. In a typical experiment a flask equipped with a magnetic stirring bar and septum was charged 4 mg (0.04 mmol) of CuCl. After flushing with dry argon, 6 ml of anhydrous THF was added. To this suspension, butylmagnesium bromide (1.00 M in THF, 2.40 mmol) was slowly added at 0 °C. Then, 1 144 mg (2.00 mmol) in THF (2 ml) was added dropwise. The mixture was stirred at 0 °C for 15 min and quenched by adding 1 ml of 3 M HCl. 2b was isolated in the same manner described above.

Confirmation of S_N2 Mechanism in the Reaction of Halomagnesium Di-tert-butylcuprate with α,β-Dimethyl-β-propiolactone (11). In a typical experiment a flask equipped with a magnetic stirring bar and septum was charged 420 mg (2.20 mmol) of CuI. After flushing with dry argon, 10 ml of anhydrous THF and 1 ml of Me_2S were added and the solution was chilled to -30 °C. t-Butylmagnesium chloride (1.00 M in THF, 4.4 mmol) was slowly added to this solution and the mixture was stirred for 30 min at this temperature. Then, a solution of 11 201 mg (2.00 mmol) in 2 ml of THF was added dropwise to the flask. The mixture was stirred at the same temperature for 1 h and allowed to warm to 0 °C for 1 h. The reaction was quenched by addition of 2 ml of 3 M HCl and then 2,3,4,4-tetramethylpentanoic acid (16c) was extracted with three 5 ml portions of 3 M NaOH from the organic layer. The alkaline solution was acidified with 3 ml of 6 M HCl and then extracted with ether. The ethereal extracts were washed with brine and dried ($MgSO_4$). Concentration gave pure 16c in a yield of 91% or 79%. Analytical glpc of the methyl esters obtained from the acid by treatment with diazomethane were performed by 3 mm x 3 m SE-30 column (90 °C). The ester obtained from a diastereo mixture (89 : 11) of had two peaks (relative retention times 1.00 (syn) and 1.07 (anti), syn : anti = 98 : 2). The ester obtained from pure cis-lactone had a single peak corresponding to syn-form.

Physical and spectral data of carboxylic acids obtained are as follows.

Butanoic Acid(2a): bp 80 °C (bath temp.)/ 2 mmHg (Kugelrohr); ^1H NMR δ 1.00 (t, J = 7 Hz, 3 H), 1.60-2.00 (m, 2 H), 2.33 (t, J = 7 Hz, 2 H), 11.80 (s, 1 H); IR (neat) 3100 (s) and 1710 (s) cm^{-1}. The IR and NMR spectra were fully identical with those of the commercial sample.

2-Methylbutanoic Acid(13a): bp 90 °C (bath temp.)/ 2 mmHg (Kugelrohr); ^1H NMR δ 0.90 (t, J = 7 Hz, 3 H), 1.08 (d, J = 6 Hz, 3 H), 1.35-1.77 (m, 2 H), 2.05-2.55 (m, 1 H), 11.15 (s, 1 H); IR (neat) 3100 (s) and 1710 (s) cm^{-1}. The IR and NMR spectra were fully identical with those of the commercial sample.

3-Methylbutanoic Acid(14a): bp 90 °C (bath temp.)/ 2 mmHg (Kugelrohr); ^1H NMR δ 0.98 (d, J = 6 Hz, 6 H), 1.93-2.18 (m, 1 H), 2.18 (d, J = 2 Hz, 2 H), 11.76 (s, 1 H); IR (neat) 3050 (s) and 1710 (s) cm^{-1}. The IR and NMR spectra were fully identical with those of the commercial sample.

2,2-Dimethylbutanoic Acid(15a):[33] bp 100 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^1H NMR δ 0.90 (t, J = 7 Hz, 3 H), 1.20 (s, 6 H), 1.65 (q, J = 7 Hz, 2 H), 10.36 (s, 1 H); IR (neat) 3080 (s) and 1710 (s) cm^{-1}. The IR and NMR spectra data were in agreement with the reported ones.

2,3-Dimethylbutanoic Acid(16a):[34] bp 100 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^1H NMR δ 0.82-1.18 (m, 9 H), 1.62-2.45 (m, 2 H), 11.18 (s, 1 H); IR (neat) 1710 (s) cm^{-1}.

Heptanoic Acid(2b): bp 120 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^1H NMR δ 0.91 (t, J = 6 Hz, 3 H), 1.25-1.65 (m, 8 H), 2.33 (t, J = 7 Hz, 2 H), 11.74 (s, 1 H); IR (neat) 3080 (s) and 1710 (s) cm^{-1}. The IR and NMR spectra were fully identical with those of the commercial sample.

2-Methylheptanoic Acid(13b):[35] bp 140 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^1H NMR δ 0.89 (br t, J = 4 Hz, 3 H), 1.17 (d, J = 7 Hz, 3 H), 1.27-2.08 (m, 8 H), 2.08-2.80 (m, 1 H), 12.12 (s, 1 H); IR (neat) 3100 (s) and 1710 (s) cm^{-1}.

3-Methylheptanoic Acid(14b):[36] bp 140 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 0.90 (t, J = 6.5 Hz, 3 H), 0.97 (d, J = 6.5 Hz, 3 H), 1.30 (br s, 6 H), 1.75-2.05 (m, 1 H), 2.05-2.35 (m, 2 H), 11.30 (s, 1 H); IR (neat) 3050 (s) and 1715 (s) cm^{-1}. The IR and NMR spectra data were in agreement with the reported ones.

2,2-Dimethylheptanoic Acid(15b):[33] bp 150 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 0.98 (t, J = 6 Hz, 3 H), 1.15 (s, 6 H), 1.35 (br s, 8 H), 11.03 (s, 1 H); IR (neat) 3060 (s) and 1715 (s) cm^{-1}. The IR and NMR spectra data were in agreement with the reported ones.

2,3-Dimethylheptanoic Acid(16b):[36]bp 150 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 0.85-1.03 (m, 6 H), 1.15 (d, J = 7 Hz, 3 H), 1.30 (br s, 6 H), 1.70-1.90 (m, 1 H), 2.20-2.50 (m, 2 H), 11.13 (s, 1 H); IR (neat) 3050 (s) and 1710 (s) cm^{-1}. The IR and NMR spectra data were in agreement with the reported ones.

4,4-Dimethylpentanoic Acid(2c):[37] bp 110 °C (bath temp.)/ 2 mmHg (Kugelrohr); ^{1}H NMR δ 0.90 (s, 9 H), 1.20-2.55 (m, 4 H), 11.57 (s, 1 H); IR (neat) 3070 (s) and 1715 (s) cm^{-1}. The IR and NMR spectra data were in agreement with the reported ones.

2,4,4-Trimethylpentanoic Acid(13c):[38] bp 120 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 0.93 (s, 9 H), 1.20 (d, J = 7 Hz, 3 H), 1.78 (d, J = 8 Hz, 1 H), 2.00 (d, J = 8 Hz, 1 H), 2.23-2.83 (m, 1 H), 12.20 (s, 1 H); IR (neat) 3100 (s), 1710 (s) and 1210 (s) cm^{-1}.

3,4,4-Trimethylpentanoic Acid(14c):[39] bp 130 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 0.87 (S, 9 H), 0.93 (d, J = 7 Hz, 3 H), 1.80-2.65 (m, 3 H), 11.33 (s, 1 H); IR (neat) 3090 (s) and 1710 (s) cm^{-1}.

2,2,4,4-Tetramethylpentanoic Acid(15c):[40] bp 140 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 0.95 (s, 9 H), 1.22 (s, 6 H), 1.63 (s, 2 H), 12.48 (s, 1 H); IR (KBr) 3100 (s), 1695 (s), 1250 (m), and 1210 (s) cm^{-1}.

2,3,4,4-Tetramethylpentanoic Acid(16c): bp 140 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 0.90-1.70 (m, 16 H), 2.20-2.70 (m, 1 H), 10.80 (s, 1 H); IR (neat) 3050 (s), 1710 (s) and 1210 (s) cm^{-1}; Anal. Calcd for $C_9H_{18}O_2$: C,68.31; H, 11.47. Found: C,68.53; H,11.42.

3-Phenylpropanoic Acid(2d): bp 180 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 2.37-2.93 (m, 4 H), 7.13 (s, 5 H), 10.33 (s, 1 H); IR (neat) 3080 (s), 1710 (s), 780 (s), and 700 (s) cm^{-1}. The IR and NMR spectra were fully identical with those of the commercial sample.

2-Methyl-3-phenylpropanoic Acid(13d):[41] bp 190 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 1.10 (d, J = 7 Hz, 3 H), 2.40-3.13 (m, 3 H), 7.20 (s, 5 H), 9.87 (s, 1 H); IR (neat) 3090 (s), 1715 (s), 780 (s), and 700 (s) cm^{-1}. The IR and NMR spectra data were in agreement with the reported ones.

3-Phenylbutanoic Acid(14d):[42] bp 190 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 1.30 (d, J = 7 Hz, 3 H), 2.43 (d, J = 2 Hz, 1 H), 2.60 (s, 1 H), 3.05-3.32 (m, 1 H), 7.25 (s, 5 H), 10.77 (s, 1 H); IR (neat) 3080 (s), 1710 (s), 780 (s), and 700 (s) cm^{-1}.

2,2-Dimethyl-3-phenylpropanoic Acid(15d):[43] bp 200 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 1.14 (s, 6 H), 2.85 (s, 2 H), 7.20 (s, 5H), 10.32 (s, 1H); IR (neat) 3080 (s), 1710 (s), 780 (s), and 700 (s) cm^{-1}.

2-Methyl-3-phenylbutanoic Acid(16d):[44] bp 200 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 1.10 (d, J = 7 Hz, 3 H), 1.25 (d, J = 7 Hz, 3 H), 2.50-2.73 (m, 1 H), 3.05-3.27 (m, 1 H), 7.25 (s, 5 H), 10.67 (s, 1 H); IR (neat) 3060 (s), 1710 (s), 780 (s), and 700 (s) cm^{-1}.

4-Pentenoic Acid(2e): bp 100 °C (bath temp.)/ 2 mmHg (Kugelrohr); ^{1}H NMR δ 2.15-2.67 (m, 4 H), 4.85-6.23 (m, 3 H), 11.53 (s, 1 H); IR (neat) 3060 (s), 1710 (s) and 915 (s) cm^{-1}. The IR and NMR spectra were fully identical with those of the commercial sample.

2-Methyl-4-pentenoic Acid(13e):[45] bp 110 °C (bath temp.)/ 2 mmHg (Kugelrohr); ^{1}H NMR δ 1.10 (d, J = 7 Hz, 3 H), 2.20-2.85 (m, 3 H), 4.80-6.20 (m, 3 H), 11.35 (s, 1 H); IR (neat) 3070 (s), 1710 (s) and 915 (s) cm^{-1}. The IR and NMR spectra data were in agreement with the reported ones.

3-Methyl-4-pentenoic Acid(14e):[46] bp 110 °C (bath temp.)/ 2 mmHg (Kugelrohr); ^{1}H NMR δ 1.10 (d, J = 7 Hz, 3 H), 2.23-3.05 (m, 3 H), 4.85-6.15 (m, 3 H), 10.13 (s, 1 H); IR (neat) 3080 (s), 1710 (s) and 915 (s) cm^{-1}. The IR and NMR spectra data were in agreement with the reported ones.

2,2-Dimethyl-4-pentenoic Acid(15e):[47] bp 120 °C (bath temp.)/ 2 mmHg (Kugelrohr); ^{1}H NMR δ 1.20 (s, 6 H), 2.28 (d, J = 7.5 Hz, 2 H), 4.75-6.05 (m, 1 H), 10.40 (s, 1 H); IR (neat) 3080 (s), 1710 (s) and 915 (s) cm^{-1}.

2,3-Dimethyl-4-pentenoic Acid(16e):[46] bp 120 °C (bath temp.)/ 2 mmHg (Kugelrohr); ^{1}H NMR δ 0.98-1.35 (m, 6 H), 2.05-2.73 (m, 2 H), 4.80-6.00 (m, 3 H), 10.55 (s, 1 H); IR (neat) 3080 (s), 1710 (s) and 915 (s) cm^{-1}. The IR and NMR spectra data were in agreement with the reported ones.

5-Hexenoic Acid(2f):[48] bp 110 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 1.33-2.55 (m, 6

H), 4.72-6.05 (m, 3 H), 11.92 (s, 1 H); IR (neat) 3080 (s), 1710 (s) and 915 (s) cm^{-1}.

2-Methyl-5-hexenoic Acid(13f): bp 120 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 1.16 (d, J = 7 Hz, 3 H), 1.30-3.00 (m, 5 H), 4.77-6.30 (m, 3 H), 12.18 (s, 1 H); IR (neat) 3080 (s), 1710 (s) and 915 (s) cm^{-1}; Anal. Calcd for $C_7H_{12}O_2$: C,65.60; H,9.44. Found: C,65.81; H,9.38.

2,2-Dimethyl-5-hexenoic Acid(15f): bp 130 °C (bath temp.)/ 1.5 mmHg (Kugelrohr); ^{1}H NMR δ 1.12 (s, 6 H), 1.70-2.32 (m, 4 H), 4.65-5.95 (m, 3 H), 11.52 (s, 1 H); IR (neat) 3080 (s), 1710 (s) and 915 (s) cm^{-1}; Anal. Calcd for $C_8H_{14}O_2$: C,67.57; H,9.92. Found: C,67.80; H,9.87.

Reaction of β-Propiolactone (1) with Allylmagnesium Bromide in the Presence of 2 mol% of CuCl. In a typical experiment a flask equipped with a magnetic stirring bar and septum was charged 4 mg (0.04 mmol) of CuCl. After flushing with dry argon, 6 ml of anhydrous THF were added. To this suspension, allylmagnesium bromide (1.00 M in THF, 2.40 mmol) was slowly added at 0 °C. Then, 1 144 mg (2.00 mmol) in THF (2 ml) was added dropwise. The mixture was stirred at 0 °C for 15 min and quenched by adding 1 ml of 3 M HCl. The organic layer was separated and aqueous layer was extracted with three 5 ml portions ether. The combined organic layer was washed with 3 M NaOH, brine and dried ($MgSO_4$). Concentration and distillation of the residue gave 6.

3-(2-Propenyl)-5-hexene-1,3-diol(6): bp 120 °C (bath temp.)/ 1 mmHg (Kugelrohr); ^{1}H NMR δ 1.65 (t, J = 7 Hz, 2 H), 2.00-2.57 (m, 4 H), 3.70 (s, 1 H), 3.75 (t, J = 7 Hz, 2 H), 4.80-6.10 (m, 6 H); IR (neat) 3350 (s) and 910 (s) cm^{-1}.; Anal. Calcd for $C_9H_{16}O_2$: C,69.19; H,10.32. Found: C,68.97; H,10.61.

Reaction of Dibutylcuprate with $\alpha,\alpha,\beta,\beta$-Tetramethyl-$\beta$-propiolactone (12). In a typical experiment a flask equipped with a magnetic stirring bar and septum was charged 420 mg (2.20 mmol) of CuI. After flushing with dry argon, 10 ml of anhydrous THF and 1 ml of Me_2S were added and the solution was chilled to -30 °C. Butylmagnesium bromide (1.00 M in THF, 4.4 mmol) was slowly added to this solution and the mixture was stirred for 30 min at this temperature. Then, a solution of 12 256 mg (2.00 mmol) in 2 ml of THF was added dropwise to the flask. The mixture was stirred at the same temperature for 1 h and allowed to warm to 0 °C for 1 h. The reaction was quenched by addition of 2 ml of 3 M HCl and then carboxylic acid was extracted with three 5 ml portions of 3 M NaOH from the organic layer. The alkaline solution was acidified with 3 ml of 6 M HCl and then extracted with ether. The ethereal extracts were washed with brine and dried ($MgSO_4$). Concentration and distillation of the residue gave 7.

2,2,3-Trimethyl-3-butenoic Acid(7): bp 100 °C (bath temp.)/ 1 mmHg (Kugelrohr); ^{1}H NMR δ 1.46 (s, 6 H), 1.85 (s, 3 H), 4.90 (br s, 2 H), 11.55 (s, 1 H); IR (neat) 3100 (s), 1710 (s) and 895 (s) cm^{-1}.; Anal. Calcd for $C_7H_{12}O_2$: C,65.60; H,9.44. Found: C,65.35; H,9.63.

Reaction of Di-tert-butylcuprate with α,α-Dimethyl-β-propiolactone (10). In a typical experiment a flask equipped with a magnetic stirring bar and septum was charged 420 mg (2.20 mmol) of CuI. After flushing with dry argon, 10 ml of anhydrous THF and 1 ml of Me_2S were added and the solution was chilled to -30 °C. t-Butylmagnesium chloride (1.00 M in THF, 4.4 mmol) was slowly added to this solution and the mixture was stirred for 30 min at this temperature. Then, a solution of 10 201 mg (2.00 mmol) in 2 ml of THF was added dropwise to the flask. The mixture was stirred at the same temperature for 1 h and allowed to warm to 0 °C for 1 h. The reaction was quenched by addition of 2 ml of 3 M HCl and then carboxylic acid was extracted with three 5 ml portions of 3 M NaOH from the organic layer. The alkaline solution was acidified with 3 ml of 6 M HCl and then extracted with ether. The ethereal extracts were washed with brine and dried ($MgSO_4$). Concentration and distillation of the residue gave 17.

2,2-Dimethylpropanoic Acid(17): bp 80 °C (bath temp.)/ 1 mmHg (Kugelrohr); ^{1}H NMR δ 0.95 (s, 9 H), 12.5 (s, 1 H); IR (neat) 3100 (s) and 1710 (s) cm^{-1}. The IR and H NMR spectra were fully identical with those of the commercial sample.

Reaction of β-Methyl-β-propiolactone (9) with Allylmagnesium Bromide in the Presence of 2 mol% of CuCl. In a typical experiment a flask equipped with a magnetic stirring bar and septum was charged 4 mg (0.04 mmol) of CuCl. After flushing with dry argon, 6 ml of anhydrous THF were added. To this suspension, allylmagnesium bromide (1.00 M in THF, 2.40 mmol) was slowly added at 0 °C. Then, 9 172 mg (2.00 mmol) in THF (2 ml) was added dropwise. The mixture was stirred at 0 °C for 15 min and quenched by adding 1 ml of 3 M HCl. The organic layer was separated and aqueous layer was extracted with three 5 ml portions ether. The combined organic layer was washed with 3 M NaOH, brine and dried ($MgSO_4$). Concentration and distillation of the residue gave 19.

4-(2-Propenyl)-6-heptene-2,4-diol(19): bp 120 °C (bath temp.)/ 1 mmHg (Kugelrohr); ^{1}H NMR δ 1.12 (d, J = 6 Hz, 3 H), 1.23-1.70 (m, 2 H), 2.00-2.40 (m, 4 H), 3.80-4.40 (m, 3 H), 4.75-6.23 (m, 6 H); IR (neat) 3500 (s), 900 (s) cm^{-1}.; Anal. Calcd for $C_{10}H_{18}O_2$: C,70.55; H,10.66. Found: C,70.47; H,10.90.

Reaction of β-Methyl-β-propiolactone (9) with Vinylmagnesium Bromide in the Presence of 2 mol% of CuCl. In a typical experiment a flask equipped with a magnetic stirring bar and septum was charged 4 mg (0.04 mmol) of CuCl. After flushing with dry argon, 6 ml of anhydrous THF were added. To this suspension, vinylmagnesium bromide (1.00 M in THF, 2.40 mmol) was slowly added at 0 °C. Then, 9 172 mg (2.00 mmol) in THF (2 ml) was added dropwise. The mixture was stirred at 0 °C for 15 min and quenched by adding 1 ml of 3 M HCl. The organic layer was separated and aqueous layer was extracted with three 5 ml portions ether. The combined organic layer was washed with 3 M NaOH, brine and dried ($MgSO_4$). Concentration and distillation of the residue gave 20.

2-Hydroxy-7-octene-4-one(20): bp 80 °C (bath temp.)/ 0.3 mmHg (Kugelrohr); ^{1}H NMR δ 1.17 (d, J = 6 Hz, 3 H), 2.00-2.70 (m, 6 H), 3.58 (s, 1 H), 3.75-4.43 (m, 1 H), 4.70-6.20 (m, 3 H); IR (neat) 3300 (s), 1725 (s), and 910 (s) cm^{-1}.; Anal. Calcd for $C_8H_{14}O_2$: C,67.57; H,9.92. Found: C,67.44; H,10.05.

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