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SIMPLE METHODS FOR THE SYNTHESES OF (E)-4- AND (E)-5-ALKENOIC ACIDS BY THE S_N2' TYPE REACTIONS OF γ-VINYL-γ-BUTYROLACTONE AND δ-VINYL-δ-VALEROLACTONE WITH ORGANOCOPPER REAGENTS

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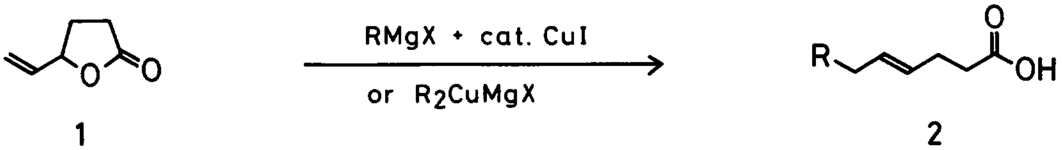
Summary: *γ-Vinyl-γ-butyrolactone and δ-vinyl-δ-valerolactone react regio- and stereoselectively with Grignard reagents in the presence of a copper(I) catalyst or with diorganocuprates to afford (E)-4- and (E)-5-alkenoic acids, respectively, in high yields. Synthetic utility of the former reaction is demonstrated in the simple synthesis of (4E,7Z)-4,7-tridecadienyl acetate.*

Nucleophilic ring-opening reaction of five- or six-membered lactones with organolithium compounds or Grignard reagents provide a useful method for natural product synthesis by virtue of carbon-carbon bond formation accompanying with proper functional groups.[1] These organometallic compounds attack generally to the carbonyl carbons of the lactones to give hydroxy ketone derivatives. On the other hand, a few example have been reported on the ring-opening between the ω-carbon and the ether oxygen of the lactones by the attack of organometallic compounds leading to carbon homologated carboxylic acids.[2,3,4] We wish to describe here simple methods for the syntheses of (E)-4- and (E)-5-alkenoic acids (2 and 6) by the regio- and stereoselective ring-opening reactions of γ-vinyl-γ-butyrolactone (1) and δ-vinyl-δ-valerolactone (5) with organocopper reagents.[5]

When γ-vinyl-γ-butyrolactone (1)[6,7] (1 equiv) was treated with butylmagnesium bromide (1.1 equiv) in THF-Me_2S (20:1) in the presence of copper(I) iodide (2 mol%) at -30 °C for 1 h, 4-decenoic acid (2; R = Bu), produced by the S_N2' type ring-opening reaction, was obtained in a high yield of 93% without any accompanying product by the S_N2 type reaction at the γ-carbon or by the attack to

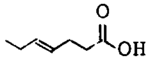
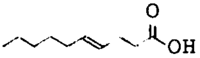
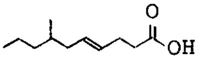
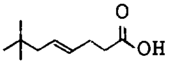
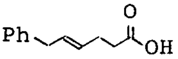
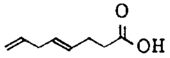
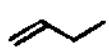
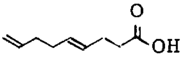
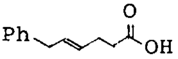
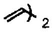
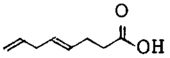
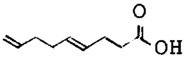


the carbonyl carbon. Vpc analysis of 2 showed the predominance of the E isomer (E:Z = 86:14). The copper-catalyzed reaction of several representative Grignard reagents with 1 was summarized in Table I. Alkyl Grignard reagents attacked regioselectively to the terminal vinyl carbon of 1 to give (E)-4-alkenoic acids in high yields. However, phenyl-, vinyl-, and allylmagnesium bromide gave the corresponding acids in low yields.

Diorganocuprates, prepared from two equivalent of Grignard reagents and one equivalent of copper(I) iodide, reacted similarly with 1 at -30 °C for 30 min and then to room temperature for 30 min. The reactions of diphenyl-, divinyl-, and diallylcuprates gave the corresponding acids in much higher yields than that of the catalytic procedure (see Table I).

Although, (E)-4-alkenoic acids have been synthesized by the ester enolate Claisen rearrangement[8] or by the Ramberg-Bäcklund rearrangement of 4-(1-bromoalkylsulfonyl)butyric acid,[9] the simplicity of the experimental procedure renders the present reaction attractive. The utility of the reaction was demonstrated in the short step synthesis of (4E,7Z)-4,7-tridecadien-1-yl acetate (4),[10] the sex pheromone of *Phthorimaea operculella* as depicted below. Bromomagnesium di-(Z)-1-heptenylcuprate, prepared from pentylmagnesium bromide, copper(I) iodide and acetylene, was allowed to react with 1 in THF-Me_2S (10:1) at -30 °C for 13 h to

Table I. Reaction of γ-Vinyl-γ-butyrolactone with Organocopper Reagents

RMgX	Product	Yield(%)	E : Z
MeMgBr[a]		87	92 : 8
BuMgBr[a]		93	86 : 14
s-BuMgCl[a]		90	83 : 17
t-BuMgCl[a]		91	78 : 12
PhMgBr[a]	Ph 	75	62 : 38
MgBr[a]		59	57 : 43
MgBr[a]		9	92 : 8
$Ph_2CuMgBr$[b]	Ph 	91	82 : 18
($_2$CuMgBr[b]		70	82 : 18
($_2$CuMgBr[b]		41	86 : 14

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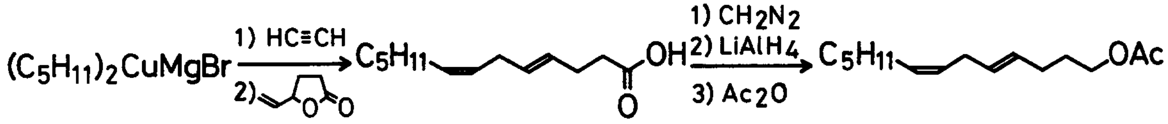
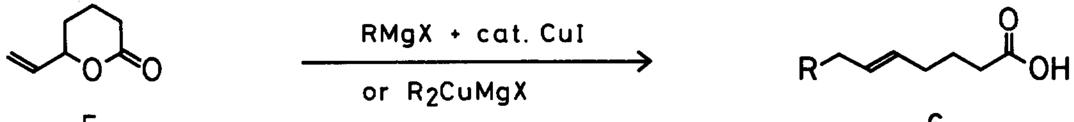
[a] All reactions were performed in THF-Me_2S (20:1) at -30 °C (1 h) in the presence of copper(I) iodide (2 mol%). All products were identified by IR and NMR spectra. [b] In these cases, diorganocuprates were used and the reactions were carried out in THF-Me_2S (10:1) at -30 °C (30 min) and then to room temperature (30 min).



3 4

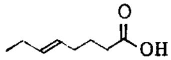
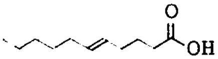
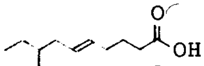
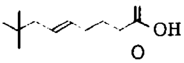
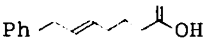
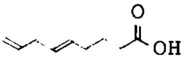
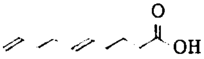
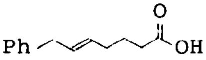
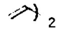
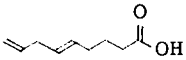
give (4E,7Z)-4,7-tridecadienoic acid (3) in 87% yield. Esterification of 3, reduction with lithium aluminum hydride and acetylation afforded 4 (ZZ:ZE = 9:91) in 97% yield.

δ-Vinyl-δ-valerolactone (5)[11] was also found to react regio- and stereoselectively with organocopper reagents as shown in Table II. Similar to the case of the reaction of γ-vinyl-γ-butyrolactone (1), S_N2' prodects of (E)-5-alkenoic acids (6) were obtained in high yields by the reaction of alkyl Grignard reagents, whereas phenyl, vinyl, and allyl Grignard reagents gave the acids in low yields.



5 6

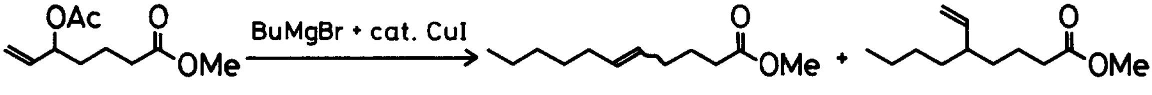
Table II. Reaction of δ-Vinyl-δ-valerolactone with Organocopper Reagents

RMgX	Product	Yield(%)	E : Z
MeMgBr[a]		70	93 : 7
BuMgBr[a]		95	88 : 12
s-BuMgCl[a]		94	83 : 17
t-BuMgCl[a]		78	75 : 25
PhMgBr[a]		56	67 : 33
 MgBr[a]		28	67 : 33
 MgBr[a]		trace	—
$Ph_2CuMgBr$[b]		57	71 : 29
()$_2$CuMgBr[b]		67	78 : 22
()$_2$CuMgBr[c]		51	92 : 8

[a] All reactions were performed in THF-Me_2S (20:1) at -45 °C (1 h) in the presence of copper(I) iodide (3 mol%). All products were identified by IR and NMR spectra. [b] Diorganocuprates were used, and the reactions were performed at -30 °C (1 h). [c] Diorganocuprate was used, and the reaction was carried out at -50 °C (1 h).

The use of divinyl- and diallylcuprates resulted in increasing the yields and the geometrical purity of the dienoic acids obtained.

Although acyclic allylic esters have been known to undergo S_N2' type reaction with organocopper reagents,[3,12] the cyclic structure was found to be essential for high regio- and stereoselectivity as confirmed by the following result. When methyl 5-acetoxy-6-heptenoate was treated with butylmagnesium bromide in the presence of copper(I) iodide (3 mol%) in THF-Me_2S at -45 °C for 1 h, methyl (E)-, (Z)-5-undecenoate (**8**) and 5-vinylnonanoate (**9**) was obtained in 98% yield in the ratio of 52:40:8.



7 **8** **9**

The regio- and stereoselective ring-opening reactions of γ-vinyl-γ-butyrolactone and δ-vinyl-δ-valerolactone provide very useful methods for six and seven carbon homologations with (E)-double bond terminating in a carboxyl function, which can be easily transformed to various functional groups.

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11. The lactone **5** was prepared by addition of lithium acetylide to methyl γ-formylbutyrate, followed by cyclization and the Lindlar reduction; bp 88 ∿ 91 °C/1.5 mmHg.
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