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Lewis Acid Mediated Reactions of Organocopper Reagents. A Remarkably Enhanced Regioselective γ-Attack of Allylic Halides and Direct Alkylation of Allylic Alcohols via $RCu \cdot BF_3$ System[1]

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Abstract: Chemical reactivities and selectivities of a new class of organocopper reagent, RCu–Lewis acid, are described. Regioselective γ-attack of allylic halides is realized irrespective of the degree of substitution at the two ends of the allylic systems, and of the structural factors (cyclic or acyclic) involved. Among the Lewis acids examined, $BF_3 \cdot OEt_2$ is the most effective with respect to the selectivity and total yield. Propargyl chloride and acetate are converted into 1,2-heptadiene by n-$BuCu \cdot BF_3$. Allylic alcohols react with 3 equiv of $RCu \cdot BF_3$ to produce the corresponding alkylation products in high yield. The stereochemistry of the reactions of $RCu \cdot BF_3$ is examined by using Goering's system, that is, 5-methyl-2-cyclohexenyl chloride, acetate, and alcohol. The substitution proceeds through a formal anti S_N2' in the case of *cis*-5-methyl-2-cyclohexenyl acetate and through a formal syn S_N2' in *trans*-5-methyl-2-cyclohexen-1-ol. On the other hand, the stereochemical integrity disappears in the reaction of *cis*-5-methyl-2-cyclohexen-1-ol and the chloride (**1**). It is proposed that the "ate" complex between RCu and BF_3 is involved as a reactive intermediate.

An important and yet frequently elusive goal of synthetic chemistry is the selective synthesis of a desired stereo- or regioisomer. Examples illustrating the importance of regioselective syntheses are manifold, control of the regiochemistry in the reaction of allylic carbanions with electrophiles being one example[2] while regiochemical control of the reaction of allylic substrates with nucleophiles is another.[3] In general, substitution reactions of allylic substrates without (or with) complete allylic rearrangement via organometallics are still unpredictable processes.[4,5] Among such reactions, several promising results to direct nucleophiles to the α position are obtained. Regioselective α-attack is achieved by using allylic substrates containing oxygen in the leaving group (OAc, OTos, etc.),[6-11] although isomerization, rearrangement, and formation of side products in many cases are reported.[8,10,11] On the other hand, in the case of the reaction of allylic halides[7] with organolithium and magnesium compounds, there are difficulties on the points of allylic transposition, geometrical isomerization, and cyclization.[12-16] Several literature sources refer to prenyl halides, cyclic allylic halides, or branched allylic compounds in which cases the problem of partial rearrangement either does not exist or is overshadowed by attendant factors.[4,17-19] Recently it was reported that acyclic allylic halides undergo cross coupling at the α position via dialkylcuprate–Me_2S system.[20]

The efforts to direct nucleophiles to the γ position are relatively scarce. Although γ-unsubstituted allylic substrates undergo a facile γ-alkylation,[10,21-23] the substitution appears to be controlled by steric factors.[19g-i] Recently exclusive syn γ-attack on the allylic system of 5-phenyl-2-cyclohexenylcarbamates was reported.[24] Consequently, the regiochemistry is highly system dependent[25] and the influencing factors are the nature of the leaving group, the degree of substitution of the two ends of the allylic system, the steric factors, the solvent system, and the nature of the nucleophile.

Previously we reported preliminary results dealing with regioselective γ-attack toward allylic halides by $RCu \cdot BF_3$ and direct alkylation of allylic alcohols.[1] We now report the full details of that work as well as the stereochemical aspects via $RCu \cdot BF_3$. The results reported here indicate that (1) regioselective γ-attack is realized irrespective of the nature of the leaving group, the degree of substitution at the two ends of the acyclic allylic systems,[26] and the structural factors (cyclic or acyclic), (2) direct displacement of the OH group of allylic alcohols is achieved via $RCu \cdot BF_3$, (3) the substitution proceeds through a formal anti S_N2' pathway in the case of *cis*-5-methyl-2-cyclohexenyl acetate and syn S_N2' in *trans*-5-methyl-2-cyclohexenol, and (4) the stereochemical integrity disappears in the reaction of *cis*- and *trans*-5-methyl-2-cyclohexenyl chloride and *cis*-5-methyl-2-cyclohexen-1-ol (eq 1).

Results and Discussion

Regiochemistry of the Reaction of Allylic Halides with Organocopper Reagents in the Presence of Lewis Acids. As we previously reported, certain observations suggest that the regiochemistry in the substitution reaction of allylic substrates with organocopper reagents must be influenced by the presence of organoboranes.[1a,27] Therefore, systematic investigation on the regiochemistry of the reaction of cinnamyl halides with organocopper reagents in the presence of various Lewis acids was carried out (Table I). As evident, an ehanced γ regiose-

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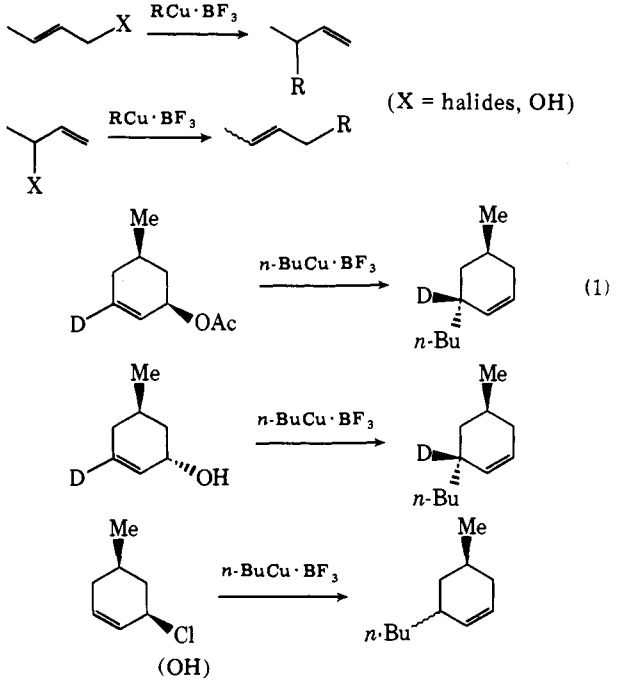
Table I. Reaction of Cinnamyl Chloride with Organocopper Reagents[a]

entry	reagent (RM)	solvent	products, %[b] PhCH(R)CH=CH₂ (γ)	PhCH=CHCH₂R (α)
1	MeCu	ether	77 (74)[c]	23 (26)[c]
2	Me_2CuLi	ether	(30)[c]	(70)[c]
3	MeCu·BEt_3	ether	87	13
4	MeCu·B(*n*-Bu)₃	ether	89 (90)[c]	11 (10)[c]
5	MeCu·$B(OCH_3)_3$	ether	79	21
6	MeCu·BF_3	ether	89 (90)[c]	11 (10)[c]
7	MeCu·BF_3	THF	99.5	0.5
8	MeCu·BCl_3	THF	99	1
9	*n*-BuCu	ether	52	48
10	*n*-BuCu	ether, LiI free[d]	56	44
11	*n*-BuCu·B(*n*-Bu)₃	ether	87	13
12	*n*-BuCu·BF_3	ether	91	9
13	*n*-BuCu·BCl_3[e]	ether	88	12
14	*n*-BuCu·$TiCl_4$[e]	ether	94	6
15	*n*-BuCu·$AlCl_3$	ether	67	33
16	*n*-BuCu·$AlEt_3$	ether	70	30
17	*n*-BuCu·B(*n*-Bu)₃	THF	99.5	0.5
18	*n*-BuCu·BF_3	THF	99.7	0.3
19	*n*-BuCu·BCl_3	THF	99	1
20	*n*-BuCu·$TiCl_4$	THF	*f*	*f*
21	*n*-BuCu from *n*-BuMgCl	THF	42	58
22	*n*-BuCu·BF_3 from *n*-BuMgCl	THF	64	36
23	*n*-Bu_2CuLi	THF	82	18
24	*n*-BuMgCl	THF	1	99
25	PhCu	ether	84 (86)[c]	16 (14)[c]
26	PhCu·BF_3	ether	84 (81)[c]	16 (19)[c]
27	PhCu·BEt_3	ether	75	25
28	PhCu·BCl_3[e]	ether	79	21
29	PhCu·BCl_3[e]	THF	50	50

[a] All reactions were carried out on a 1-mmol scale with the same procedure as described in the Experimental Section. Normally, cinnamyl chloride was used except where otherwise indicated. [b] By GLC. Total yields were usually excellent except where otherwise indicated. Only small amounts of byproducts (<4%), such as reduction products, the dimer of cinnamyl unit, cinnamyl iodide, and/or RI (alkyl iodide), were detected in some cases. [c] Cinnamyl bromide was used. [d] *n*-BuCu·P(*n*-Bu)₃ complex free from LiI was prepared as previously described: Whitesides, G. M.; Casey, C.P.; Krieger, J. K. *J. Am. Chem. Soc.* **1971**, *93*, 1379. [e] Total yields were ca. 60%. [f] Cinnamyl chloride was recovered.



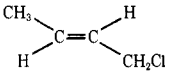
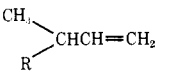
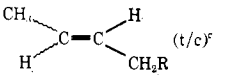
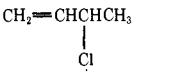
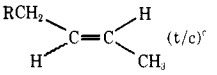
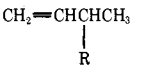
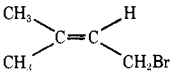
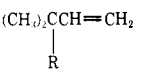
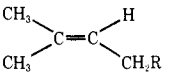
(1)

lectivity is observed in alkylcopper–Lewis acid systems. RCu·BF_3 is the most effective with respect to the selectivity and total yield among the Lewis acids examined (entries 6, 7, 12, and 18). THF is superior to ether for directing to the γ position, though titanium tetrachloride complex in THF gives quite an unsatisfactory result (entry 20). It is noteworthy that both *n*-BuCu and *n*-BuCu·BF_3 from *n*-BuMgCl are less regioselective even in THF than those from *n*-BuLi (entries 21 and 22). The result of entry 24 suggests a simple and very promising procedure for directing alkyl groups to the α position; actually such a reaction is frequenty carried out in an ether solvent.[16] Unfortunately, the regiochemical control of phenylcopper systems (entries 25–29) is not successful. This may be due to the complex formation between BF_3 and the π electrons of the aromatic ring. However, utilization of 2 equiv of BF_3 does not exert any appreciable influence on the regiochemistry.

Of particular interest is the question whether the enhanced γ regioselectivity will be a reflection of the complex formation between Lewis acids and LiI present in the reaction mixture. It seems that the difference between entries 9 and 10 is negligible, though the comparison is not completely adequate because of the presence of P(*n*-Bu)₃ in the latter. The effect of excess amounts of LiI upon the regioselectivity can be ignored (see also Table II); the dimeric product of the cinnamyl unit slightly increased in the presence of LiI. Further, if such a complex formation is an important factor, PhCu·BF_3 system should be equally effective. Since I^- is a soft base, a relatively soft acid (BR_3) will form a stronger complex with LiI than a hard acid (BF_3).[28] This leads to an expectation that RCu·BR'_3 must direct the R group to the γ position with greater regioselectivity than RCu·BF_3. However, the experiment gives a reversed result (entry 11 vs. 12). These considerations suggest that other factors, except (or in addition to) complex formation, play a major role in the control of the regiochemistry.

Reaction of various allylic halides with organometallics was examined to establish a generality of the enhanced γ regioselectivity of the RCu·BF_3 system (Table II). In contrast to cinnamyl chloride, a remarkable salt effect of LiI is observed

Table II. Reaction of Allylic Halides with Organometallic Reagents[a]

entry	allylic halide/RM	solvent	γ product, %[b]	α product, %[b]
				
1	*n*-BuLi[d]	ether	46	54
2	*n*-BuMgCl	THF	10	90 (100/~0)
3	*n*-Bu_2CuLi	ether	4	96 (99/1)
4	*n*-BuCu	ether	68	32
5	*n*-BuCu	THF	79	21
6	*n*-BuCu, 2 equiv of LiI[e]	THF	30	70 (85/15)
7	*n*-BuCu·B(*n*-Bu)$_3$	ether	73	27
8	*n*-BuCu·BF_3	ether	94	6
9	*n*-BuCu·BF_3	THF	98	2
10	*n*-BuCu·$TiCl_4$[f]	ether	98	2
11	PhCu	ether	84	16 (97/3)
12	PhCu·BF_3[d]	ether	84	16
				
13	*n*-BuLi[d]	ether	92 (82/18)	8
14	*n*-BuMgCl	THF	79 (40/60)	21
15	*n*-Bu_2CuLi	ether	78 (54/46)	22
16	*n*-BuCu	ether	90 (42/58)	10
17	*n*-BuCu·BF_3	ether	96 (55/45)	4
18	*n*-BuCu·BF_3	THF	~100 (80/20)	
19	*n*-BuCu·$TiCl_4$[f]	ether	97 (70/30)	3
20	Ph_2CuLi	ether	81 (58/42)	19
21	PhCu	ether	94 (57/43)	6
22	PhCu·BF_3	ether	98 (59/41)	2
	$CH_3CH{=}CHCH{=}CHCH_2Cl$		$CH_3CH{=}CHC(R)HCH{=}CH_2$	$CH_3CH{=}CHCH{=}CHCH_2R$ $CH_3C(R)HCH{=}CHCH{=}CH_2$
23	*n*-BuCu·BF_3	THF	~100	g
				
24	MeLi[d]	ether	12	88
25	Me_2CuLi	ether	trace	~100
26	MeCu	ether	60	40
27	MeCu·B(*n*-Bu)$_3$	ether	80	20
28	MeCu·BF_3 (1:0.5)[h]	ether	74	26
29	(1:1)[h]	ether	94	6
30	(1:2)[h]	ether	95	5
31	MeCu·BF_3	THF	95	5
32	MeCu·BCl_3[d]	THF	90	10
33	*n*-Bu_2CuLi	ether	trace	~100
34	*n*-BuCu	ether	79	21
35	*n*-BuCu·B(*n*-Bu)$_3$	ether	90	10
36	*n*-BuCu·BF_3	ether	90	10
37	*n*-BuCu·BCl_3	THF	67	33
38	PhLi	ether	trace	~100
39	PhCu	ether	80	20
40	PhCu·BF_3	ether	80	20

[a] All reactions were carried out on a 1-mmol scale. Total yields were usually excellent except where otherwise indicated. [b] By GLC. [c] Trans/cis ratio. [d] Total yields were about 50–60%. [e] See footnotes to Table I. [f] Considerable amounts of byproducts were detected. [g] Not detected. [h] The ratio of MeCu to BF_3.

in crotyl chloride (entries 5 and 6). Importance of the ratio of RCu to BF_3 is clearly indicated in entries 28–30; the ratio of 1:1 is essential. Here also, RCu·BF_3 in THF is the most effective and such an enhanced regioselectivity is not detected or is negligible in the case of PhCu (entries 11 and 12, 21 and 22, and 39 and 40). Consequently, it is now clear that highly regioselective γ-attack is accomplished generally via RCu·BF_3 irrespective of the degree of substitution of the two ends of the allylic system.

Regiochemistry of the Reaction of Propargyl Chloride and Acetate. The similar α/γ problem arises in the reaction of propargyl derivatives with organometallics. Although the regiochemistry is also system dependent, it is generally recognized that the reaction of organocopper reagents proceeds through γ-attack (allene formation).[29-31] In some cases, direct substitution (S_N2 type) to produce acetylenic derivatives is realized by blocking the terminal position of the acetylene with the Me_3Si group.[32] On the other hand, widely divergent results are reported in the reaction with Grignard reagents or organolithium.[33] Accordingly, the reaction of propargyl chloride, acetate, and alcohol with RCu·BF_3 was briefly examined; the chloride and acetate were converted into the corresponding

Table III. Reaction of Allylic Alcohols and Acetate with RCu-Lewis Acids[a]

entry	substrate (1 mmol)/RM (mmol)	γ product, %[b]	α product, %[b]	total yield, %[b]
	$C_6H_5CH{=}CHCH_2OH$	$C_6H_5CH(R)CH{=}CH_2$	$C_6H_5CH{=}CHCH_2R$	
1	*n*-BuCu·BF_3 (1)	83	17	17
2	*n*-BuCu·BCl_3 (1)	*c*	*c*	*c*
3	*n*-BuCu·BF_3 (2)	91	9	66
4	*n*-BuCu·BF_3 (3)	91	9	97
5	*n*-BuCu·$TiCl_4$(3)	trace	trace	trace
6	MeCu·BF_3 (3)	95	5	96
7	*n*-BuCu (2)	*c*	*c*	*c*
8	*n*-Bu_2CuLi(2)	*c*	*c*	*c*
	$CH_3CH{=}CHCH_2OH$	$CH_3CH(R)CH{=}CH_2$	$CH_3CH{=}CHCH_2R$	
9	*n*-BuCu·BF_3 (3)	86	14	99
	$CH_2{=}CHCH(OH)CH_3$	$RCH_2CH{=}CHCH_3$	$CH_3CH(R)CH{=}CH_2$	
10	*n*-BuCu·BF_3 (2)	90 (55/45)[d]	10	44
11	*n*-BuCu·BF_3 (3)	94 (55/45)[d]	6	86
	$CH_3CH{=}CHCH{=}CHCH_2OH$	$CH_3CH{=}CHC(R)HCH{=}CH_2$	$CH_3CH{=}CHCH{=}CHCH_2R$ $CH_3CH(R)CH{=}CHCH{=}CH_2$	
12	*n*-BuCu·BF_3 (2)	100	*e*	70
	$(CH_3)_2C{=}CHCH_2OH$	$(CH_3)_2C(R)CH{=}CH_2$	$(CH_3)_2C{=}CHCH_2R$	
13	*n*-BuCu·BF_3 (3)	98	2	60
	$(CH_3)_2C(OH)CH{=}CH_2$	$(CH_3)_2C{=}CHCH_2R$	$(CH_3)_2C(R)CH{=}CH_2$	
14	*n*-BuCu·BF_3 (3)	20	80	85
	$C_6H_5CH{=}CHCH_2OAc$	$C_6H_5CH(R)CH{=}CH_2$	$C_6H_5CH{=}CHCH_2R$	
15	*n*-Bu_2CuLi (1)	trace	99	50
16	*n*-BuCu·BCl_3 (1)	60	40	23
17	*n*-BuCu·BF_3 (2)	75	25	78
18	*n*-BuCu·BF_3 (3)	62	38	92
19	*n*-BuCu·$AlCl_3$ (3)	68	32	85

[a] All reactions were performed on a 1-mmol scale in ether. [b] By GLC analysis. The stereochemistry of the minor product was not determined. [c] Not detected. [d] Trans/cis ratio. [e] The α- and ω-alkylated products were not detected.

allene (R = *n*-Bu) in high yields and 1-heptyne was not detected. In contrast to the allylic alcohols, the reaction of propargyl alcohol was quite sluggish even in the presence of excess *n*-BuCu·BF_3 and only trace amounts of the allene were detected with GLC.

Reaction of Allylic Alcohols and Their Derivatives with RCu-Lewis Acids. The reaction of allylic acetates with RCu-Lewis acids was examined as a logical extension of the work on allylic halides. During this study, a new reaction was encountered, involving the replacement of the hydroxy group of allylic alcohols by an alkyl function in the reaction of RCu·BF_3 with such alcohols. The results are summarized in Table III. Although the reaction of allylic alcohols with 1 or 2 equiv of *n*-BuCu·BF_3 did produce the alkylation products (entires 1, 3, and 10), the best result was obtained when 3 molar equiv of the reagent was used. As expected, the corresponding alkylcopper and cuprate reagents did not give the desired products at all (entries 7 and 8). Use of other Lewis acids such as BCl_3 (entry 2), B(*n*-Bu)$_3$, and $TiCl_4$ (entry 5) gave quite unsatisfactory results. It was essential to use ether as a solvent; utilization of THF led to poor results. The reaction of cinnamyl acetate with *n*-BuCu·BF_3 or *n*-BuCu·$AlCl_3$ also gave the alkylation products (entries 16–19), but the regioselectivity was relatively low.

Some other features of the data in Table III deserve comment. Crotyl alcohol and its isomer, 1-buten-3-ol, are converted into 3-methyl-1-heptene and 2-octene, respectively (entries 9–11). Therefore, the reaction of these alcohols does not involve a common intermediate such as 1-methylallyl cation or radical. A similar result is obtained in the case of crotyl chloride and its isomer (Table II, entries 7–9 vs. 17–19). In contrast to these alcohols, both prenyl alcohol and its isomer, 3-methyl-1-buten-3-ol, gave 3,3-dimethyl-1-heptene as a major product (entries 13 and 14). This suggests that the latter alcohol undergoes isomerization to prenyl alcohol under the reaction conditions. Another possibility is that the latter alcohol, substituted with an allyl and two methyl groups, undergoes facile ionization under the influence of BF_3 (or RCu·BF_3) and the resulting 1,1-dimethylallyl cation is immediately trapped with RCu (or RCu·BF_3).[34]

In connection with these observations, the role of BF_3 was investigated. It is known that the complex formation between alcohols and BF_3 is a facile process.[35] Therefore, it might be thought that complexes can react with an alkylating reagent. However, this possibility was eliminated, though not completely, by a control experiment.[1b] Consequently, as mentioned later, the reaction must involve a cyclic transition state since S_N2'-type substitution occurs even in a positionally unbiased system. Although the reaction of allylic alcohols proceeds with less regioselectivity than that of allylic halides, direct alkylation of allylic alcohols via an organocopper reagent is the first example[36] and synthetically useful; allylic alcohols are easily handled in comparison with allylic halides, which often are highly reactive.

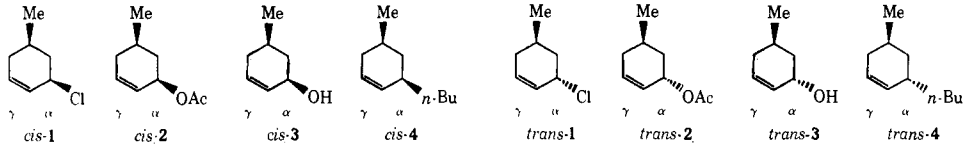
The reaction of other allylic substrates with RCu·BF_3 was also examined. Allyl phenyl ether was converted into 1-heptene (26% yield) under the influence of 3 equiv of *n*-BuCu·BF_3. Similar reaction of allylamine, allylammonium bromide, and allyl sulfide gave trace amounts of 1-heptene. Phenyl iodide, benzyl chloride, cyclohexyl bromide, 1-bromoadamantane, and benzyl alcohol did not react with excess amounts of *n*-BuCu·BF_3, while *n*-amyl iodide and diphenylchloromethane gave the corresponding butylated products in 10–20% yields. Consequently, it is possible to carry out a chemoselective alkylation of the allylic and propargyl derivatives in the presence of these functional groups.

Stereochemical Aspects. Stereochemistry of the S_N2' reaction has been of synthetic and mechanistic interest for many years.[3,37] In this connection, stereochemistry of the formal S_N2' reaction via an organometallic is of current interest. The mode of substitution is shown to be exclusively anti (trans) in both cyclohexenyl systems[19g,h,23c] and acyclic allylic ethers,[23b] while

Table IV. Reaction of 5-Methyl-2-cyclohexenyl Derivatives with Organocopper Reagents[a]

entry	cyclohexenyl derivative (cis/trans ratio)		product (*cis*-**4**/*trans*-**4** ratio)		
			n-BuCu·BF_3	*n*-Bu_2CuLi	*n*-BuCu
1	*cis*-**1**	(97/3)	60/40	65/35	51/49
2	*cis*- and *trans*-**1**	(60/40)	67/33		
3	*cis*- and *trans*-**1**	(37/63)	67/33		
4	*cis*-**2**	(90/10)	23/77	12/88	
5	*cis*-**3**	(97/3)	59/41		
6	*trans*-**3**	(17/83)	22/78		
7	*cis*-**2**-γ-*d*		**4**-α-*d*		
8	*cis*-**3**-γ-*d*		**4**-α-*d*		
9	*cis*-**3**-α-*d*		**4**-γ-*d*		

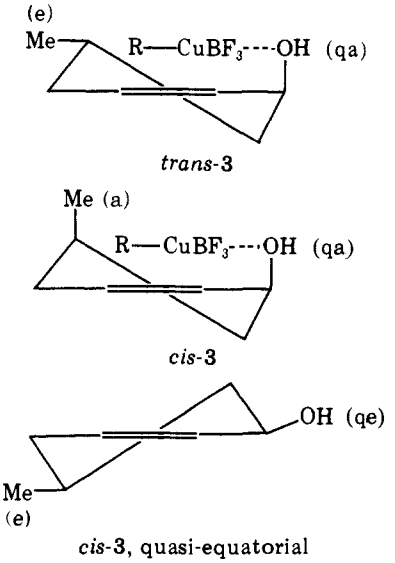
[a] All reactions were carried out as described in the Experimental Section. Three equivalents of *n*-BuCu·BF_3 was used in the reaction of **3**; the product (**4**) was obtained in 47–52% yields. The reaction of **1** proceeded smoothly and the product was obtained in high yield. Deuterium was labeled as indicated (>98% d). *cis*-**2**-γ-*d* indicates that deuterium is substituted at γ position of *cis*-**2**, and analogous notation is used for other systems.



exclusive syn (cis) γ-attack on the cyclohexenyl carbamate systems is reported.[24] Therefore, we examined the stereochemistry of the formal S_N2' reaction via RCu·BF_3 by using Goering's cyclohexenyl system. The results are listed in Table IV.

The reaction of the allylic halide (**1**) proceeds with complete loss of the stereochemistry (entries 1–3) regardless of the reagent types. This may be due to a labile characteristic of chloride as a leaving group, which leads to an allylic intermediate or which causes a facile isomerization of the starting materials under the reaction conditions. Although it is now clear that the stereochemical integrity disappears in the reaction of **1**, the regiochemical integrity (S_N2' type) must be presumably retained as is apparent from the results of reactions of crotyl chloride and its isomer (Table II). Unfortunately, **1**-α-*d* or **1**-γ-*d* could not be prepared in reasonably pure form. The reaction of *cis*-**2** with *n*-BuCu·BF_3 or *n*-Bu_2CuLi proceeds via anti S_N2' as would be expected from the literature[19g,h,23b,c] (entries 4 and 7).

The reaction of **3** is a puzzling system; the stereochemical integrity of *cis*-**3** disappears in a similar manner as that of **1** (entry 5), while *trans*-**3** retains its configuration (entry 6). In both cases, the regiochemical integrity (S_N2' type) is retained (entries 8 and 9). Examination of the composition of the recovered alcohols revealed that the trans isomer reacted faster than the cis isomer. These observations are tentatively explained in terms of steric hindrance during the attack of the reagent toward *cis*-**3**.



cis-**3**, quasi-equatorial

For the case of a cyclohexenyl derivative disposed in a half-chair conformation, the bonds undergoing rupture and formation are both quasi-axial. Further, it is reasonable to assume a cyclic transition state since a formal S_N2' is observed in this positionally unbiased system (entries 8 and 9). Therefore, *trans*-**3** may be expected to be less sterically hindered and more energetically favored than *cis*-**3**, so that it would react faster than *cis*-**3**. Thus, *trans*-**3** leads readily to *trans*-**4** via a syn S_N2' type reaction. On the other hand, *cis*-**3** is more sterically hindered and less energetically favored and thus may be energetically similar to or higher than *cis*-**3**, *quasi-equatorial*, leading to the mixture of *cis*- and *trans*-**4**. Consequently, the stereochemistry is more system dependent than the regiochemistry, at least in the present system, and will be determined by the nature of the leaving group and conformational and configurational factors.[38,39]

Concerning the Reactive Intermediate. The enhanced γ regioselectivity, the direct alkylation of allylic alcohols, and the stereochemical aspects make it desirable to obtain better insight into the reactive intermediate. Treatment of cinnamyl chloride with BF_3·OEt_2 followed by the addition of *n*-BuCu exhibited similar regioselectivity as the reaction of normal *n*-BuCu free from BF_3, though total yields of butylated products became low. Interaction between BF_3 and LiI is not a major factor for the high regioselectivity as already mentioned. Consequently, complex formation between RCu and BF_3 is most probable, and the present observations seem to be a reflection of such a complex. Although the coordination of BF_3 with donor atoms, such as N, O, P, and S, is well known,[35,40] the complexes between BF_3 and carbon atom as a donor are relatively scarce. To our knowledge, the complexes reported so far are $[Me_3Sn]^+[CF_3BF_3]^-$ [41] and $K[CF_3BF_3]$,[42] the structure of which is determined by X-ray diffraction methods. Complexes between basic transition metal organometallics and BF_3 are also reported.[43] Since it is widely accepted that lithium, sodium, and magnesium borates are formed from the reaction of alkyllithium, sodium, and magnesium compounds with trialkylboranes,[44] it is reasonable that the similar ate complexes of copper are produced from the reaction between alkylcoppers and trialkylboranes.[27,45] Actually, it is reported that copper methyltrialkylborates, prepared from the reaction of lithium trialkylborates with copper halides, exhibit high γ regioselectivity (96%) toward cinnamyl

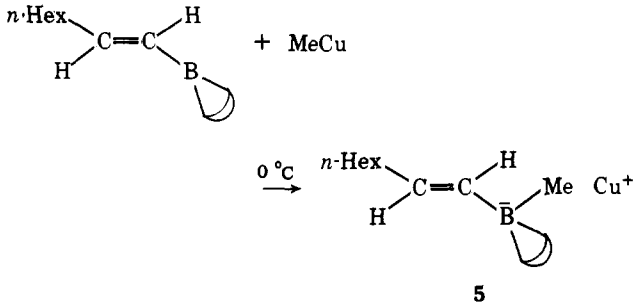
chloride.[46]

Therefore, it is proposed that the complex RCu·BF$_3$ possesses an ate complex type structure, RBF$_3$$^-Cu^+$, at low temperature. Since CuF is unknown,[47] this ate complex presumably does not give RBF$_2$ easily.

$$RCu + BF_3 \rightleftharpoons RBF_3^-Cu^+ \not\rightarrow RBF_2 + CuF$$

The reaction mixture of *n*-BuCu with BF$_3$ at −78 °C was allowed to warm to room temperature. GLC examination of the mixture revealed the formation of only trace amounts of tri-*n*-butylborane. This is a marked contrast to the reaction of alkylmagnesium and lithium compounds with BF$_3$, which gives excellent yields of trialkylboranes.[48] The oxidation of the mixture with H$_2$O$_2$–NaOH gave only trace amounts of *n*-BuOH.[49] These results indicate that the compounds having *n*-Bu–boron bonds, such as *n*-Bu$_3$B and *n*-BuBF$_2$, are not involved in the mixture. Instead, RCu·BF$_3$ or more preferably RBF$_3$$^-Cu^+$ presumably dissociates into RCu and BF$_3$ upon heating. Preparation of *n*-BuCu·BF$_3$ at −30 °C and subsequent reaction with cinnamyl chloride exhibited the same regioselectivity as that at −70 °C. Thus, the complex is stable at least at −30 °C. Without further knowledge of the exact structure of RCu·BF$_3$, it is difficult to postulate any convincing mechanism for the reaction. However, the following results strongly suggest involvement of the ate complex as an intermediate.

Dark green ate complex **5**, prepared from 1-octenyl-9-BBN and methylcopper in ether at 0 °C, is stable at 0 °C left overnight.[50] This complex does not dissociate into 1-octenylcopper and methyl-9-BBN or into 1-octenyl-9-BBN and methylcopper, while copper bis(1-hexenyl)di-*n*-butylborate undergoes a facile dissociation into 1-hexenylcopper.[27,45] The regiochemical behavior of **5** to crotyl chloride was compared with



5

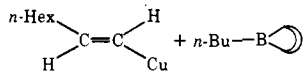
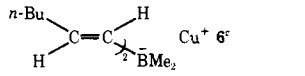
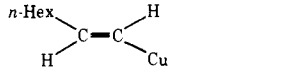
that of other related copper derivatives. The results are summarized in Table V.[51] The ate complex **5** exhibited higher regioselectivity than free 1-octenylcopper (entry 1 vs. 5). The mixture between 1-octenylcopper and *n*-butyl-9-BBN showed a similarly high regioselectivity (entry 3). On the other hand, the regioselectivity of **6** was close to that of free 1-octenylcopper (entry 4 vs. 5), suggesting a facile dissociation of **6** into 1-hexenylcopper. Consequently, it is now clear that formation of ate complexes causes an enhanced γ regioselectivity. Finally, the postulation of the cyclic transition state, involving the pentavalent aluminate in the reduction of certain allylic halides with LiAlH$_4$,[39,52] should be recalled when the mechanism of the present reactions is considered.

Experimental Section

^{1}H NMR spectra were recorded on a JEOL JNM-MH-100 instrument; chemical shifts (δ) are expressed in parts per million relative to Me$_4$Si. IR spectra were recorded on a JASCO IRA-1 spectrophotometer. Mass spectra were recorded on a Hitachi GC-M-52 instrument (22 eV). Elemental analyses were performed by the Kyoto University Microanalytical Laboratories, and the results are within the accepted limits (±0.3%). All temperatures were uncorrected.

Reagents. Reagent grade solvents were purified by standard techniques and kept over a drying agent. Methyllithium in ether was prepared by standard procedure,[53a] and *n*-butyllithium in hexane was a commercial product. Phenyllithium[53b] and *n*-butylmagnesium chloride[53c] were prepared. The titrations were performed by Gilman's[54] and Eastham's[55] methods. Cuprous iodide was purchased and purified.[56] Organoboranes, such as B(*n*-Bu)$_3$, *n*-Bu-9-BBN, and 1-octenyl-9-BBN, were prepared by the reported procedures.[57] Other simple chemicals were purchased and used as such. LiI was prepared in situ from the reaction of *n*-BuLi with MeI since it was highly hygroscopic.

Table V. Reaction of Alkenylcopper Derivatives with Crotyl Chloride[a]

entry	copper derivative	γ-attack, %	α-attack, %
1	**5**	87.5	12.5
2	**5** + 3-chloro-1-butene[b]	87.5	12.5
3		84	16
4		73	28
5		77.5	22.5

[a] All reactions were carried out in ether at −30 °C. The ratio was determined by GLC. [b] Instead of crotyl chloride, 3-chloro-1-butene was used. [c] Prepared from bis(1-hexenyl)chloroborane with 3 equiv of MeCu.[27]

Reaction of RCu–Lewis Acids with Allylic Halides and Related Compounds. The following procedure for the reaction of cinnamyl chloride with *n*-BuCu·BF$_3$ is representative. In a 200-mL flask, equipped with a magnetic stirrer and maintained under N$_2$, were placed 1.9 g (10 mmol) of CuI and 20 mL of dry THF. *n*-BuLi in hexane (1.3 M, 10 mmol) was added at −30 °C and the resulting mixture (black) was stirred at this temperature for 5 min. The mixture was then cooled to −70 °C and BF$_3$·OEt$_2$ (47%, 1.3 mL, 10 mmol) was slowly added. The color changed from black to very black. After the mixture was stirred for a few minutes, cinnamyl chloride (1.53 g, 10 mmol) was slowly added by a syringe, and the mixture was allowed to warm to room temperature by stirring. The mixture was directly analyzed by GLC or was filtered through the column of alumina using light petroleum ether. The olefin thus obtained in an essentially pure form was distilled under reduced pressure through Kugelrohr: 1.64 g (3-phenyl-1-heptene), 94%, bp 65–66 °C (5 mmHg).

The same procedure was employed for other Lewis acids and allylic halides. Boron trichloride and aluminum trichloride were dissolved in ether and these solutions were added to RCu at −70 °C. Triethylaluminum in hexane solution was purchased and used as such. Although the reaction of PhCu–Lewis acids was carried out as described above, a slightly different condition was used in the reaction of MeCu–Lewis acids; MeCu was prepared at 0 °C (yellow) and then cooled to −70 °C. The product ratio was determined by GLC using a column of DC550 (2 m). In some cases, the GC–mass instrument was used for the analysis (SE-30, 1 m). Prenyl bromide was prepared from the reaction of isoprene with HBr. 2,4-Hexadienyl chloride was prepared by Dr. Y. Naruta in our laboratories from the reaction of 2,4-hexadien-1-ol, which was purchased from Tokyo Kasei Co., Ltd., with Ph$_3$P–CCl$_4$.[58] The chloride was contaminated with the regioisomers even by using this procedure and purified by fractional distillations. The procedure via SOCl$_2$[59] or via PBr$_3$,[60] which had been used for the synthesis of the corresponding bromide, was less effective for the selective synthesis of the desired chloride: bp 55–58 °C (10 mmHg); $n^{20}$$_D$ 1.5010 (lit.[59] 1.5000); ^{1}H NMR (CCl$_4$) δ 1.76 (3 H, d, *J* = 6 Hz), 3.96 (2 H, d, *J* = 6 Hz), 5.0–6.4 (4 H, m); *m/e* (M$^+$) 116, 118. The reaction of 2,4-hexadienyl chloride with *n*-BuCu·BF$_3$ was carried out as described above. GLC examination of the reaction mixture revealed that the reaction was very clean and a single peak appeared at the region expected for the butylated product. The usual workup followed by distillation gave 3-*n*-butyl-1,4-hexadiene (cis and trans mixture) in 83% yield; bp 100–103 °C (20 mmHg); IR (cm^{-1}, in CCl$_4$), 1640, 995, 970, 909; ^{1}H NMR (CCl$_4$) δ 0.90 (3 H, t, *J* = 7 Hz), 1.23 (6 H, bs), 1.62 and 1.63 (3 H, d, *J* = 6 Hz), 2.50 (1 H, m), 4.70–5.90 (5 H, m); *m/e* (M$^+$) 138. Anal. Calcd for C$_{10}$H$_{18}$: C, 86.88; H, 13.12. Found: C, 86.68; H, 13.31.

The same procedure was used for the reaction of allylic alcohols and acetate. In some cases, excess amounts of RCu-Lewis acids were used (Table III). 3,3-Dimethyl-1-butene, 2-methyl-2-pentene, *cis*- and *trans*-2-octene, and *trans*-1-phenyl-2-butene were commercially available. Authentic samples of 3-phenyl-1-butene, *trans*-1-phenyl-1-butene, 3-phenyl-1-heptene, *trans*-1-phenyl-1-heptene, 3,3-diphenyl-1-propene, and 3-methyl-1-heptene were kindly given by Dr. Y. Tanigawa, which were prepared according to the reported methods (ref 11b and 23c). *trans*-1,3-Diphenylpropene,[61] 2-methyl-2-octene,[62] 2-methyl-4-phenyl-2-butene,[63] 3,3-dimethyl-1-heptene,[64] and 3-methyl-3-phenyl-1-butene[65] were prepared according to the previous literature. The spectroscopic characteristics of these authentic samples were compared with those of the reaction products listed in Tables I-III. Both materials were completely identical in all respects.

Stereochemical Aspects. The synthesis of the cyclohexenyl derivatives has been described in an earlier paper.[66] 5-Methyl-1,3-cyclohexadione was prepared from the reaction of ethyl crotonate with ethyl acetoacetate in the presence of sodium ethoxide,[67] mp 126-128 °C (50% yield) (lit.[67] 126-127 °C). Treatment of this dione with ethanol in the presence of *p*-toluenesulfonic acid produced 5-methyl-3-ethoxy-2-cyclohexenone in 90% yield, bp 108 °C (4 mmHg) (lit.[68] 83 °C (0.1 mmHg)). Reduction of ethoxycyclohexenone with $LiAlH_4$ in ether gave 5-methyl-2-cyclohexenone in 69% yield,[69] bp 87 °C (20 mmHg) (lit.[69] 74 °C (8 mmHg)). Further reduction with $LiAlH_4$ produced 5-methyl-2-cyclohexenol in 82% yield,[70] bp 82 °C (20 mmHg) (lit.[70] 74 °C (8 mmHg)). GLC examination using CW-20M (2 m) revealed that the ratio of cis to trans isomer was 93:7. On the other hand, the reduction with $Al(O\text{-}i\text{-}Pr)_3$ gave the corresponding alcohol, in which cis:trans = 60:40, in 76% yield.[71] Resolution of partially resolved *cis*- and *trans*-5-methyl-2-cyclohexenol was carried out via their nitrobenzoates as previously described.[70] 5-Methyl-2-cyclohexenyl chloride was prepared from the reaction of resolved or partially resolved *cis*- and *trans*-5-methyl-2-cyclohexenol with $SOCl_2$,[66] bp 71 °C (50 mmHg) (42% yield) (lit. 65 °C (25 mmHg)).[66] The configurations of the isomeric chlorides were related to those of the isomeric alcohols; they were readily distinguished by the IR bands at 7.81, 10.93, and 13.03 μ for cis isomer and at 8.00, 9.52, and 13.4 μ for trans isomer.[66] Both isomers exhibited essentially identical ^1H NMR spectra. 5-Methyl-2-cyclohexenyl acetate was prepared from the corresponding alcohol and acetyl chloride in pyridine in 73% yield, bp 77-78 °C (20 mmHg) (lit.[66] 83-84 °C (25 mmHg)). The ratio of cis to trans isomer was determined by GLC using a DC 550 column (1 m). *cis*-**2**-γ-*d*, *cis*-**3**-γ-*d*, and *cis*-**3**-α-*d* were prepared from 5-methyl-3-ethoxy-2-cyclohexenone as described in an earlier paper.[19g] Total deuterium contents were determined from mass spectra. The deuterium distribution was determined from the total deuterium and relative peak areas for the C_5 and the γ (or α) proton signals in expanded 220-MHz NMR spectra (Varian HR-220), and was found to be discretely labeled as indicated in Table IV. Preparation of deuterium-labeled *trans*- or *cis*-**1** was unsuccessful; deuterium was scrambled at the α and γ position of **1** when *cis*-**3**-γ-*d* or *cis*-**3**-α-*d* was treated with $SOCl_2$. Butylated product, 5-methyl-3-butylcyclohexene [bp 95 °C (20 mmHg); ^1H NMR (CCl_4) δ 0.95 (3 H, d, J = 7 Hz), 0.95 (3 H, t, J = 7 Hz), 1.28 (6 H, bs), 1.60-1.80 (3 H, m), 1.95 (3 H, m), 5.52 (2 H, m)], was reduced to 3-methyl-1-butylcyclohexane via the hydroboration-protonolysis procedure.[57] Authentic material of this hydrocarbon was prepared according to the reported procedure.[72] The ratio of cis to trans isomer was determined by GLC using a capillary column (squalane, 0.25 i.d., 45 m) as previously reported.[73]

Concerning the Reactive Intermediate. *trans*-1-Octenyl-9-borabicyclo[3.3.1]nonane was prepared as previously reported:[57,74] bp 92-96 °C (0.03 mmHg); ^1H NMR (CCl_4) δ 0.96 (3 H, t, J = 6 Hz), 1.00-2.00 (22 H, m), 2.10-2.30 (2 H, m), 6.08 (1 H, d, J = 18 Hz), 6.68 (1 H, d-t, J = 18 and 6 Hz). *trans*-1-Octenylcopper was prepared from the corresponding lithium and CuI in ether. The reaction of these copper derivatives with crotyl chloride and its isomer was carried out as described above. 3-Methyl-(4*E*)-1,4-undecadiene (γ-attack product of **5** to crotyl chloride): bp 115-125 °C (20 mmHg); IR (cm^{-1}, direct) 1640, 990, 965, 910; ^1H NMR (CCl_4) δ 0.90 (3 H, t, J = 6 Hz), 1.04 (3 H, d, J = 6 Hz), 1.20-1.44 (8 H, m), 1.84-2.10 (2 H, m), 2.64-2.88 (1 H, m), 4.88 (1 H, d-d, J = 18 and 2 Hz), 5.20-5.36 (2 H, m), 5.70 (1 H, d-d-d, J = 18, 10, and 6 Hz). Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.37; H, 13.33. (2*E*,5*E*)-2,5-Dodecadiene (α-attack product of **5** to crotyl chloride and the γ-attack product to 3-chloro-1-butene in which case (2*Z*,5*E*) isomer was also produced):[51] bp 125-130 °C (20 mmHg); IR (cm^{-1}, direct) 965; ^1H NMR (CCl_4) δ 0.90 (3 H, t, J = 6 Hz), 1.24-1.36 (8 H, m), 1.60-1.68 (3 H, m), 1.94-2.02 (2 H, m), 2.58-2.72 (2 H, m), 5.28-5.40 (4 H, m). Anal. Calcd for $C_{12}H_{22}$: C, 86.66; H, 13.34. Found: C, 86.63; H, 13.10. 3-Methyl-(4*E*)-1,4-nonadiene (γ-attack product of **6** to crotyl chloride): bp 80-90 °C (30 mmHg); IR (cm^{-1}, direct) 1640, 990, 965, 910; ^1H NMR (CCl_4) δ 0.93 (3 H, t, J = 6 Hz), 1.10 (3 H, d, J = 7 Hz), 1.16-1.78 (4 H, m), 1.83-2.16 (2 H, m), 2.66-3.16 (1 H, m), 5.00-5.40 (2 H, m), 5.56-5.71 (2 H, m), 5.83-6.50 (1 H, m). Anal. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.60; H, 13.22. (2*E*,5*E*)-2,5-Decadiene (α-attack product of **6** to crotyl chloride): bp 80-90 °C (30 mmHg); IR (cm^{-1}, direct) 965; ^1H NMR (CCl_4) δ 0.93 (3 H, t, J = 6 Hz), 1.16-1.56 (4 H, m), 1.66-1.83 (3 H, m), 1.96-2.25 (2 H, m), 2.63-2.90 (2 H, m), 5.50-5.83 (4 H, m). Anal. Calcd for $C_{10}H_{18}$: C, 86.88; H, 13.12. Found: C, 86.71; H, 13.10.

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Tunneling Model for Hydrogen Abstraction Reactions in Low-Temperature Solids. Applications to Reactions in Alcohol Glasses and Acetonitrile Crystals[1]

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Abstract: A simple and internally consistent quantitative model for hydrogen-abstraction reactions in low-temperature solids, which implicitly incorporates zero point energy effects which allow for finite reaction rates at $T = 0$ K, is derived and applied to new measurements of H-abstraction rate constants by methyl radicals in methanol and ethanol glasses at $T = 13$–99 K and in acetonitrile and methyl isocyanide crystals at 69–128 K. Nonlinear least-squares fits of the model to the experimental data yield effective one-dimensional barriers to reaction whose heights are virtually independent of the analytic form used for the potential energy barrier, and are somewhat larger than the activation energies measured for the corresponding reactions in the gas phase. This model predicts that values of the isotopic rate constant ratio k_H/k_D will be larger than 10^{12} at $T = 0$ K.

Quantum-mechanical tunneling has long been believed to make a dominant contribution to the rates of many chemical reactions at low temperatures.[5,6] However, it is only relatively recently that convincing experimental evidence of this behavior has begun to appear. In most studies,[7-17] the evidence that the reactions considered proceeded mainly by tunneling consisted of (1) pronounced curvature in Arrhenius plots, (2) anomalously small activation energies, and (3) anomalously large[10,14]

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