containing an α,β-unsaturated ketone moiety such as 4-(2,6,6-trimethyl-2-cyclohexen-1-yl)-3-buten-2-one (α-ionone, **6**), 4-(2,6,6-trimethyl-1-cyclohexen-1-yl)-3-buten-2-one (β-ionone, **7**), and L-*p*-mentha-6,8-dien-2-one (L-carvone, **4**) afforded their corresponding epoxides **6′**, **7′**, and **4′**, respectively in mostly quantitative yields; no epoxidation of the double bond in the α,β-unsaturated ketone moiety was detected. Earlier work[7] demonstrated that epoxidations of α- and β-ionone (**6** and **7**) with hydrogen peroxide or phthalic monoperacid afforded the epoxides **6′** and **7′**, respectively, as the major products whose yields are lower than those obtained by our method using the reaction of nitrobenzenesulfonyl chloride with $O_2^{-}\cdot$. Epoxidations of chalcones or stilbene yielded excellent yields of their epoxides at −35 °C. Recently, Curci et al. reported that epoxidation of olefins involved peroxide-reactive intermediate of dioxirane generated in the reaction of potassium caroate ($KHSO_5$) with ketones.[8] In the presence of dimethyl sulfoxide as a trapping agent for an activated oxygen of **2**, dimethyl sulfone was obtained quantitatively along with 2-nitrobenzenesulfonate (quantitative yields). Without olefins, the oxidation of nitrobenzenesulfonyl chloride with $O_2^{-}\cdot$ gave the nitrobenzenesulfonates. In the absence of nitrobenzenesulfonyl chlorides, olefins **4** and **6** were recovered quantitatively under the same reaction conditions: no direct epoxidations between olefins and $O_2^{-}\cdot$ occurred. Thus, the obtained results can be accounted by the formation of an oxidizing reagent such as peroxysulfonate intermediate **2** in this oxidation system, though the reaction mechanism is not clear. When the epoxidations using **1a**, **1b**, and **1c** were compared with each other, **1a** gave the better yield of epoxide (**8**, X = H), in the shorter reaction time than those from **1b** and **1c**.[9]

Acknowledgment. We gratefully acknowledge financial support from the Asan Foundation.

Registry No. **1a**, 1694-92-4; **1b**, 1656-44-6; **1c**, 98-74-8; **1d**, 121-51-7; **3**, 5989-27-5; **3′**, 1195-92-2; **4**, 6485-40-1; **4′**, 56423-45-1; **5**, 25093-48-5; **5′**, 2886-87-5; **6**, 127-41-3; **6′**, 37677-81-9; **7**, 79-77-6; **7′**, 23267-57-4; **8** (X = H), 94-41-7; **8** (X = Br), 2403-27-2; **8** (X = OMe), 959-23-9; **8′** (X = H), 5411-12-1; **8′** (X = Br), 29425-81-8; **8′** (X = OMe), 40327-51-3; **9**, 530-48-3; 1,1-diphenylethylene oxide, 882-59-7; 1,2-diphenylethylene oxide, 17619-97-5; potassium superoxide, 12030-88-5; PhCH=CHPh, 588-59-0.

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(14) ^{1}H NMR (60 MHz, $CDCl_3$) δ 1.00 (3 H, Me, epoxide), 1.10–1.60 (6 H), 1.05 (6 H, Me), 2.17 (3 H, Me, CO), 5.92 (1 H, C=C), 6.52 (1 H, =CCO).

(15) ^{1}H NMR (60 MHZ, $CDCl_3$) δ 4.05, 4.15 (2 H, epoxide), 2.50 (3 H, Me).

(16) ^{1}H NMR (60 MHz, $CDCl_3$) δ 3.30 (2 H, epoxide), 7.40 (10 H, C_6H_5).

(17) "The Aldrich Library of NMR Spectra"; Aldrich Chemical Co.: Milwaukee, WI, Vol. 4, p 103.

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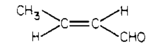
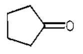
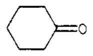
Regioreversed Addition of Crotylmagnesium Chloride to Carbonyl Compounds in the Presence of $AlCl_3$

Summary: The reaction of carbonyl compounds with crotylmagnesium chloride in the presence of $AlCl_3$ at −78 °C gives predominantly products in which the allylic group is attached at the less substituted position (α-adduct).

Sir: The reaction of unhindered carbonyl compounds with substituted allylic organometallic reagents (**1**) such as M = Li,[1] Mg,[1,2] Cu,[3] Zn,[1] Cd,[1] B,[4] Al,[1] Si,[5] Sn,[6] Ti,[7] Zr,[8] Cr,[9] and Mn,[10] generally results in products in which the allylic group is attached at the more highly substituted position (γ-adduct) (eq 1). The reaction of this type is becoming increasingly important as a basic synthetic strategy for stereoregulated synthesis of acyclic systems.[11] With hindered ketones such as di-*tert*-butyl ketone and di-isopropyl ketone, α-adduct is sometimes obtained because of the reversible addition of allylic organometallic reagents.[12]

Table I. Reaction of Carbonyl Compounds with Crotylmagnesium Chloride in the Presence of $AlCl_3$[a]

	product ratio,[b] %		
carbonyl compd	α-adduct (*E*:*Z*)	γ-adduct (*erythro*: *threo*)	total yield,[c] %
C_6H_5CHO[d]	85 (83:17)	15 (50:50)	92
C_6H_5CHO	87 (78:22)	13 (50:50)	92
C_6H_5CHO[e]	80 (95:5)	20 (50:50)	(95)
C_6H_5CHO[f]	84 (77:23)	16 (50:50)	(88)
CH_3CHO	83 (84:16)	17 (41:59)	(90)
CH_3CH_2CHO	94 (81:19)	6 (17:83)	85
$CH_3(CH_2)_2CHO$[g]	83 (84:16)	17 (31:69)	90
$CH_3(CH_2)_2CHO$	85 (84:16)	15 (40:60)	(95)
$CH_3(CH_2)_2CHO$[e]	78 (96:4)	22 (40:60)	(95)
$CH_3(CH_2)_3CHO$	86 (81:19)	14[h]	90
$CH_3(CH_2)_8CHO$	89 (83:11)	11[h]	82
$(CH_3)_2CHCHO$	84 (92:8)	16 (44:56)	90
$(CH_3)_2CHCH_2CHO$	87 (87:13)	13 (50:50)	88
	83 (85:15)	17 (44:56)	90
	84 (67:33)	16	90
	83 (66:34)	17	92
$C_6H_5C(O)CH_3$	70 (62:38)	30 (50:50)	94

[a] All reactions were carried out on a 1-mmol scale as described in the text, except where otherwise indicated.
[b] By GLC analyses using a column of CW-6000-5%-2m. The ratio of *erythro/threo* was determined by ^{1}H NMR and/or GLC.
[c] Isolated combined yield (GLC yield).
[d] One equivalent of $AlCl_3$ was used.
[e] THF was used as a solvent.
[f] HMPA (1 equiv) was added to the Mg-Al mixture.
[g] Two equivalents of $AlCl_3$ were used.
[h] Not determined.

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(1) Courtois, G.; Miginiac, L. *J. Organomet. Chem.* **1974**, *69*, 1 and references cited therein.

(2) (a) Benkeser, R. A. *Synthesis* **1971**, 347. (b) Kharasch, M. S.; Reinmuth, O. "Grignard Reactions of Nonmetallic Substances"; Prentice-Hall: Englewood Cliffs, NJ, 1954.

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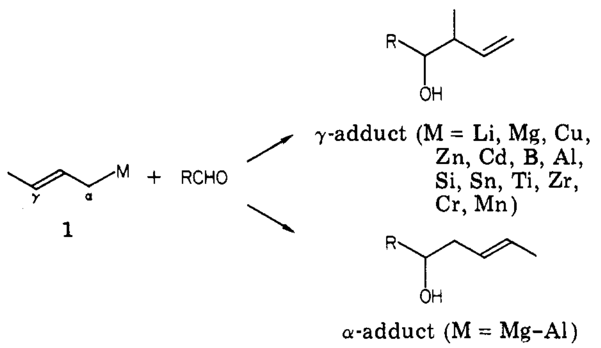
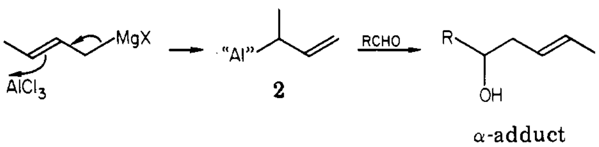
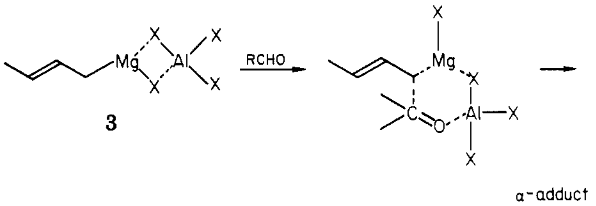


(1)

(2)



(3)



(4)

On the other hand, despite great potential importance of the regioreversed addition (shown in eq 2), such a transformation with unhindered carbonyl compounds appears totally unprecedented[13] and this problem has been one of long-standing concerns in organic chemistry. In this communication, we report that the Mg-Al system provides, for the first time, a solution to this problem. The results are summarized in the Table I.

The following procedure for the synthesis of 1-phenylpent-3-en-1-ol is representative. In a 50-mL flask equipped with a magnetic stirrer and maintained under N_2 was placed crotylmagnesium chloride in ether (1.1 mmol, 0.25 M) at −78 °C, and then $AlCl_3$ in ether (3 mmol, 2 M) was slowly added at this temperature. After 5–10 min, benzaldehyde (1 mmol, 0.1 mL) was added. The resulting mixture was allowed to warm to 0 °C and quenched with saturated NH_4Cl solution. The isomer ratio indicated in the Table I was obtained by the GLC examination of this reaction mixture. The usual workup followed by simple Kugelrohr distillation gave the mixture of α- and γ-adduct in 92% yield. Further purification through a column of silica gel with hexane–ether (20:1) as an eluant gave the desired isomer.

As is apparent from Table I, α-adduct is obtained with 83–94% regioselectivity regardless of the structure of aldehydes and the procedure is also applicable to ketones. Usually ether is used as a solvent. THF solvent causes slight decrease of α-adduct but produces the *E* isomer with greater stereoselectivity. Lewis acids other than $AlCl_3$ were also examined, but $TiCl_4$, $SnCl_4$, and $SnCl_2$ gave γ-adduct exclusively. $EtAlCl_2$ and BF_3 afforded α-adduct as a major product, though the degree of the regioselectivity was lower than that with $AlCl_3$. While the discussion of the mechanism of this regioselective C–C bond formation would be premature at this time, the following two routes may be conceivable: (i) the transmetalation of crotylmagnesium reagent to aluminum reagent via S_E2' process[14] followed by rapid S_E2' reaction of the resulting α-metallylaluminum reagent (**2**) with carbonyl compounds (eq 3); (ii) formation of the Mg–Al-bridged species (**3**)[15] followed by the coordination of carbonyl group to aluminum atom to produce α-adduct through a six-membered cyclic transition state (eq 4). The intermediate, **2** or **3**, is presumably stable only at low temperature and must undergo a facile rearrangement into crotylaluminum reagent at higher temperature. Actually, when the mixture of crotylmagnesium chloride and $AlCl_3$ was temporarily kept at 0 °C and then treated with an aldehyde at −78 °C, γ-adduct was produced quantitatively. Irrespective of the precise mechanism, it is now possible to carry out a previously unavailable organic transformation through crotylmagnesium chloride. The reaction of the Mg–Al system with other substrates and the reaction of other allylic organometallics–Al systems are being pursued.

Registry No. C_6H_5CHO, 100-52-7; CH_3CHO, 75-07-0; CH_3CH_2CHO, 123-38-6; $CH_3(CH_2)_2CHO$, 123-72-8; $CH_3(CH_2)_3CHO$, 110-62-3; $CH_3(CH_2)_8CHO$, 112-31-2; $(CH_3)_2CHCHO$, 78-84-2; $(CH_3)_2CHCH_2CHO$, 590-86-3; $C_6H_5C(O)CH_3$, 98-86-2; $AlCl_3$, 7446-70-0; (*E*)-1-phenyl-3-penten-1-ol, 75851-77-3; (*Z*)-1-phenyl-3-penten-1-ol, 75851-76-2; (*E*)-4-hexen-2-ol, 54560-70-2; (*Z*)-4-hexen-2-ol, 65709-88-8; (*E*)-5-hepten-3-ol, 64884-87-3; (*Z*)-5-hepten-3-ol, 64884-86-2; (*E*)-6-octen-4-ol, 60340-29-6; (*Z*)-6-octen-4-ol, 60340-30-9; (*E*)-7-nonen-5-ol, 85355-76-6; (*Z*)-7-nonen-5-ol, 85355-77-7; (*E*)-12-tetradecen-10-ol, 85355-78-8; (*Z*)-12-tetradecen-10-ol, 85355-79-9; (*E*)-2-methyl-5-hepten-3-ol, 66248-77-9; (*Z*)-2-methyl-5-hepten-3-ol, 75851-75-1; (*E*)-2-methyl-6-octen-4-ol, 75851-71-7; (*Z*)-2-methyl-6-octen-4-ol, 75851-70-6; (*E,E*)-2,6-octadien-4-ol, 85355-80-2; (*E,Z*)-2,6-octadien-4-ol, 85355-81-3; (*E*)-1-(2-butenyl)cyclopentanol, 85355-82-4; (*Z*)-1-(2-butenyl)cyclopentanol, 85355-83-5; (*E*)-1-(2-butenyl)cyclohexanol, 85355-84-6; (*Z*)-1-(2-butenyl)cyclohexanol, 85355-85-7; (*E*)-2-phenyl-4-hexen-2-ol, 85355-86-8; (*Z*)-2-phenyl-4-hexen-2-ol, 85355-87-9; (*E*)-2-butenal, 123-73-9; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; crotyl chloride, 591-97-9.

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[13] $(\eta^3$-1,1-Dimethylallyl)nickel bromide reacts with benzil to give 1,2-diphenyl-2-hydroxy-5-methylhex-5-en-1-one predominantly but does not react with ordinary substrates such as cyclohexanone and cyclohexenone (Hegedus, L. S.; Wagner, S. D.; Waterman, E. L.; S-Hansen, K. *J. Org. Chem.* **1975**, *40*, 593). For the reaction of π-allyl and (π-2-methylallyl)nickel complexes with carbonyl compounds, see: Semmelhack, M. F. *Org. React.* (N.Y.) **1972**, *19*, 115. Crotyltrimethylsilane reacts with butanal in the presence of F^- to produce α-adduct together with γ-adduct, and the regioselectivity is not great (Hosomi, A.; Sirahata, A.; Sakurai, H. *Tetrahedron Lett.* **1978**, 3043). See also: Chan, T. H.; Kang, G. J. *Ibid.* **1982**, *23*, 3011.

[14] Usually such a transformation from Mg to Si, Sn, Zn, Cd, or Hg takes place without any allylic rearrangement.[1] See also: Hosomi, A.; Iguchi, H.; Sakurai, H. *Chem. Lett.* **1982**, 223.

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Directed Metalation of Tertiary Benzamides. Silicon Protection of Ortho Sites and Ortho Methyl Groups

Summary: Metalation of 2-trimethylsilyl or 2-bis(trimethylsilyl)methyl benzamides occurs selectively at the 6-position, providing regiospecific routes to various trisubstituted benzenes.

Sir: The directed ortho metalation[1] of aromatic tertiary amides,[2] secondary amides,[3] and 2-oxazolines[4] (**1**) provides

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