

# ORGANOMETALLIC COMPOUND WITH LEWIS BASE—IV<sup>a</sup> DIMERIZATION OF METHYL CROTONATE BY ALUMINUM ALKYL-TERTIARY AMINE COMPLEX

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**Abstract**—Aluminum alkyl-tertiary amine complex was found to induce the catalytic dimerization of methyl crotonate (MCr) to dimethyl 2-methylpent-4-ene-1,3-dicarboxylate (1) and dimethyl 2-methylpent-*cis*-3-ene-1,3-dicarboxylate (2). The dimerization to dimer 1 is initiated by the abstraction of the  $\gamma$ -hydrogen of the MCr molecule. Dimer 2 is formed through the isomerization of dimer 1. The complex of AlR<sub>3</sub> with a bidentate ligand, sparteine, produces dimer 1, selectively. The complex of AlR<sub>3</sub> with monodentate ligand NEt<sub>3</sub>, on the other hand, induces the isomerization of dimer 1 to the *cis*-form of dimer 2. The coordination number of aluminum alkyl-tertiary amine complex seems to control the dimerization mechanism of MCr.

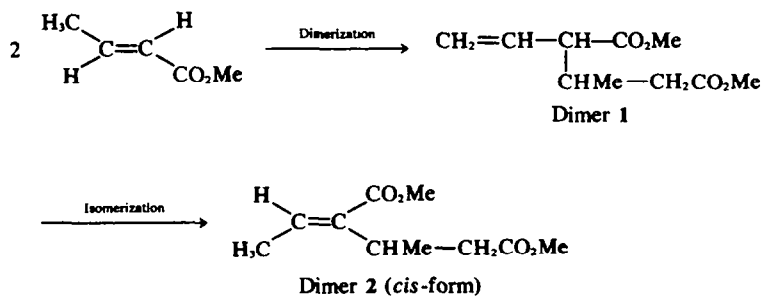
## INTRODUCTION

Lewis base added as complexing agent to aluminum alkyl not only activates the aluminum-alkyl bond but also controls the mode of reaction catalyzed by the complex.

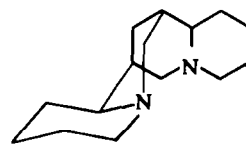
As described in our previous papers, aluminum alkyl complexed with certain kinds of Lewis base shows catalytic activity for the polymerization of

formed through an isomerization reaction of the assumed intermediate, dimer 1, although they did not detect the dimer 1 in their reaction system.<sup>4</sup>

Thus, the selective dimerization of MCr to dimer 1 by aluminum alkyl-sparteine complex and the selective isomerization of dimer 1 to the *cis*-form of dimer 2 by aluminum alkyl-NEt<sub>3</sub> complex are characteristic of the aluminum alkyl-tertiary amine



(1)



Sparteine

acrylonitrile and methyl methacrylate,<sup>1,2</sup> and aluminum alkyl-sparteine complex catalyzed a selective dimerization reaction of methyl crotonate (MCr) to dimer 1.<sup>3</sup>

Further study revealed that the dimerization reaction by aluminum alkyl-NEt<sub>3</sub> complex was accompanied with a selective isomerization reaction of dimer 1 to *cis*-form of dimer 2.

Saegusa *et al.* reported that Cu<sub>2</sub>O-isocyanide system dimerized MCr to a mixture of dimer 2 and its *trans*-isomer.<sup>4</sup> These dimers were considered to be

complex. More detailed study of these dimerization and isomerization reactions is described herein as part of a general investigation of the chemistry of AlR<sub>3</sub>-Lewis base complex system.

## EXPERIMENTAL

**Materials.** All the solvents were purified by conventional method: benzene(Bz), diethyl ether (Et<sub>2</sub>O) and n-pentane(n-Pent) were distilled over sodium benzophenone under purified N<sub>2</sub>. Al(*i*Bu)<sub>3</sub>, AlEt<sub>3</sub>, and AlMe<sub>3</sub> were distilled under reduced pressure. Sparteine(Spar) was prepared from sparteine sulfate by neutralization with KOH, and then distilled over calcium hydride: b.p.

\*Part III: see Ref 2.

120°C/1.8 mmHg,  $[\alpha]_D^{25} - 5.13$  (benzene).  $\text{NEt}_3$  and hexamethylphosphoric triamide (HMPA) were distilled over calcium hydride, and pyridine was distilled over barium oxide.  $\alpha, \alpha'$ -Dipyridyl (Dip) and PPh<sub>3</sub> were recrystallized from *n*-hexane solution. Tetramethyl-*o*-phenylenediamine (TMPDA) was prepared by the method described in our previous paper.<sup>2</sup> 8-(Dimethylamino)quinoline (DMAQ) was prepared from 8-hydroxyquinoline.<sup>5</sup> Methyl crotonate (MCr) and methyl acrylate (MA) were purified by conventional method. Methyl  $\alpha$ -isopropylacrylate (MPra) was also prepared by the method described previously.<sup>2</sup>

**Preparation of methyl 4-methyl-trans-2-hexenoate (MMH).** Active amyl alcohol was oxidized to 2-methylbutanal by  $\text{K}_2\text{Cr}_2\text{O}_7\text{-H}_2\text{SO}_4$  system,<sup>6</sup> b.p. 94°, yield 60%. 2-Methylbutanal (0.4 mol) was reacted with malonic acid (0.4 mol) in the presence of 45 ml of pyridine for 3 h at 80°. The mixture was then poured into a mixture of  $\text{H}_2\text{O}$  (30 ml) and  $\text{H}_2\text{SO}_4$  (15 ml) at 0°. From the ether extract, *trans*-4-methyl-2-hexenoic acid (0.15 mol) was obtained by distillation under reduced pressure; b.p. 114°/13 mmHg, yield 37%. A mixture of *trans*-4-methyl-2-hexenoic acid (0.15 mol),  $\text{Ag}_2\text{O}$  (0.15 mol) and MeI (0.15 mol) in  $\text{Et}_2\text{O}$

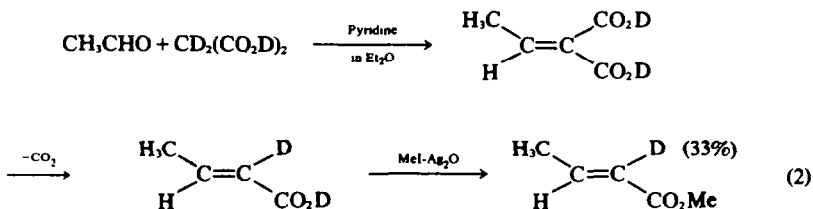
(Calcd. 200). (Found: C, 59.7; H, 8.0, Calcd. for 1: C, 60.0; H, 8.0%).

**Dimer (2)** (Dimethyl 2-methylpent-*cis*-3-ene-1,3-dicarboxylate)\*: NMR (in  $\text{CCl}_4$ );  $\tau$  3.30 (q, 1H,  $\text{H}-\overset{|}{\text{C}}=\text{C}$ ),  $\tau$  6.34 (s, 3H,  $\text{C}=\text{C}-\text{CO}_2\text{CH}_3$ ),  $\tau$  6.42 (s, 3H,  $-\text{CH}_2\text{CO}_2\text{CH}_3$ ),  $\tau$  6.59-6.95 (m, 1H,  $\text{CH}_3-\overset{|}{\text{C}}\text{H}-$ ),  $\tau$  7.19-7.67 (m (ABX type), 2H,  $-\text{CH}_2-\text{CO}_2\text{CH}_3$ ),  $\tau$  8.14 (d, 3H,  $\text{CH}_3-\overset{|}{\text{C}}=\text{C}$ ),  $\tau$  8.83 (d, 3H,  $\text{CH}_3-\overset{|}{\text{C}}\text{H}$ ). Principal IR bands ( $\text{cm}^{-1}$ ) (liquid

film); 1745, 1720 vs ( $\nu_{\text{C=O}}$ ), 1645 w ( $\nu_{\text{C=C}}$ ). Molecular weight by mass spectrometry; 200 (Calcd. 200). (Found: C, 59.9; H, 8.1, Calcd. for 2: C, 60.0; H, 8.0%).

**Gas volumetry of ethane generated by the reaction of MCr with  $\text{AlEt}_3$ -Spar complex.** Before the reaction, MCr and  $\text{AlEt}_3$ -Spar solns were saturated with purified ethane which was made free from oxygen and moisture by passing through a benzene solution of  $\text{AlEt}_3$ . MCr was then added to a mixture of  $\text{AlEt}_3$  and Spar solns, and the volume of generated ethane was measured by a gas burette.

**Preparation of partially deuterated MCr.** MCr partially deuterated at the  $\alpha$ -position was prepared as follows:



(180 ml) was refluxed with stirring for 18 h, and then filtered.  $\text{Et}_2\text{O}$  and MeI were removed from the filtrate by distillation, and a further distillation under reduced pressure gave MMH (0.097 mol); b.p. 45°/6 mmHg, yield 65%. The thus obtained MMH proved to be an exclusively *trans*-form from the large value ( $J = 15.6$  Hz) of coupling constant between the two olefinic protons.

**Dimerization of MCr.** MCr was added to a mixture of aluminum alkyl and Spar or  $\text{NEt}_3$  solutions. After a given time of reaction, the mixture was poured into water containing a small amount of HCl. The ether extract of the reaction product was distilled, giving at 90°-110°/10 mmHg dimers of MCr, i.e. dimer 1 and dimer 2. Dimer 1 and dimer 2 were separated by gas chromatograph. The thus obtained dimers were subjected to structure determination and optical activity measurement. The yield of dimer, the consumption of MCr monomer and the amount of produced methanol were determined by gas chromatography.

**Dimer (1)** (Dimethyl 2-methylpent-4-ene-1,3-dicarboxylate): NMR (in  $\text{CCl}_4$ );  $\tau$  4.05-4.47 (m, 1H,  $\text{CH}_2=\overset{|}{\text{C}}\text{H}-$ ),  $\tau$  4.79-5.07 (m, 2H,  $\text{CH}_2=\overset{|}{\text{C}}\text{H}-$ ),  $\tau$  6.38 (s, 3H,  $\text{CO}_2\text{CH}_3$ ),  $\tau$  6.42 (s, 3H,  $\text{CO}_2\text{CH}_3$ ),  $\tau$  6.99-7.35 (m, 1H,  $\text{CH}_2=\overset{|}{\text{C}}\text{H}-$ ),  $\tau$  7.47-8.19 (m, 3H,  $-\overset{|}{\text{C}}\text{H}(\text{CH}_3)-\overset{|}{\text{C}}\text{H}_2-$ ),  $\tau$  9.11 (d, 3H,  $\text{CH}_3-\overset{|}{\text{C}}\text{H}$ ). Principal IR bands ( $\text{cm}^{-1}$ ) (liquid film); 1745 vs ( $\nu_{\text{C=O}}$ ), 1645 w ( $\nu_{\text{C=C}}$ ), 930 ( $\delta_{\text{C-H}}$  of  $-\text{CH}=\text{CH}_2$ ). Molecular weight by mass spectrometry; 197

A mixture of *d*<sub>2</sub>-malonic acid (0.10 mol), acetaldehyde (0.10 mol) and pyridine (0.10 mol) in 10 ml of  $\text{Et}_2\text{O}$  was heated at 90° for 16 h in a closed vessel. The mixture was poured into 25 ml of 5N HCl cooled at 0°. Crude deuterated crotonic acid (0.06 mol) was obtained from the ether extract. A mixture of the crude deuterated crotonic acid (0.06 mol),  $\text{Ag}_2\text{O}$  (0.08 mol) and MeI (0.08 mol) in 70 ml of  $\text{Et}_2\text{O}$  was refluxed with stirring for 22 h, and then filtered.  $\text{Et}_2\text{O}$  and MeI were removed from the filtrate by distillation, and the further distillation give partially deuterated MCr (0.03 mol) at 118-120°. The NMR spectrum of the partially deuterated MCr showed that  $\alpha$ -hydrogen was 33% deuterated and  $\beta$ - and  $\gamma$ -hydrogens were scarcely deuterated (< 2%).

**Reaction of partially deuterated MCr with  $\text{AlEt}_3$ -Spar complex.** Partially deuterated MCr (25 mmol) was added to a mixture of  $\text{AlEt}_3$  (5 mmol) and Spar (5 mmol) in 5.5 ml of benzene, and was stirred at 30° for 2 h. Purified  $\text{N}_2$  was bubbled into the mixture for 20 min to purge generated ethane which was collected in a trap cooled by liquid  $\text{N}_2$ . The thus obtained ethane was analyzed by mass spectrometry to prove that the proportion of deuterated ethane to total ethane was very small ( $\approx 2\%$ ).

**Codimerizations of MMH with methyl acrylate derivatives.**  $\text{AlEt}_3\text{-NEt}_3$  (1:1) complex was reacted with an equimolar amount of MMH for 2 h at 30°. The comonomer methyl acrylate deriv was then added to this mixture. After 21 h of reaction at 30°, the mixture was poured into water containing a small amount of HCl. The codimer of MMH was isolated by gas chromatograph from the ether extract containing unreacted monomers and a small amount of by-products.

MMH-methyl  $\alpha$ -isopropylacrylate (MPra) codimer (Di-

\*These NMR data of dimer 2 agree with those reported for the *cis* isomer in the *cis-trans* mixture.<sup>4</sup>

methyl 2,7-dimethylnon-6-ene-3,5-dicarboxylate): NMR (in CCl<sub>4</sub>);  $\tau$  4.95–5.23 (m, 1H, C=CH),  $\tau$  6.43 (s, 6H, CO<sub>2</sub>CH<sub>3</sub> × 2),  $\tau$  6.94 (sext(AM<sub>2</sub>X type), 1H,

C=C-CH-CO<sub>2</sub>CH<sub>3</sub>),  $\tau$  8.40 (*cis*) and  $\tau$  8.44 (*trans*) (2s, 3H, H<sub>3</sub>C-C=C),  $\tau$  7.80–8.38 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>-C=C, -CH<sub>2</sub>-CH-CO<sub>2</sub>CH<sub>3</sub> and -CH(CH<sub>3</sub>)<sub>2</sub>),  $\tau$  8.92–9.20 (m, 9H, CH<sub>3</sub>CK<sub>2</sub> and -CH(CH<sub>3</sub>)<sub>2</sub>). Principal IR bands (cm<sup>-1</sup>) (liquid film); 1745 vs ( $\nu_{C=O}$ ), 1635 vw ( $\nu_{C=C}$ ). (Found: C, 66.99; H, 9.76, Calcd. for C<sub>15</sub>H<sub>26</sub>O<sub>4</sub>: C, 66.67; H, 9.63%).

MMH-MCr codimer (Dimethyl 2,5-dimethylhept-4-ene-1,3-dicarboxylate): NMR (in CCl<sub>4</sub>);  $\tau$  4.90–5.15 (m, 1H, C=CH),  $\tau$  6.52 (s, 6H, CO<sub>2</sub>CH<sub>3</sub> × 2),  $\tau$  6.84–7.16

(m, 1H, C=C-CH-CO<sub>2</sub>CH<sub>3</sub>),  $\tau$  7.60–8.20 (m, 5H, CH<sub>2</sub>CH<sub>2</sub>-C=C and -CH(CH<sub>3</sub>)-CH<sub>2</sub>-CO<sub>2</sub>CH<sub>3</sub>),  $\tau$  8.38 (*cis*) and  $\tau$  8.46 (*trans*) (2s, 3H, H<sub>3</sub>C-C=C),  $\tau$  8.96–9.40 (m, 6H, CH<sub>3</sub>CH<sub>2</sub>- and >CHCH<sub>3</sub>). Principal IR bands (cm<sup>-1</sup>) (liquid film); 1745 vs ( $\nu_{C=O}$ ), 1635 vw ( $\nu_{C=C}$ ). (Found: C, 64.20; H, 8.58, Calcd. for C<sub>13</sub>H<sub>22</sub>O<sub>4</sub>: C, 64.46; H, 9.09%).

MMH dimer (Methyl 3,7-dimethylnon-6-ene-4-methoxycarbonylmethyl-5-carboxylate): NMR (in CCl<sub>4</sub>);  $\tau$  4.90–5.20 (m, 1H, C=CH),  $\tau$  6.48 (s, 3H, C=C-CH-CO<sub>2</sub>CH<sub>3</sub>),  $\tau$  6.51 (s, 3H, CH<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>),  $\tau$  6.87 (t,

1H, C=C-CH-CO<sub>2</sub>CH<sub>3</sub>),  $\tau$  7.50–8.23 (m, 6H, CH<sub>2</sub>CH<sub>2</sub>-C=C and CH<sub>3</sub>-CH-CH<sub>2</sub>-CO<sub>2</sub>CH<sub>3</sub>),  $\tau$  8.33 (*cis*) and  $\tau$  8.40 (*trans*) (2s, 3H, H<sub>3</sub>C-C=C),  $\tau$  8.80 (m, 2H, CH-CH<sub>2</sub>-CH<sub>3</sub>),  $\tau$  8.93–9.40 (m, 9H, CH<sub>2</sub>CH<sub>2</sub>-C=C and CH<sub>3</sub>-CH-CH<sub>2</sub>-CH<sub>3</sub>). Principal IR band (cm<sup>-1</sup>) (liquid film);

1740 vs ( $\nu_{C=O}$ ). (Found: C, 67.54; H, 9.48, Calcd. for C<sub>16</sub>H<sub>28</sub>O<sub>4</sub>: C, 67.61; H, 9.86%).

**Diastereomer distribution of dimer 1.** In benzene, the NMR spectrum of CH-CH<sub>3</sub> part of dimer 1 shows the

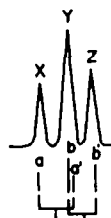


Fig. 1. NMR spectrum of CH-CH<sub>3</sub> part of dimer 1 in benzene and their assignments.

signals shown in Fig 1. These signals are considered to be an overlapping of two kinds of doublet (a, a' and b, b'), which come from the two diastereomers. Assuming a'/a=b'/b (a > a', b > b'), the ratio of diastereomers can be obtained from the observed X, Y, Z areas.

## RESULTS AND DISCUSSION

### 1. General feature of dimerization of methyl crotonate

The results of the dimerization of methyl crotonate(MCr) by the complexes of AlEt<sub>3</sub> with various Lewis bases are shown in Table 1. The dimerization products are dimer 1 and dimer 2. NMR spectra of

Table 1. Dimerization of methyl crotonate by AlEt<sub>3</sub>-Lewis base complex<sup>a</sup>

Lewis base	pK <sub>a</sub>	Reaction time (hr)	Dimer yield (%) <sup>b</sup>	Dimer composition(%)		Polymn. Activity <sup>c</sup>	
				1	2	AN	MMA
Spar	9.5	2	163	100	trace	○	○
			339	99	1		
NEt <sub>3</sub>	10.9	2	44	97	3	○	○
			268	69	31		
Dip <sup>d</sup>	4.1	22	0	—	—	○	○
TMPDA <sup>e</sup>	6.4 <sup>h</sup>	22	0	—	—	○	×
DMAQ <sup>f</sup>	5.1 <sup>i</sup>	22	0	—	—	○	×
	4.8 <sup>j</sup>						
Pyridine	5.2	22	0	—	—	×	×
PPh <sub>3</sub>		22	0	—	—	○	○
HMPA <sup>g</sup>		22	0	—	—	○ <sup>k</sup>	×
None	—	22	0	—	—	×	×

<sup>a</sup> AlEt<sub>3</sub> = 3.30 mmol, Lewis base = 3.30 mmol (bidentate ligand) or 6.60 mmol (monodentate ligand), MCr = 33.0 mmol. Solvent: benzene 5.5 ml. Reaction temperature: 30°C.

<sup>b</sup> Total dimer yield based on AlEt<sub>3</sub>.

<sup>c</sup> Polymerization activity of the AlEt<sub>3</sub>-Lewis base complex for AN and MMA.<sup>2</sup> ○: active, ×: inactive.

<sup>d</sup> α,α'-Dipyridyl

<sup>e</sup> Tetramethyl-*o*-phenylenediamine

<sup>f</sup> 8-(Dimethylamino)quinoline

<sup>g</sup> Hexamethylphosphoric triamide

<sup>h</sup> Value for *para*-form

<sup>i</sup> Value for *N,N'*-dimethylaniline

<sup>j</sup> Value for quinoline

<sup>k</sup> Unpublished data

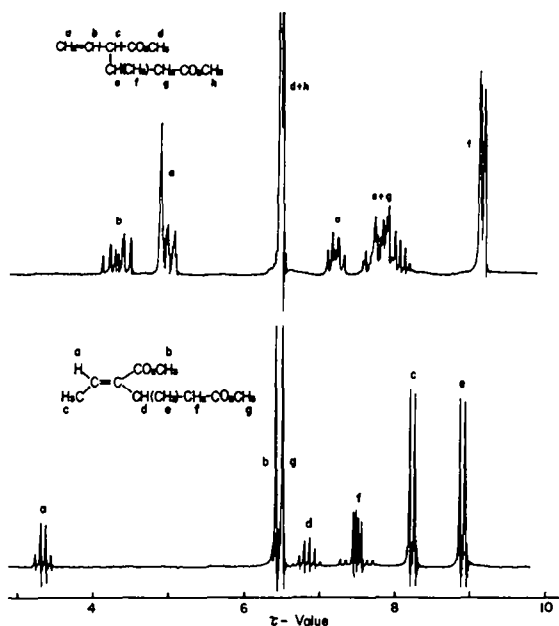


Fig 2. 100 MHz-<sup>1</sup>H-NMR spectra of dimer 1 and dimer 2 in CCl<sub>4</sub> at room temperature.

dimer 1 and dimer 2 are shown in Fig 2. It is to be noted that dimer 2 is only *cis* in form.

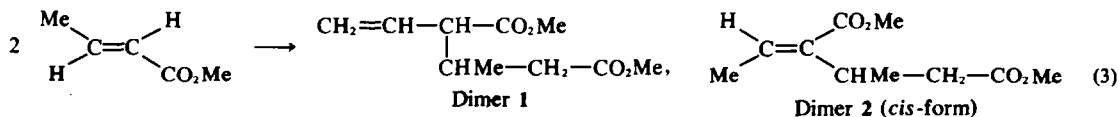


Table 1 also contains rough features on the activities of the complexes for the polymerization of acrylonitrile (AN) and methyl methacrylate (MMA). The complexes active as catalysts for the polymerization of AN and MMA are not necessarily active catalysts for the dimerization of MCr, only the complexes with highly basic tertiary amines, such as Spar and NEt<sub>3</sub>, being active.

The time-conversion curves of the dimerization reaction of MCr by AlEt<sub>3</sub>-Spar and AlEt<sub>3</sub>-NEt<sub>3</sub> complexes are shown in Fig 3. The AlEt<sub>3</sub>-Spar complex produces almost only dimer 1, though it does produce a small amount of dimer 2 after a prolonged reaction time. In the case of the AlEt<sub>3</sub>-NEt<sub>3</sub> complex, on the other hand, the amount of dimer 2 increases remarkably with reaction time while the amount of dimer 1 decreases after passing the maximum point. This result indicates that dimer 2 is produced through the isomerization reaction of dimer 1.

It was reported in our previous paper<sup>2</sup> that the monodentate ligand NEt<sub>3</sub> forms only an equimolar 4-coordinated complex 3 with AlEt<sub>3</sub> even in the presence of excess NEt<sub>3</sub>, in contrast to the biden-

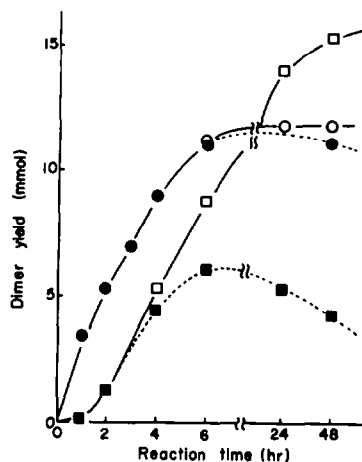


Fig 3. Dimerization of methyl crotonate by AlEt<sub>3</sub>-Spar and AlEt<sub>3</sub>-NEt<sub>3</sub> complexes. AlEt<sub>3</sub>-Spar complex: ○ 1 + 2, ● 1. AlEt<sub>3</sub>-NEt<sub>3</sub> complex: □ 1 + 2, ■ 1. Reaction temperature: 30°C. Solvent: benzene 5.5 ml. MCr = 33 mmol, MCr/AlEt<sub>3</sub> = 10, Spar/AlEt<sub>3</sub> = 1, NEt<sub>3</sub>/AlEt<sub>3</sub> = 2.

tate ligand Spar which forms an associated pseudo 5-coordinated complex 4.

For the dimerization of MCr, AlEt<sub>3</sub>-NEt<sub>3</sub> system shows the largest catalytic activity when the ratio of NEt<sub>3</sub>/AlEt<sub>3</sub> is one, the excess NEt<sub>3</sub> having no influence on the activity, as is shown in Fig 4. This

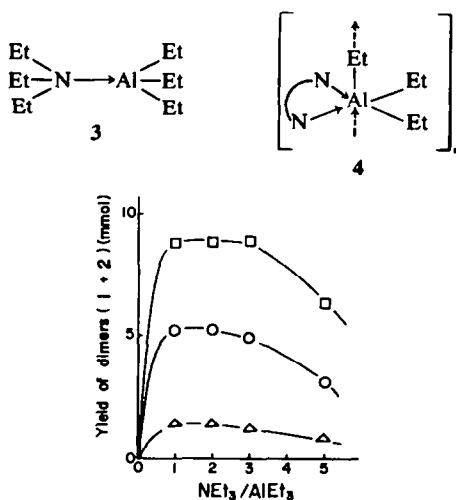


Fig 4. Reactivity of AlEt<sub>3</sub>-NEt<sub>3</sub> system for the dimerization reaction of methyl crotonate at various NEt<sub>3</sub>/AlEt<sub>3</sub> ratios. Reaction temperature: 30°C. AlEt<sub>3</sub> = 3.3 mmol, MCr = 33 mmol. Solvent: benzene 5.5 ml. Reaction time: △ 2 hr, ○ 4 hr, □ 6 hr.

fact may suggest that the above mentioned equimolar 4-coordinated  $\text{AlEt}_3\text{-NEt}_3$  complex **3** operates as the active species.

## 2. Dimerization of methyl crotonate to Dimer 1

In the early stage of the dimerization reaction, the generation of ethane was detected by gas chromatography and the amount of ethane was measured by gas volumetry. The results are shown in Fig 5. This fact implies that the dimerization was initiated by the hydrogen abstraction from MCr molecule with the activated  $\text{Et-Al}$  bond.

The hydrogen of MCr to be abstracted is either  $\alpha$ - or  $\gamma$ -hydrogen; the latter may be more probable from the structure of the product dimer **1**. To confirm this conjecture, a 33%  $\alpha$ -deuterated, and less than 2%  $\beta$ - and  $\gamma$ -deuterated, MCr ( $\alpha$ - $d_1$ -methyl crotonate) was submitted to the dimerization reaction by  $\text{AlEt}_3\text{-Spar}$  complex. Mass spectroscopic analysis of the generated ethane showed that the deuterated ethane content in the total ethane was about 2%. This result indicates that the  $\alpha$ -hydrogen of MCr was scarcely abstracted by the  $\text{AlEt}_3\text{-Spar}$  complex. It follows that the hydrogen abstraction reaction should occur at the  $\gamma$ -hydrogen of MCr.

Thus, the mechanism of dimerization of MCr to dimer **1**, initiated by  $\gamma$ -hydrogen abstraction, is considered to be as follows:

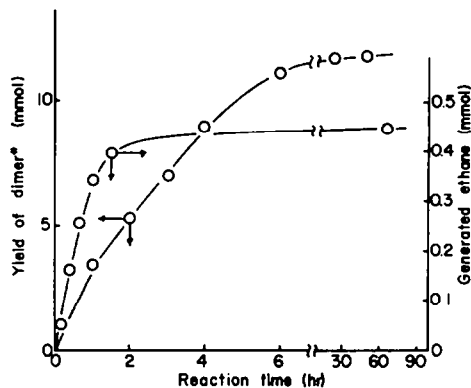
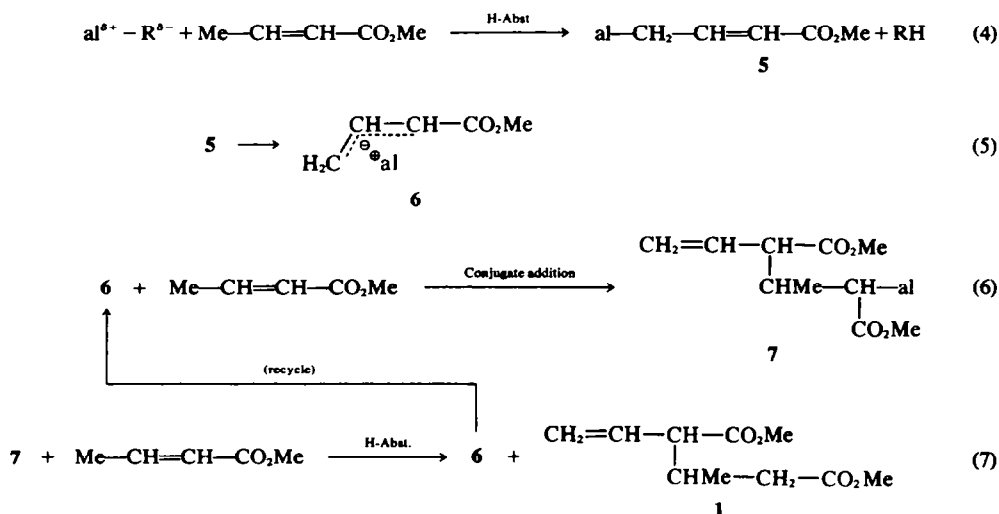


Fig 5. Generation of ethane in the dimerization reaction of methyl crotonate by  $\text{AlEt}_3\text{-Spar}$  complex. Reaction temperature:  $30^\circ\text{C}$ .  $\text{AlEt}_3 = 3.3$  mmol, Spar =  $3.3$  mmol, MCr =  $33$  mmol. Solvent: benzene  $5.5$  ml. (\*Dimer is almost only **1**.)

attacks the MCr molecule to produce conjugate addition product **7**. The species **7** seems to undergo the hydrogen abstraction reaction much more readily than further conjugate additions to MCr molecules, because the carbon-carbon double bond in MCr is sterically hindered by the  $\beta$ -methyl group. In fact, high molecular weight product is scarcely detected in this reaction system. The



where al stands for the  $\text{Et}_2\text{Al-Spar}$  complex residue.

The acidic  $\gamma$ -hydrogen of MCr molecule is abstracted by aluminum alkyl-tertiary amine complex to form **5**, which may possess a delocalized structure, **6**. The fact that active catalysts for the polymerization of MMA and AN are not necessarily active for the dimerization of MCr, as shown in Table 1, may be correlated with their ability in hydrogen abstraction reaction. The species **6**

hydrogen abstraction of **7** from MCr molecule leads to dimer **1** and the species **6**. Thus, through the reproduction of **6**, the dimerization reaction of MCr proceeds catalytically.

Methyl 4-methyl-*trans*-2-hexenoate (MMH), which also has a  $\gamma$ -hydrogen, was codimerized with some methyl acrylate derivatives by  $\text{AlEt}_3\text{-NEt}_3$  complex. The codimer of MMH with methyl acrylate (MA) was not obtained, due to the high polymerizability of MA. On the other hand, MMH

Table 2. Codimerizations of methyl 4-methyl-*trans*-2-hexenoate(MMH) with methyl acrylate derivatives by AlEt<sub>3</sub>-NEt<sub>3</sub> complex<sup>a</sup>

Comonomer		Yield of codimer (mmol)	Chemical shift of MeC=C(τ) <sup>f</sup>	
R <sup>1b</sup>	R <sup>2b</sup>		<i>trans/cis</i> <sup>f</sup>	<i>trans</i> <i>cis</i>
MA <sup>c</sup>	H	0	—	—
MPrA <sup>d</sup>	H	4.99	1.2	8.46 8.38
MCr	Me	4.77 <sup>e</sup>	1.6	8.44 8.40
MMH	secBu	3.23	9.0	8.40 8.33

<sup>a</sup>Reaction temperature: 30°C. Reaction time: 21 hr. AlEt<sub>3</sub> = NEt<sub>3</sub> = MMH = Comonomer = 11 mmol. Solvent: benzene 16 ml. Comonomer was added after MMH was reacted with AlEt<sub>3</sub>-NEt<sub>3</sub> complex for 2 hr at 30°C.

<sup>b</sup>R<sup>1</sup>, R<sup>2</sup> are substituent groups of methyl acrylate derivatives, as given in Eq (8).

<sup>c</sup>Methyl acrylate.

<sup>d</sup>Methyl α-isopropylacrylate.

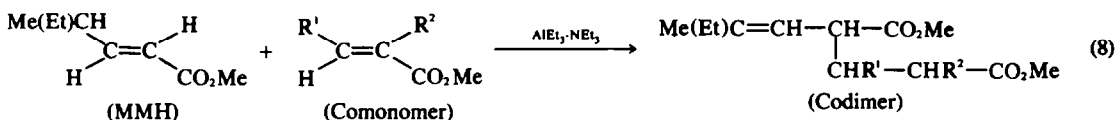
<sup>e</sup>In addition, 2.66 mmol of MCr dimer 2 was obtained.

<sup>f</sup>The ratio of the geometrical isomers (*trans/cis*) was determined by the area ratio of two kinds of NMR signal of olefinic Me protons (Me-C=C) in codimer.

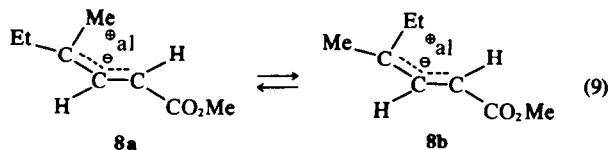
gave codimers with non-polymerizable monomer such as methyl α-isopropylacrylate(MPrA) or MCr, as is shown in Table 2.

The structures of the dimers were exclusively those of the dimer 1 type. The *trans/cis* ratios of

The steric requirement, caused by the β-substituent (R<sup>1</sup>) of the comonomer, at the transition state of the conjugate addition reaction would be smaller in **8a** than in **8b**, which results in the predominant formation of the *trans*-isomer. There-



codimers are dependent on the bulkiness of the β-substituent group (R<sup>1</sup>) in the comonomer: the ratio of *trans/cis* increases with the bulkiness of R<sup>1</sup>. This result could be explained in terms of the following equilibrium of the delocalized structure of MMH anion.

Table 3. Specific rotation of dimer 1 obtained by AlR<sub>3</sub>-Spar complex<sup>a</sup>

R	Solvent	MCr/Al	[α] <sub>D</sub> <sup>25</sup> (in benzene)
Et	Bz	1	+1.15
Me	n-Pent	1	+1.30
Et	Bz	10	+0.68
Et	Et <sub>2</sub> O	10	+0.21
Me	Bz	10	+0.23
iBu	Bz	10	+0.32
cf.	Spar		-5.13

<sup>a</sup>Dimerization condition. Reaction temperature: 30°. AlR<sub>3</sub> = Spar = 33 mmol. Solvent: 40 ml (MCr/Al = 1) or 55 ml (MCr/Al = 10).

fore, the selection of *trans*-form will become more predominant as the bulkiness of R<sup>1</sup> increases.

The dimer of MCr obtained by aluminum alkyl-Spar complex shows optical activity, as is shown in Table 3. This asymmetric synthesis is a direct evidence that dimerization reaction did take place on

the AlR<sub>3</sub>-Spar complex under chiral circumstance of the ligand, Spar.

### 3. Isomerization of dimer 1 to dimer 2

Dimer 1 was isomerized to dimer 2 rapidly by reaction with AlEt<sub>3</sub>-NEt<sub>3</sub> complex, as is shown in Fig 6.

On the other hand, the AlEt<sub>3</sub>-Spar complex isomerized dimer 1 to dimer 2 only with great difficulty. Dimer 2 obtained by these isomerization reactions is exclusively *cis*-form. This result and the variation of the dimer composition with reaction time, as is shown in Fig 3, lead to the conclusion that dimer 2 is formed through an isomerization reaction of pre-produced dimer 1.

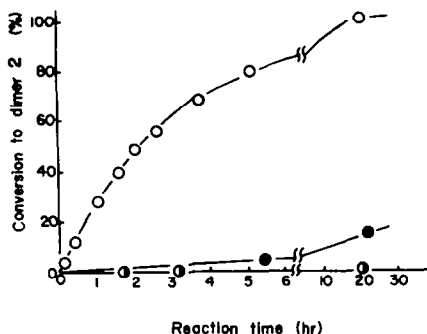
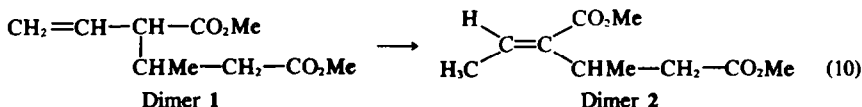


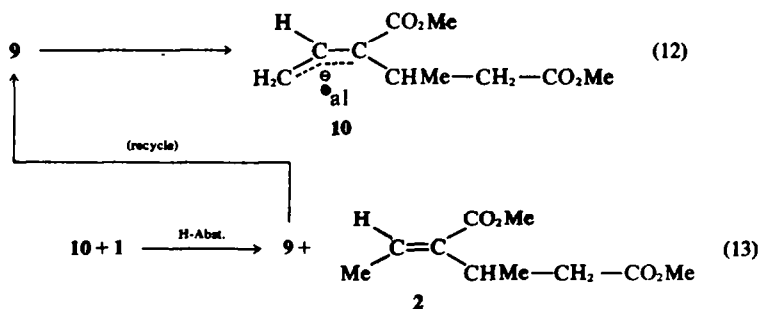
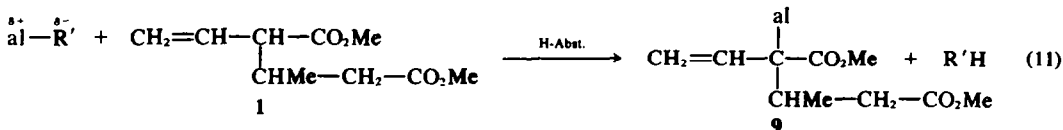
Fig. 6. Isomerization of dimer 1 to dimer 2. ○ AlEt<sub>3</sub>-NEt<sub>3</sub>, (1:1), ● AlEt<sub>3</sub>-Spar (1:1), ◐ AlEt<sub>2</sub>H-NEt<sub>3</sub>, (1:1). Reaction temperature: 30°. Dimer 1 = 10 mmol, Dimer 1/Al = 3. Solvent: benzene 5.5 ml.



and that the selective production of dimer 1 by AlEt<sub>3</sub>-Spar complex is due to the low rate of the isomerization reaction by this complex.

AlEt<sub>2</sub>H-NEt<sub>3</sub> complex did not isomerize dimer 1 to dimer 2. Therefore, this isomerization was not induced by the trace amount of aluminum hydride as is often seen in the isomerization of olefin by transition metal catalyst.

The most probable isomerization mechanism may be as follows:



The absence of the isomerization reaction in the case of the cation R<sub>2</sub>Al<sup>+</sup>-Spar system could be explained in terms of the significant steric repulsion between the bidentate ligand and -CHMe-CH<sub>2</sub>-CO<sub>2</sub>Me group in 10.

#### 4. Carbonyl addition of the AlR<sub>3</sub>-tertiary amine complex

As is shown in Fig 7, at higher temperature, such as 50°, the dimerization reaction shows features different from the reaction at around 30°; i.e. the dimerization reaction did not proceed beyond a certain low conversion. The reacted MCr turned almost quantitatively into dimer 1 because the observed ratio of the amount of reacted MCr to that of dimer 1 was approximately 2 to 1. Besides this dimerization reaction, methanol up to almost one-third of the total mole amount of aluminum-ethyl bond was detected upon acid hydrolysis of the reaction system. These results indicate that a concurrent carbonyl addition reaction takes place, transforming the active aluminum-alkyl bond into aluminum alkoxide, which is inactive for the dimerization of MCr.

#### 5. Dimerizations by various catalyst systems

The yields and the compositions of the dimers, formed with several kinds of aluminum alkyl-tertiary amine complex in various solvents, are shown in Table 4. The reactivity of AlEt<sub>3</sub>-Spar decreased remarkably in a polar solvent, Et<sub>2</sub>O, whereas the reactivity of AlEt<sub>3</sub>-NEt<sub>3</sub> complex was almost independent of the nature of solvents. In the former case, polar solvent molecules might occupy the sixth coordination site of the pseudo 5-

coordinated AlEt<sub>3</sub>-Spar complex 4, becoming an inactive catalyst species for the dimerization reaction. On the other hand, there would be little possibility for polar solvents to coordinate to aluminum atom in the 4-coordinated AlEt<sub>3</sub>-NEt<sub>3</sub> complex 3.

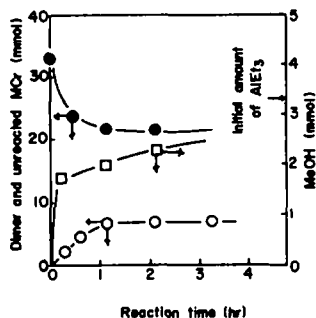


Fig 7. Dimer yield\*, MCr consumption and amount of produced MeOH in the dimerization of MCr by  $\text{AlEt}_3$ -Spar complex at  $50^\circ\text{C}$ . Dimer yield (○), amount of unreacted MCr (●), and amount of produced MeOH (□).  $\text{AlEt}_3 = 3.3$  mmol, Spar = 3.3 mmol, MCr = 33 mmol. Solvent: benzene 5.5 ml. (\*Dimer is almost 1. Note that one mole of dimer is produced from two moles of MCr.)

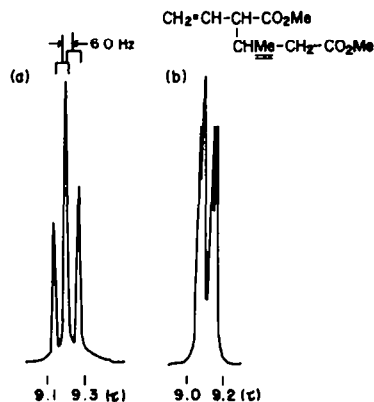


Fig 8. The  $\text{CH}-\text{CH}_3$  part of the 100 MHz- $^1\text{H}$ -NMR spectra of dimer 1 obtained by  $\text{AlEt}_3$ -Spar complex. The area ratio of higher doublet/lower doublet is 35/65. Measured at room temperature in benzene (a) and  $\text{CCl}_4$  (b).

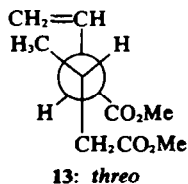
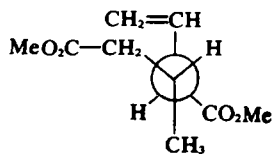
Table 4. Composition of dimer of MCr and the ratio of diastereomers of dimer 1 obtained by  $\text{AlR}_3$ -Spar and  $\text{AlR}_3$ - $\text{NEt}_3$  complexes<sup>a</sup>

Amine	R	Solvent	Total dimer yield (mmol)	Composition of dimer (mmol)		Ratio of diastereomers of dimer 1 <sup>b</sup>
				1	2	
Spar	Et	Bz	9.51	9.51	trace	35/65
Spar	Et	n-Pent	9.36	9.36	trace	36/64
Spar	Et	$\text{Et}_2\text{O}$	2.33	2.33	trace	34/66
Spar	Me	Bz	5.75	5.75	trace	35/65
Spar	iBu	Bz	4.41	4.41	trace	38/62
$\text{NEt}_3$	Et	Bz	8.77	6.14	2.63	47/53
$\text{NEt}_3$	Et	n-Pent	10.36	7.04	3.32	42/58
$\text{NEt}_3$	Et	$\text{Et}_2\text{O}$	8.35	5.64	2.71	43/57
$\text{NEt}_3$	Me	Bz	1.25	1.13	0.12	42/58
$\text{NEt}_3$	iBu	Bz	1.78	1.03	0.75	41/59

<sup>a</sup> Dimerization condition: reaction time 6 h, reaction temperature  $30^\circ$ , MCr = 33 mmol,  $\text{MCr}/\text{AlR}_3 = 10$ , Spar/ $\text{AlR}_3 = 1$ ,  $\text{NEt}_3/\text{AlR}_3 = 2$ , Solvent 5.5 ml.

<sup>b</sup> Ratio of diastereomers of dimer 1 is determined by the area ratio of the lower signal of  $\text{CH}-\text{CH}_3$  group of dimer 1 in NMR spectrum to the higher one.

In the NMR spectrum of dimer 1, two kinds of doublet signal of the  $\text{CH}-\text{CH}_3$  group were observed. The separation of the two signals was fairly large in aromatic solvents such as benzene and pyridine (6.0 Hz in benzene, 5.3 Hz in pyridine), whereas separation was small in  $\text{CCl}_4$  or  $\text{CS}_2$  (1.6 Hz in  $\text{CCl}_4$ , 1.5 Hz in  $\text{CS}_2$ ), as is shown in Fig 8. These two kinds of signal may be assigned tentatively to those of *erythro*- and *threo*-forms of dimer



1. The so-called collision complex formation between the Me group of dimer 1 and aromatic solvent<sup>7</sup> seems to be responsible for the large separation of the two signals in aromatic solvents. The ratio of diastereomers of dimer 1 was determined from the area ratio of the two signals of  $\text{CH}-\text{CH}_3$ , as is shown in Table 4. It is of much interest that the distribution of diastereomers is dependent neither on R in  $\text{AlR}_3$  nor on solvents, but on the tertiary amine.

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