SELECTIVE OLIGOMERIZATION OF α-SUBSTITUTED ACRYLATES WITH ORGANOALUMINUM AND MAGNESIUM COMPOUNDS

KAZUMI YAMAGUCHI

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CONTENTS

Chapter 1

INTRODUCTION

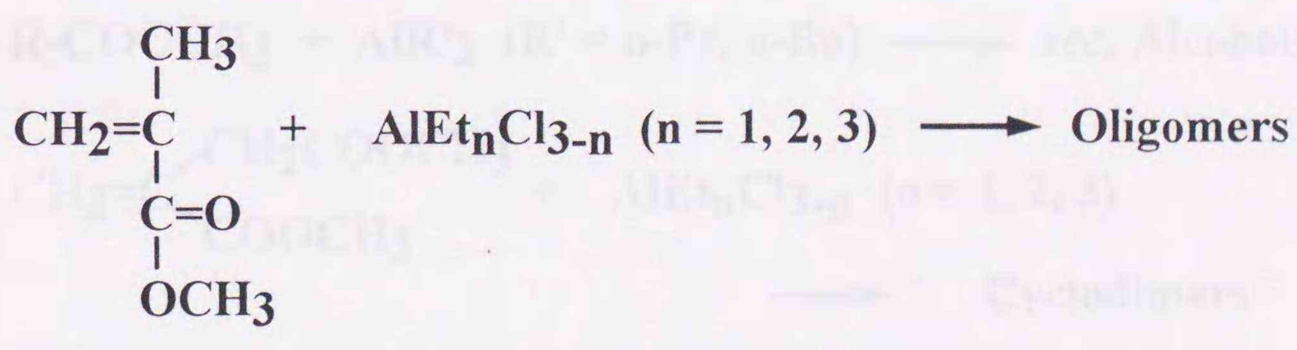
Until the last three decades the chemistry of organic compounds in which carbon is covalently bound to aluminum, silicon, and boron formed only a small part of organic chemistry. Owing to rapid recent advances in our understanding of the properties and reactions of these compounds, the chemistry occupies the greater part of organic chemistry at present.

Among organometallic compounds Grignard reagents have long played a central role in organic chemistry[1]. Organoaluminum compounds known for hundred years, however, attracted little attention until two discoveries by Karl Ziegler and his colleagues at the Max-Planck-Institute in Mulheim. The first discovery is the direct synthesis of trialkylaluminums from aluminum metal, olefins and hydrogen. The second is the formation of carbon-carbon bonds by the addition of aluminum compounds to olefins, which proved the key to a vast new area of polymer chemistry. On an industrial scale, the organoaluminum compounds are used mainly as a component of Ziegler-Natta catalysts in the polymerization of olefins, although their use in the manufacture of long-chain alcohols and olefins for the detergent and plasticiser industries is of growing importance[2]. Recently, alkylaluminum compounds have been widely used in organic synthesis as alkylating and reducing agents which are applied to the elaboration of the carbon skeleton of complex molecules.[3,4] Although reduction is dominantly found on reactions of α,β-unsaturated esters with the alkylaluminum compounds, conjugated addition is occasionally induced[5,6].

The oligomerizations of vinyl monomers have attracted an increasing interest as effective tools for establishing the mechanism and the stereochemistry of the polymerization[7-16]. The oligomers formed in side-reactions also have been noted as useful and interesting intermediates in organic synthesis. The polymers of acrylate and methacrylate are very important material. In addition, selective oligomerizations of acrylic acid derivatives were extensively studied. Useful polyfunctional compounds were prepared by DABCO catalyzed aldol condensation[17] and lithio enolate initiated cyclodimerization[18].

The present study concerns with oligomerizatin of acrylate and methacrylate by use of organometallic compounds, mainly, organoaluminum compounds. In order to elucidate the polymerization mechanism of acrylate monomers, the reactions of acrylic and methacrylic esters with alkylaluminum compounds and Grignard reagents are studied in this thesis.

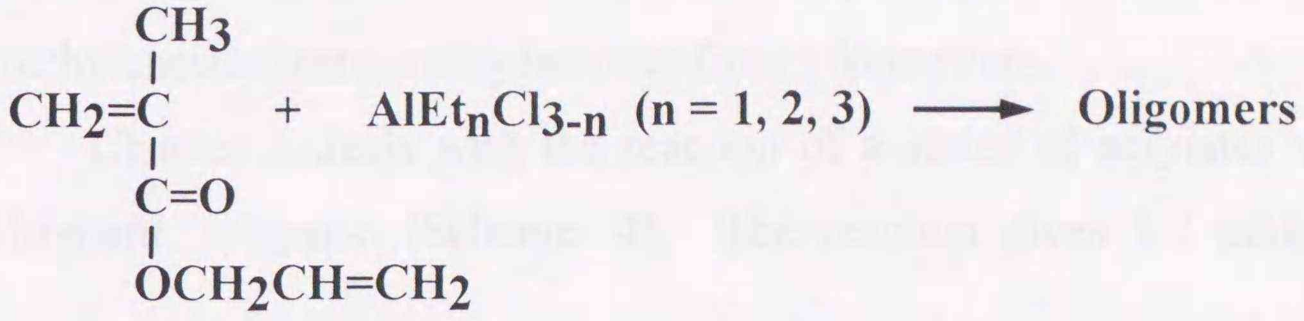
In Chapter 2, the oligomerization of methyl methacrylate with alkylaluminum compounds and the structural elucidation of the resulting oligomer are described (Scheme 1). Effects of the molar ratio of aluminum compound to methyl methacrylate (Al/M) on the



Scheme 1

molecular weight and the conversion are examined. Isolation of cyclic trimers from the oligomeric mixture and the formation mechanism of oligomers are also described.

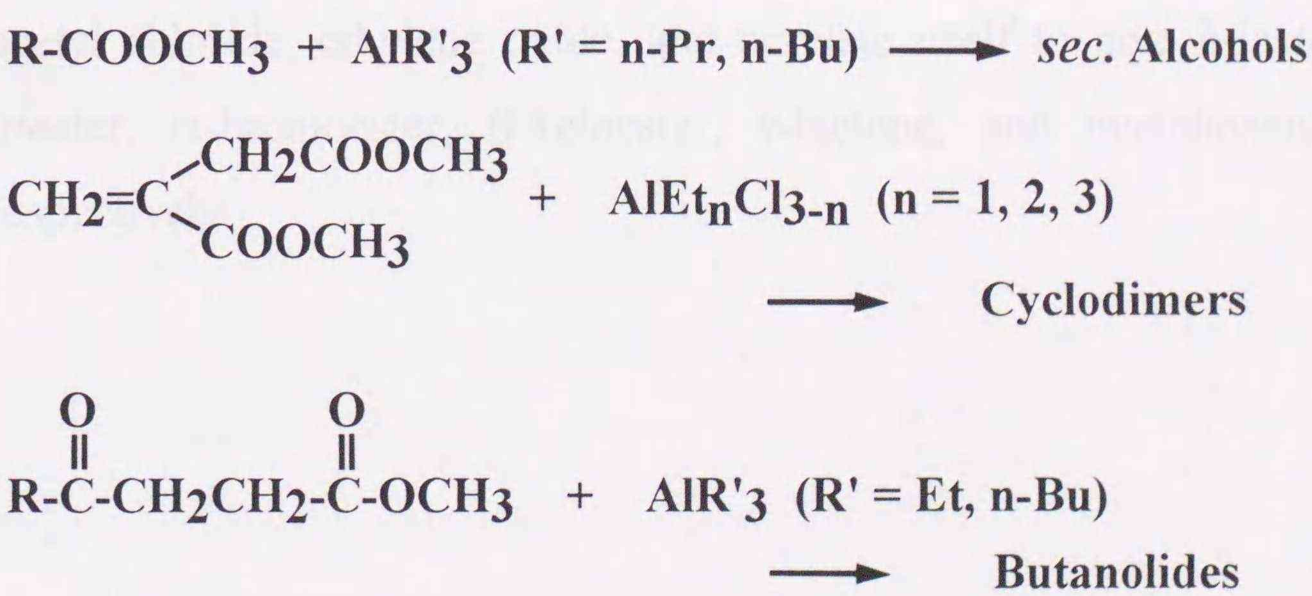
Chapter 3 deals with the oligomerization of allyl methacrylate by alkylaluminum compounds (Scheme 2). Claisen-type rearrangement



Scheme 2

of allyl group occurrs in the oligomerization. The rearranged products are 2-methyl-2-propyl-4-pentenoic acid corresponding to unimer and 1-allyl hydrogen 4-allyl-2,4-dimethyl-2-propylglutarate to dimer in the cases of triethylaluminum and diethylaluminum coloride, respectivery. Ethylaluminum dichloride causes Friedel-Crafts-type reaction between allyl methacrylate and solvent.

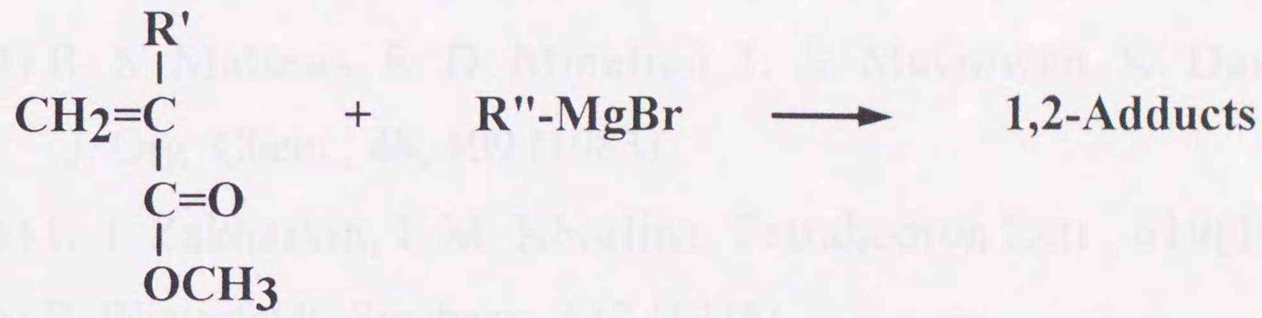
Chapter 4 deals with the reactions of simple esters, namely, dimethyl methylenesuccinate and β-ketoesters with alkylaluminum compounds (Scheme 3). The reaction of aliphatic esters with



Scheme 3

trialkylaluminums induces reduction, thereby resulting with the formation of selectively secondary alcohols. Cyclopentanone and bicyclic lactone derivatives are selectively prepared from dimethyl methylenesuccinate, and γ-lactones from γ-ketoesters.

Chapter 5 deals with the reaction of a series of acrylates with Grignard reagents (Scheme 4). The reaction gives 1:2 adducts,



Scheme 4

namely, dimethyl 2,2,4-trisubstituted glutarates corresponding to a linear dimer. The diastereoselectivity in the dimerization is caused by a difference in bulkiness between the two alkyl groups on the acrylate and the Grignard. The long-lived 2:1 adduct anion is subject to further reaction with electrophiles such as aldehyde, carbon dioxide, bromine, acetyl chloride, ethylene oxide, and acrylate itself to give δ-lactone, triester, α-bromoester, β-ketoester, γ-lactone, and cyclohexanone, respectively.

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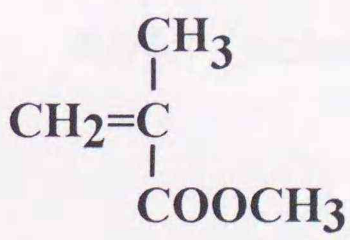
Chapter 2

OLIGOMERIZATION
OF
METHYL METHACRYLATE
IN THE PRESENCE
OF
ETHYLALUMINUM COMPOUNDS

2-1 Introduction

The oligomerization of methyl methacrylate (MMA) by thermal[1], radical[2] and anionic[3-5] initiation generally caused to form a regular linkage of monomeric units. There were some cases producing a functional end group[6-8] and a cyclic β-ketoester group[9-11]. On the other hand, an acceleration of propagation in the free radical polymerization of vinyl monomers having carbonyl or cyano groups, such as methyl methacrylate and acrylonitrile, was found in the presence of Lewis acid type complexing agents like organoaluminum compounds[12-18]. The cyclopolymerizations of *o*-allylphenyl acrylate[19] and methacrylate[20] in the presence of diethylaluminum chloride ($AlEt_2Cl$), preferentially produced oligomers of the methacrylate. In this chapter, the oliomerization of MMA by ethylaluminum dichloride ($AlEtCl_2$), diethylaluminum chloride ($AlEt_2Cl$), and triethylaluminum ($AlEt_3$), and the structural analysis of the oligomers will be described.



Methyl methacrylate (MMA)

2-2 Results and Discussion

2-2-1 Polymerization Behavior in the Presence of Ethylaluminum Compounds.

Experimental results of the radical polymerization in the presence of organoaluminum compounds were shown in Figures 1, 2, and 3.

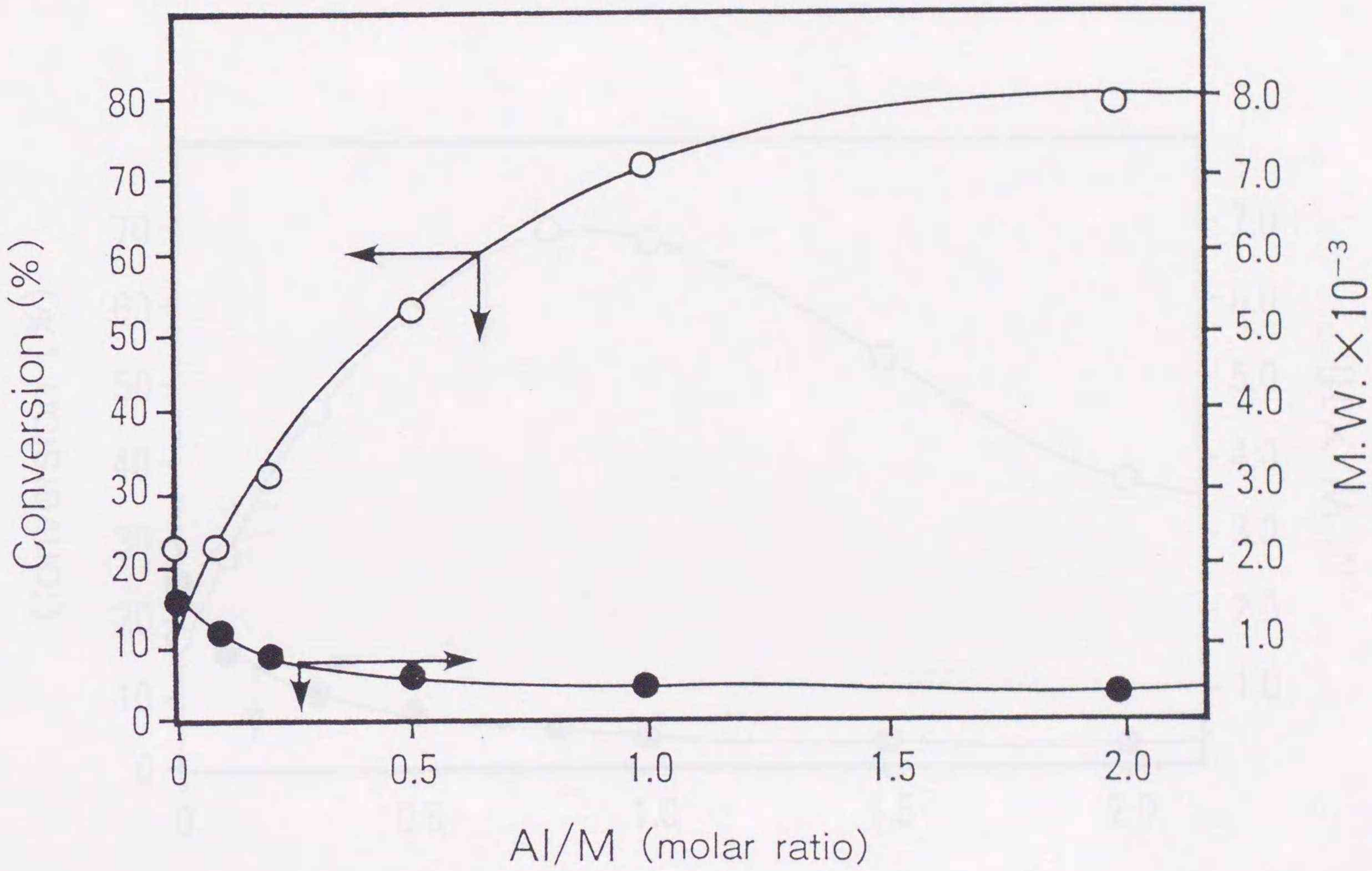


Figure 1. Effect of the Al/M molar ratio on the polymerization of methyl methacrylate in the presence of $AlEt_3$: Conversion within 7h (○); molecular weight of the product (●) ; [M], 1.0 M ; [AIBN], 6 mM ; temp, 40 ℃ .

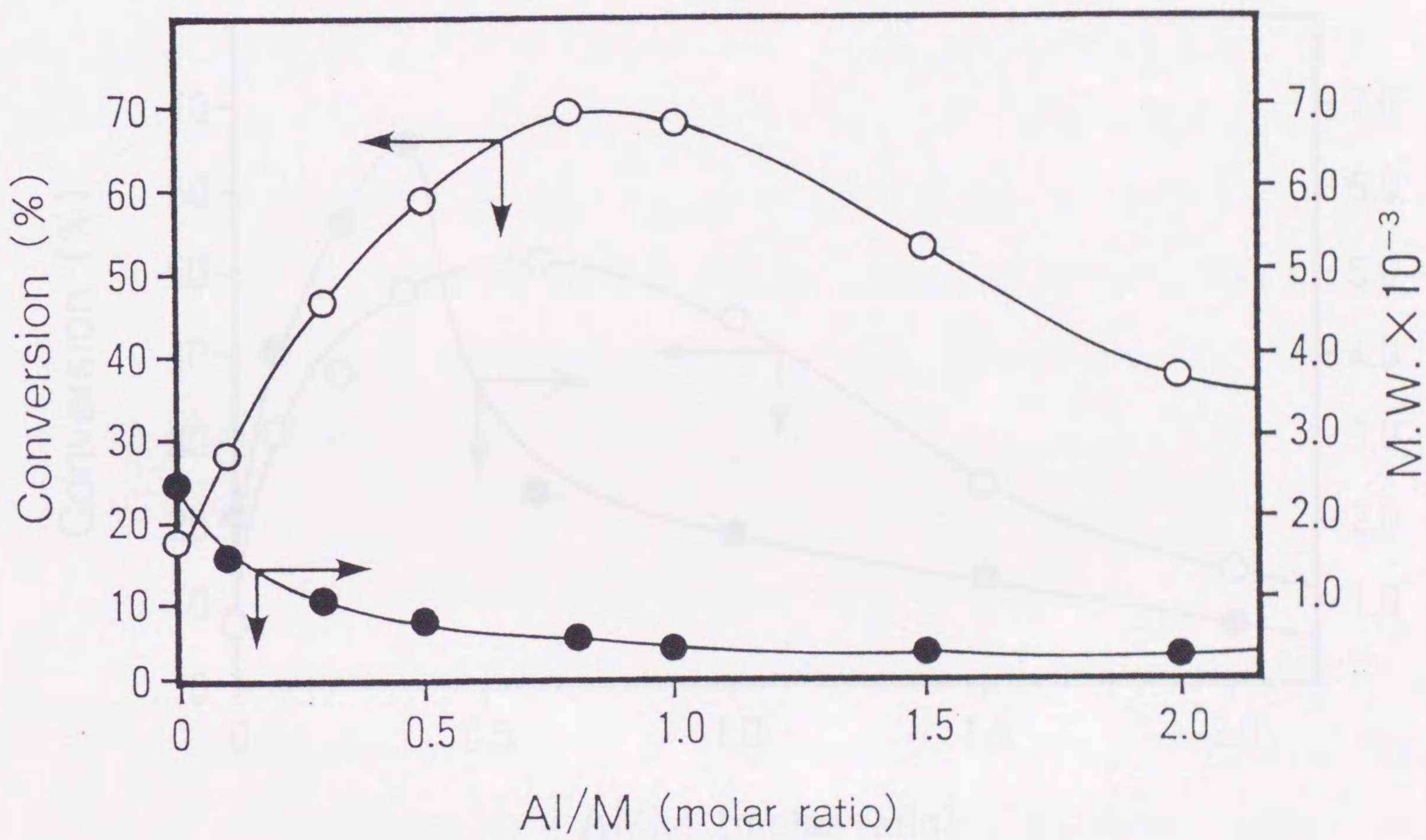


Figure 2. Effect of the Al/M molar ratio on the polymerization of methyl methacrylate in the presence of $AlEt_2Cl$: Conversion within 14h (○); molecular weight of the product (●) ; [M], 1.0 M ; [AIBN], 6 mM ; temp, 40 ℃ .

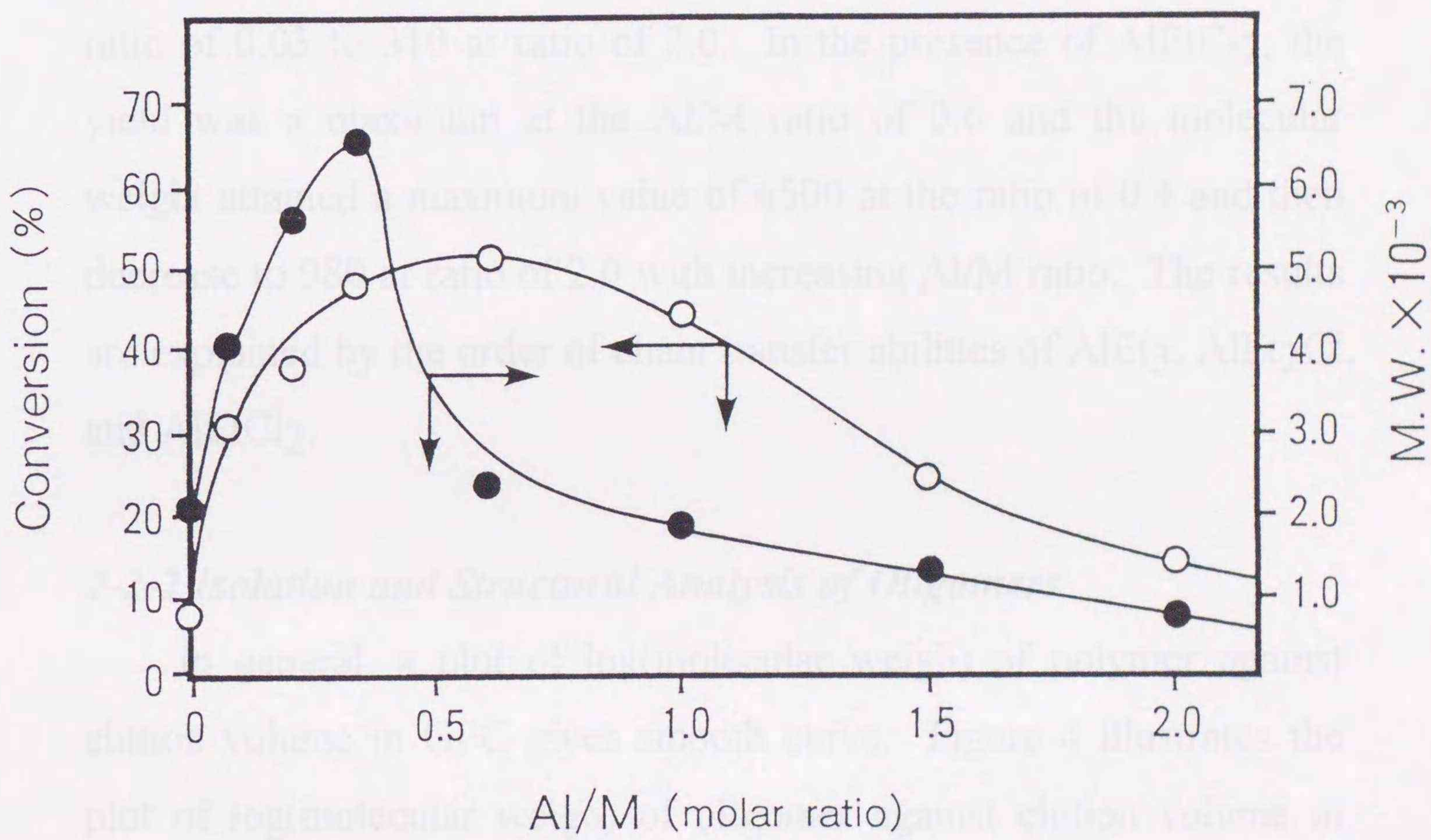


Figure 3. Effect of the Al/M molar ratio on the polymerization of methyl methacrylate in the presence of $AlEtCl_2$. Conversion within 14h (○); molecular weight of the product (●) ; [M], 1.0 M ; [AIBN], 6 mM ; temp, 40 ℃.

The product changed from white powder to viscous oil with decrease in molecular weight. In the presence of $AlEt_3$, the yield was monotony increased with increase in the molar ratio of aluminum compound to the monomer (Al/M), and the molecular weight was monotony decreased from 1570 at ratio of 0.03 to 410 at ratio of 2.0. In the presence of $AlEt_2Cl$, the yield of oligomer was a maximum at the ratio of 0.8, but the molecular weight was decreased from 2400 at ratio of 0.03 to 310 at ratio of 2.0. In the presence of $AlEtCl_2$, the yield was a maximum at the Al/M ratio of 0.6 and the molecular weight attained a maximum value of 6500 at the ratio of 0.4 and then decrease to 980 at ratio of 2.0 with increasing Al/M ratio. The results are explained by the order of chain transfer abilities of $AlEt_3$, $AlEt_2Cl$, and $AlEtCl_2$.

2-2-2 Isolation and Structural Analysis of Oligomers

In general, a plot of log(molecular weigh) of polymer against elution volume in GPC gives smooth curve. Figure 4 illustrates the plot of log(molecular weigh) of oligomer against elution volume in GPC. The Figure shows that the structure of lower oligomer (<1500) is different from higher oligomer (1500<). As shown in Figuers 5 and 6, the IR and the ^{1}H NMR spectra of oligomer are also different from those of ordinary poly (methyl methacrylate). In order to determination of structure of oligomer, the oligomer was separated by liquid chromatography. A chromatogram of a typical sample is illustrated in Figure 7. The recovery of oligomer amounted to 82%. The structures of isolated oligomers were shown in Scheme 1.

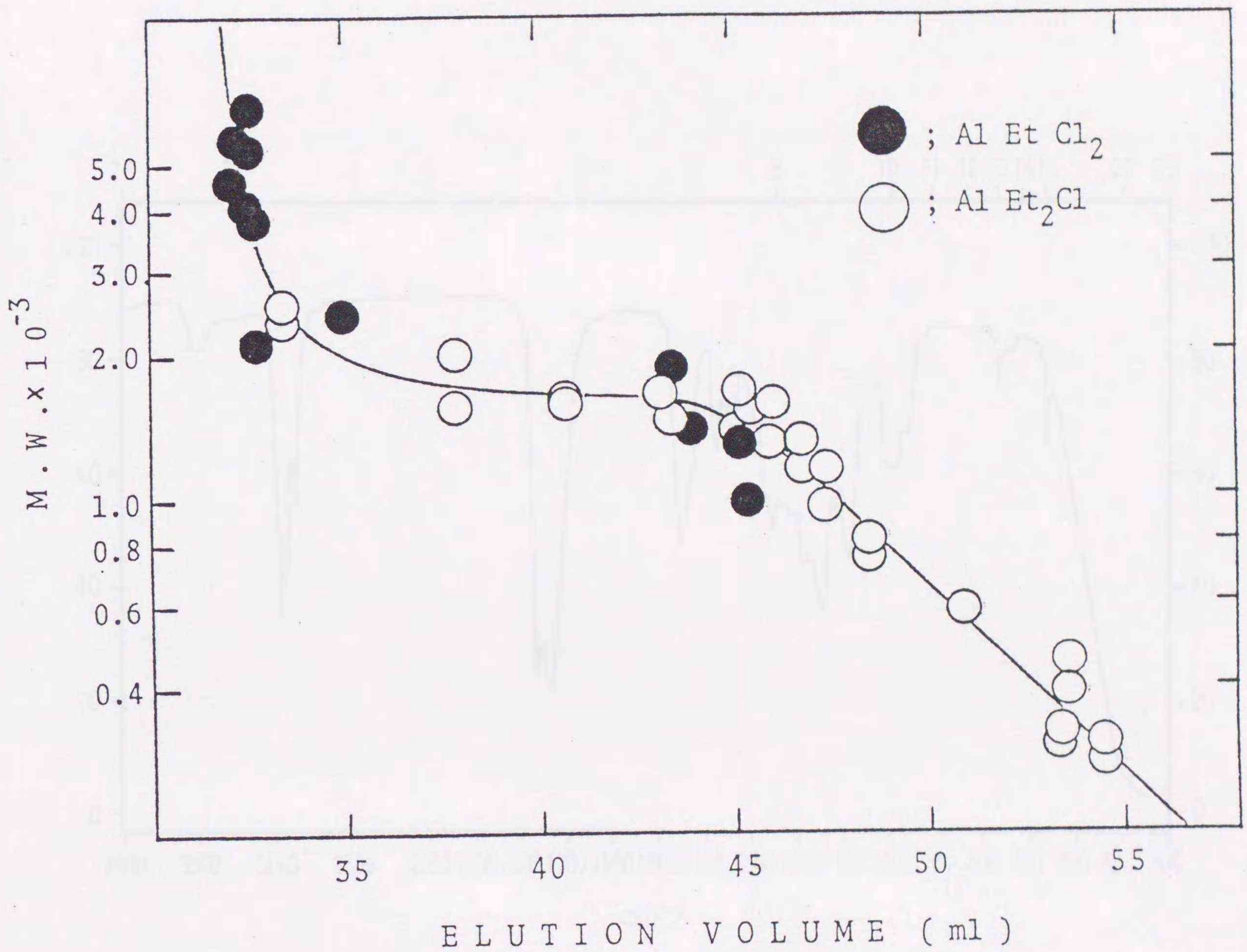


Figure 4. A plot of log(molecular weigh) of oligomer against elution volume in GPC: column, Shodex 802-803-804; flow rate 1.0 ml/min; temp. 20 ℃.

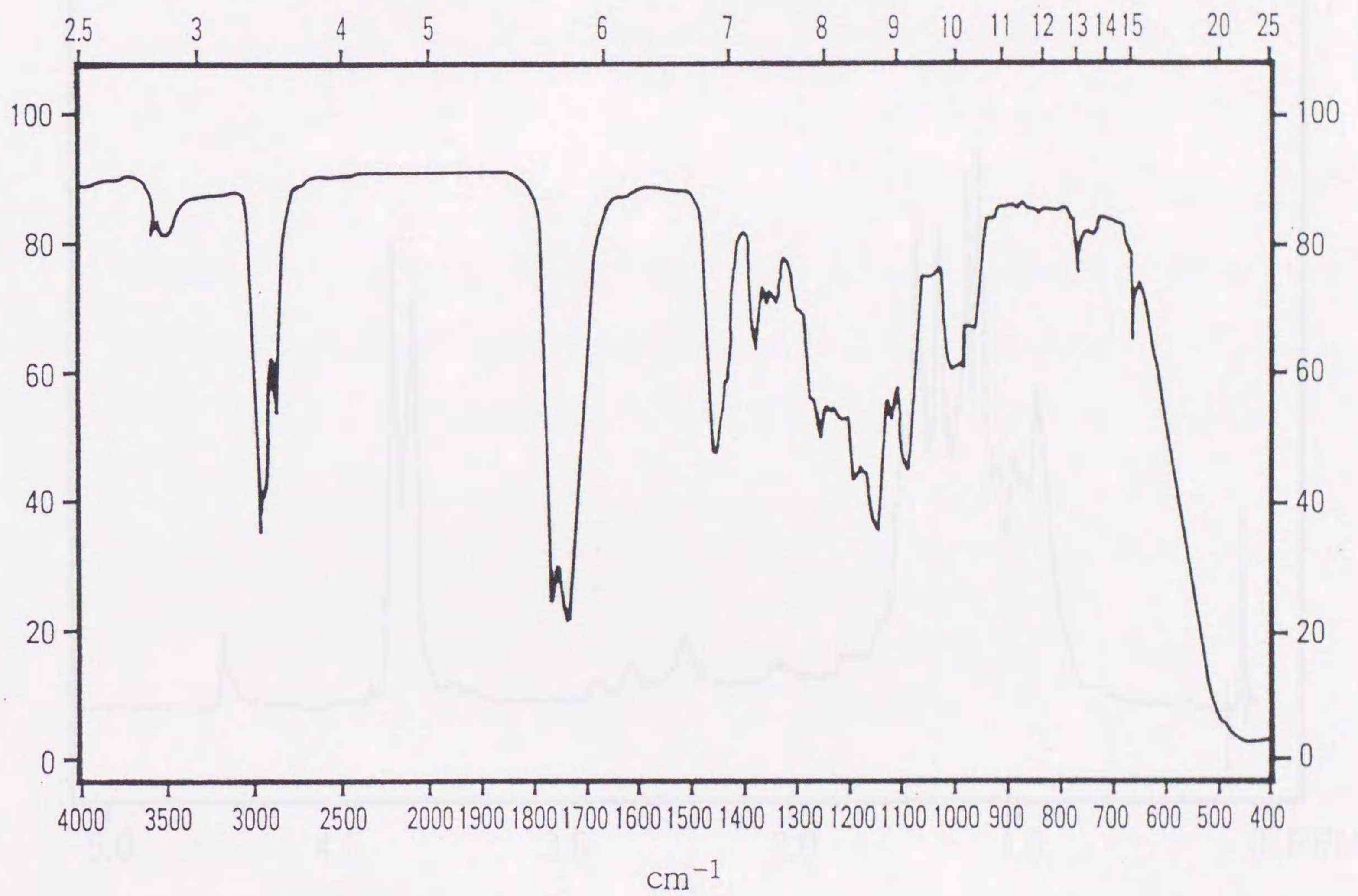


Figure 5. IR spectrum of the product obtained from the polymerization of methyl methacrylate in the presence of $AlEt_2Cl$: [M], 1.0 M; Al/M molar ratio, 2.0; [AIBN], 6 mM; temp. 40 ℃.

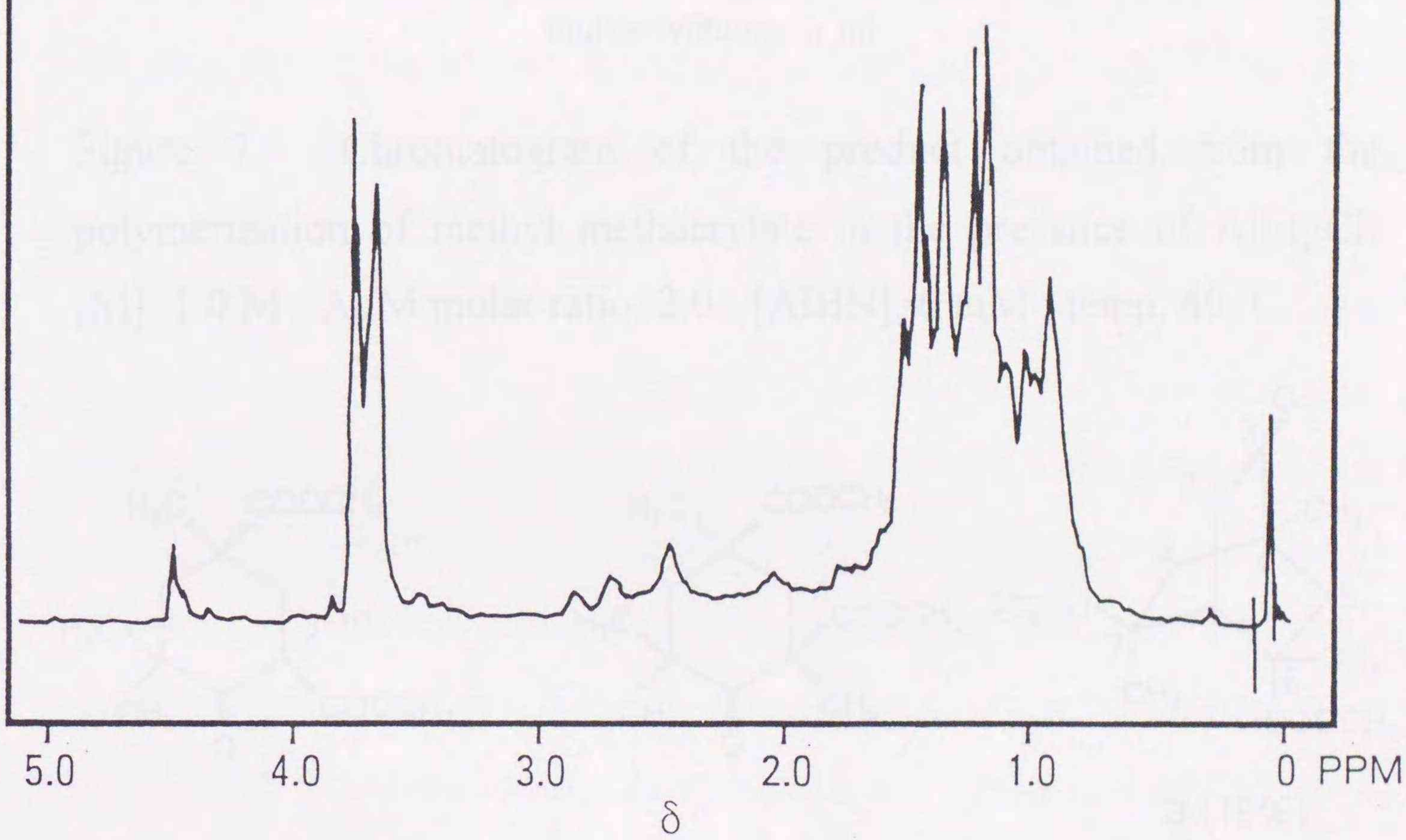


Figure 6. ^1H NMR spectrum of the product obtained from the polymerization of methyl methacrylate in the presence of $AlEt_2Cl$: Al/M molar ratio, 2.0; temp. 40 ℃.

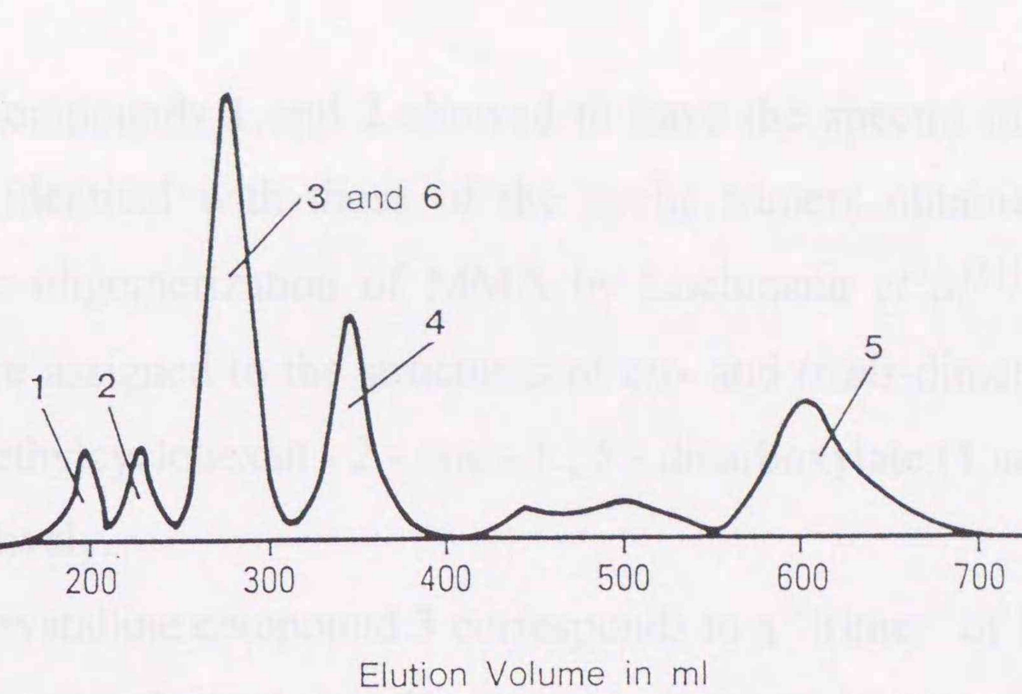
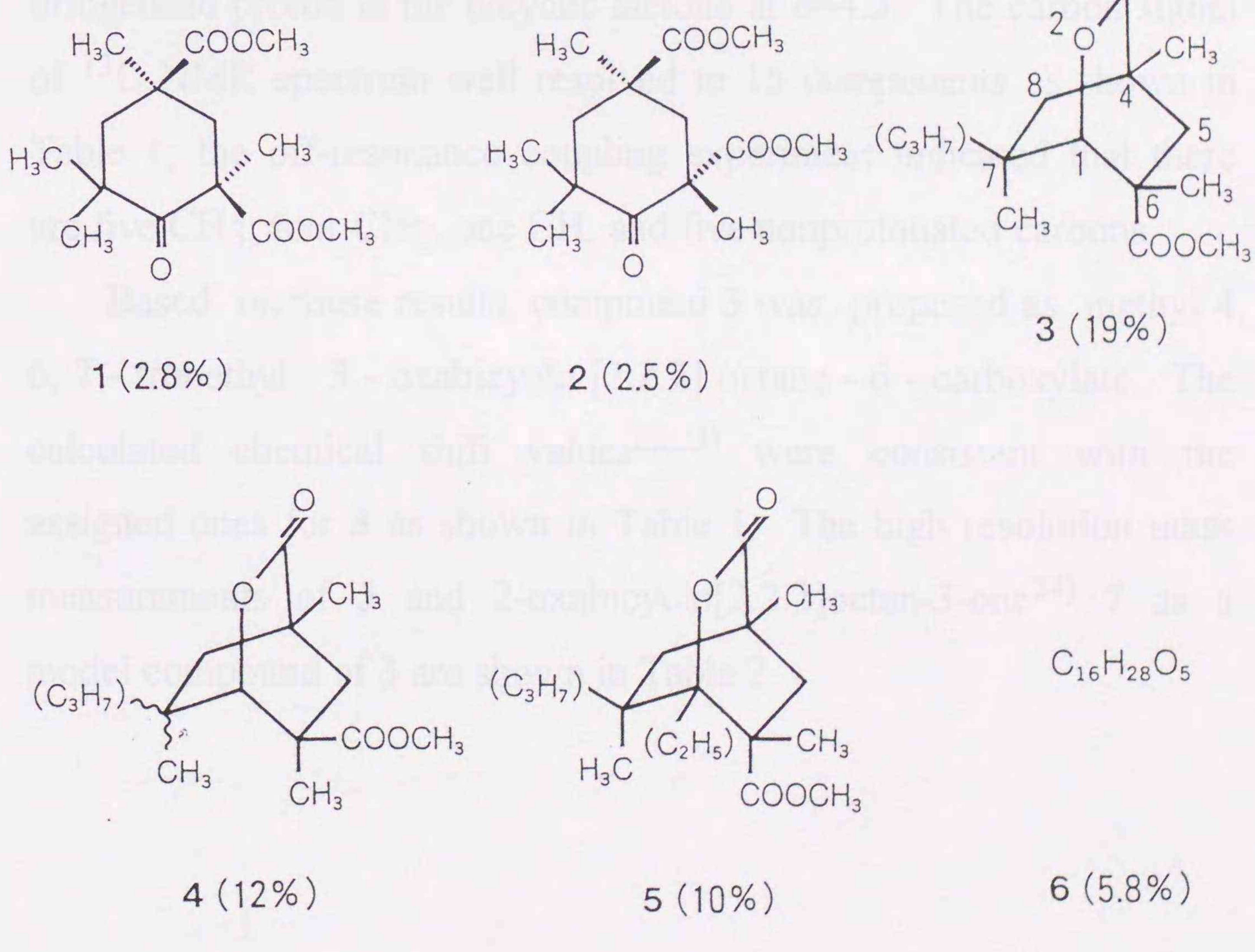


Figure 7. Chromatogram of the product obtained from the polymerization of methyl methacrylate in the presence of $AlEt_2Cl$: [M], 1.0 M ; Al/M molar ratio, 2.0 ; [AIBN], 6 mM ; temp, 40 ℃ .



Scheme 1

Compounds **1** and **2** showed to have the spectra of IR and ^1H NMR identical with those of the cyclic trimers obtained from the anionic oligomerization of MMA by Lochmann *et al*[21) ; therefore, they are assigned to the structures of *cis*- and *trans*-dimethyl 1,3,3,5-tetramethylcyclohexan - 2 - one - 1 , 5 - dicarboxylate (**1** and **2**) , respectively.

Crystalline compound **3** corresponds to a "trimer" of MMA. The IR spectrum showed the characteristic band at 1735 and 1768 cm^{-1}. Thus, the compound contains two different C=O groups, one from the ester group of MMA unit and the other from the lactone group. The ^1H NMR spectrum showed one ester methyl proton at δ=3.7, one terminal methyl proton in the alkyl group at δ = 1.0 and one bridgehead proton in the bicyclic lactone at δ=4.3. The carbon signal of ^{13}C NMR spectrum well resolved to 15 components as shown in Table 1; the off-resonance coupling experiment indicated that there are five CH_3, four CH_2, one CH, and five nonprotonated carbons.

Based on these results, compound **3** was proposed as methyl 4, 6, 7 - trimethyl - 3 - oxabicyclo [2.2.2] octane - 6 - carboxylate. The calculated chemical shift values[22,23) were consistent with the assigned ones for **3** as shown in Table 1. The high resolution mass measurements of **3** and 2-oxabicyclo[2.2.2]octan-3-one[24) **7** as a model compound of **3** are shown in Table 2.

Table 1. Comparison of observed and calculated ^{13}C NMR chemical shifts for the methyl methacrylate "trimer" **3**[a)]

δ(obs.)[b)]	Multiplicity[c)]	Assignment[d)]	δ(calc.)[e)]
14.53	q	C-f	14.8
16.75	t	C-e	17.5
21.07	q	C-b	20.1
24.04	q	C-a or C-c	22.8(C-c)
25.41	q	C-a or C-c	23.1(C-a)
37.70	s	C-4 or C-7	37.8(C-7)
38.24	s	C-4 or C-7	40.3(C-4)
40.72	t	C-d	39.1
45.31	t	C-5 or C-8	45.7(C-5)
47.77	t	C-5 or C-8	45.9(C-8)
48.16	s	C-6	46.3
52.70	q	C-h	-
85.30	d	C-1	93.7
175.13	s	C-g	-
176.62	s	C-3	-

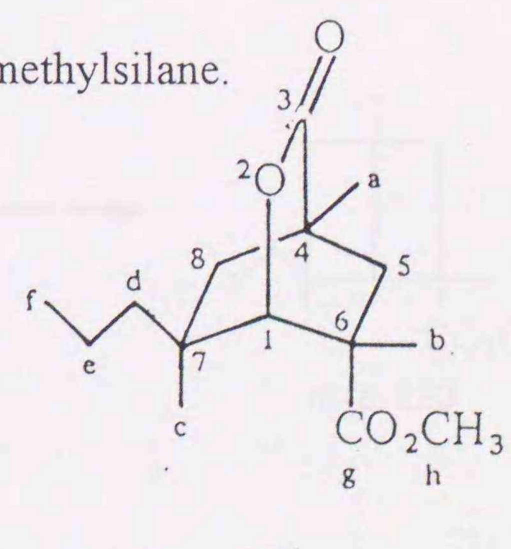
a) In $CDCl_3$ at room temperature.

b) Chemical shift in ppm downfield from tetramethylsilane.

c) Multiplicity in off-resonance spectrum.

d) Numbering system shown in structure formula of methyl 4,6,7-trimethyl-3-oxo-7-propyl-2-oxabicyclo[2.2.2]octane-6-carboxylate **3**.

e) Chemical shift calculated for **3**.

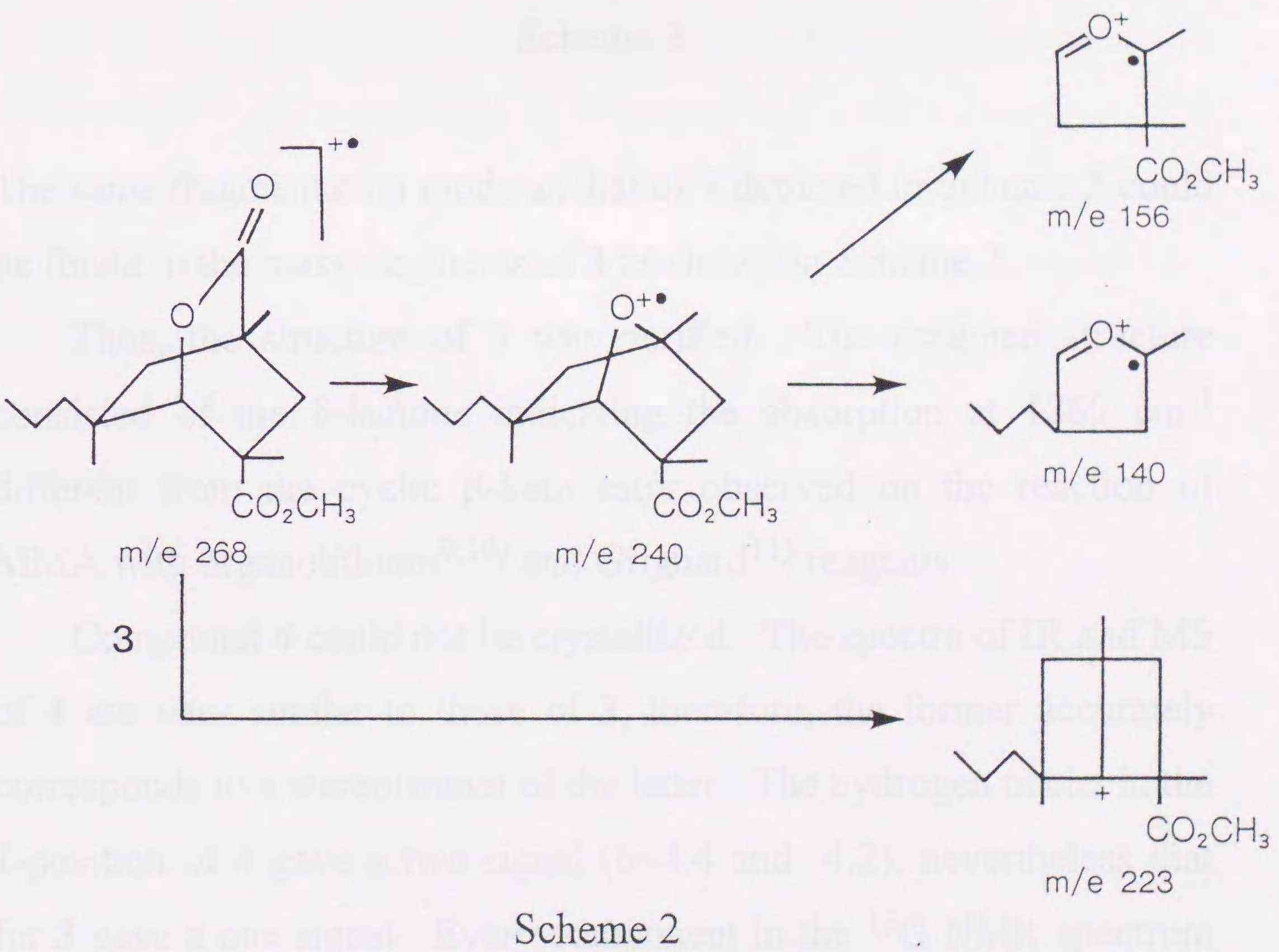


3

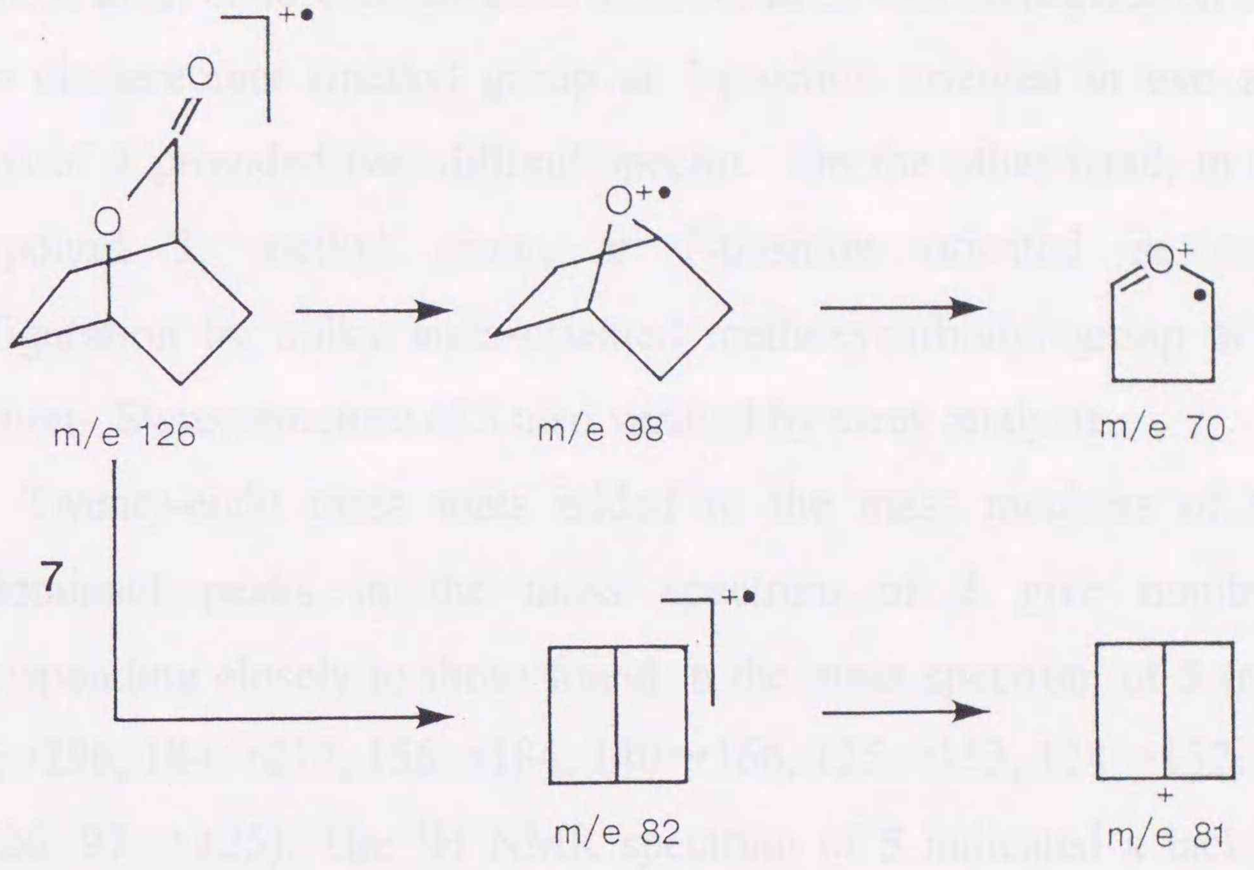
Table 2. High resolution mass measurements of the methyl methacrylate "trimer" **3** and 2-oxabicyclo[2.2.2]octan-3-one **7**

Compound	m/e (intensity[a]), elemental composition)
3	268 (M^+ , 4.9 , $C_{15}H_{24}O_4$) , 240 (14.4 , $C_{14}H_{24}O_3$) , 223 (8.9 , $C_{14}H_{23}O_2$) , 209 (27.4 , $C_{13}H_{21}O_2$) , 184 (27.0 , $C_9H_{12}O_4$) , 168 (12.1 , $C_{10}H_{16}O_2$) , 165 (16.2 , $C_{12}H_{21}$) , 163 (22.5 , $C_{12}H_{14}$) , 156 (100.0 , $C_8H_{12}O_3$) , 140 (16.2 , $C_9H_{16}O$)
7	127 (M^+ , 1.4 , $C_7H_{10}O_2$) , 126 (29.4 , -) , 98(4.8 , $C_6H_{10}O$) , 83(3.5,-) , 82 (39.2,C_6H_{10}) , 81 (3.1,-) , 70(32.0,C_4H_6O) , 67 (100.0 , C_5H_7)

a) Relative intensity , % of ion, present in maximum amount.



Scheme 2



Scheme 3

The same fragmentation mode as that of **7** depicted in Scheme 3 could be found in the mass fragments of **3** as shown in Scheme 2.

Thus, the structure of **3** was verified. The assigned structure consisted of the δ-lactone indicating the absorption at 1760 cm^{-1} different from the cyclic β-keto ester observed on the reaction of MMA with organolithium[9,10] and Grignard[11] reagents.

Compound **4** could not be crystallized. The spectra of IR and MS of **4** are very similar to those of **3**; therefore, the former accurately corresponds to a stereoisomer of the latter. The hydrogen nuclei in the 1-position of **4** gave a two signal (δ=4.4 and 4.2), nevertheless that for **3** gave a one signal. Every component in the ^{13}C NMR spectrum was split into a doublet in the case of **4**, though observed as a singlet in the case of **3**. It is concluded that the methyl group in 6-position is oriented in an endo-configuration at **3**, but in an exo-configuration at **4**. Two diastereomer (methyl group at 7-position oriented in exo and endo) of 4 provided two diffrent spectra. On the other hand, in the compound 3, methyl group at 7-position oriented in endo configuration by bulky endo-oriented methoxycarbonyl group at 6-position. Stereostructure of 3 also verified by x-ray analysis.

Twenty-eight mass units added to the mass numbers of the predominant peaks in the mass spectrum of **3** give numbers corresponding closely to those found in the mass spectrum of **5** (m/e 268→296, 184→212, 156→184, 140→168, 125→153, 124→152, 98 →126, 97→125). The ^1H NMR spectrum of **5** indicated a lack of hydrogen in position 1. The ^{13}C NMR spectrum and off-resonance ^1H NMR information indicated the substitution of an alkyl group at this position, as well. Compound **5**, therefore, is a 1-ethyl derivative of **3** or **4**. Every component also in ^{13}C NMR spectrum of **5** was split into a doublet as shown in the case of **4**. These findings suggest that compound **5** is assigned to the structure of methyl-1-ethyl-4,6,7-trimethyl - 3 - oxo - 7 - propyl - 2 - oxabicyclo [2. 2. 2] octane -6-exo-carboxylate.

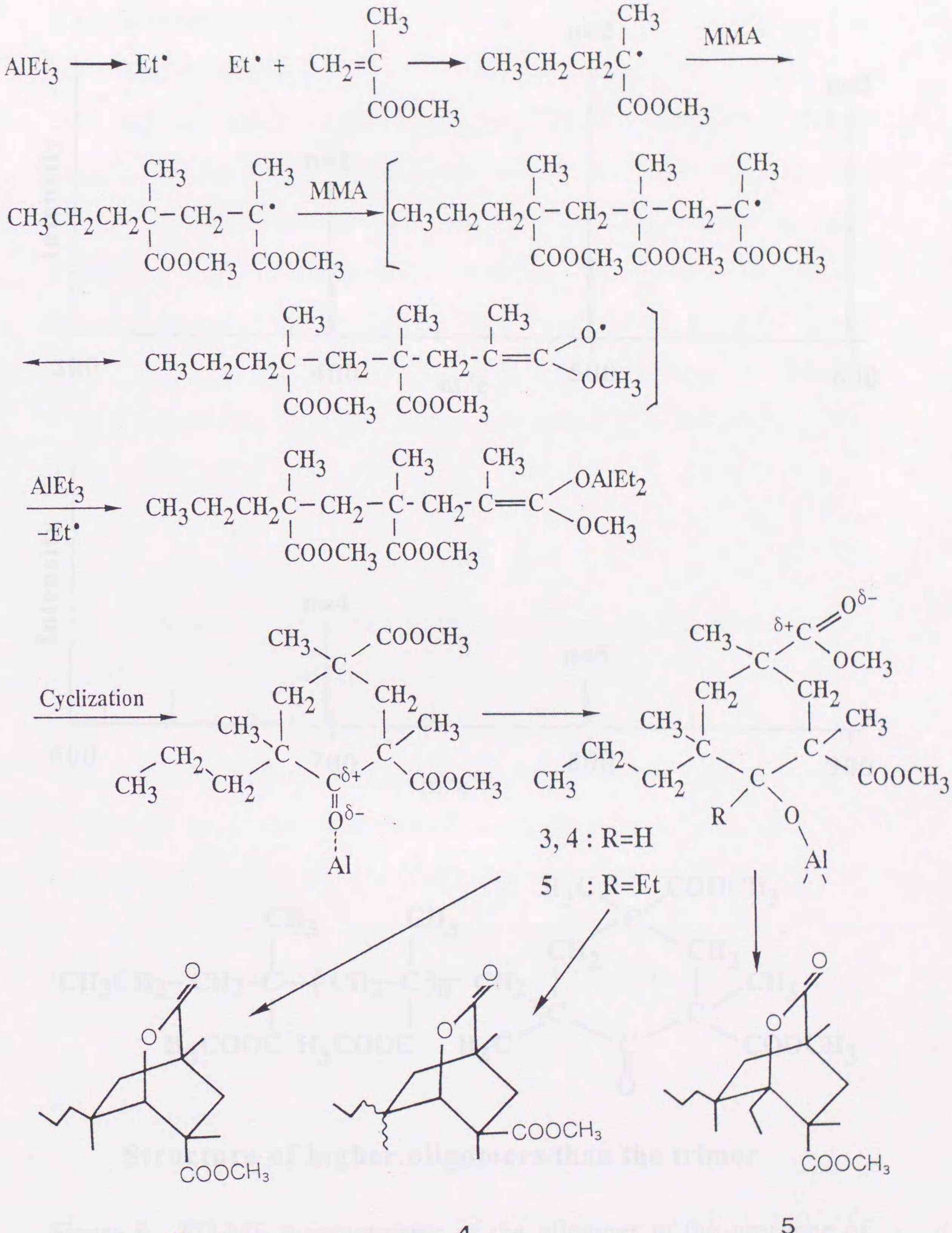
Compound **6** was obtained together with **3** by liquid chromatographic separation and was not able to be completely separated from **3**.

2-2-3 Reaction Mechanism

The mechanism of formation of the bridged bicyclic lactone **3** is of interest. The reaction between MMA and organoaluminum compound gives a 1:1 complex[25,26] which is responsible for the radical propagation. Under the experimental condition the evolved gases were ethylene and ethane, but the amount of the former was approximately three times lager than that of the latter. Therefore, the overall reaction may be described by Scheme 4. The reaction is initiated by the ethyl radical. Chain transfer with $AlEt_2Cl$ is the main termination process producing the ethyl radical as chain carrier. As shown in Fig 8 (m/e 398, 498, 598, 698, 798), higher oligomers than the trimer also have the ethyl group as initial end group and the cyclohexanone structure as terminal end group. Scheme 4 seems to be common to the oligomerization of methacrylate with organoaluminum compounds.

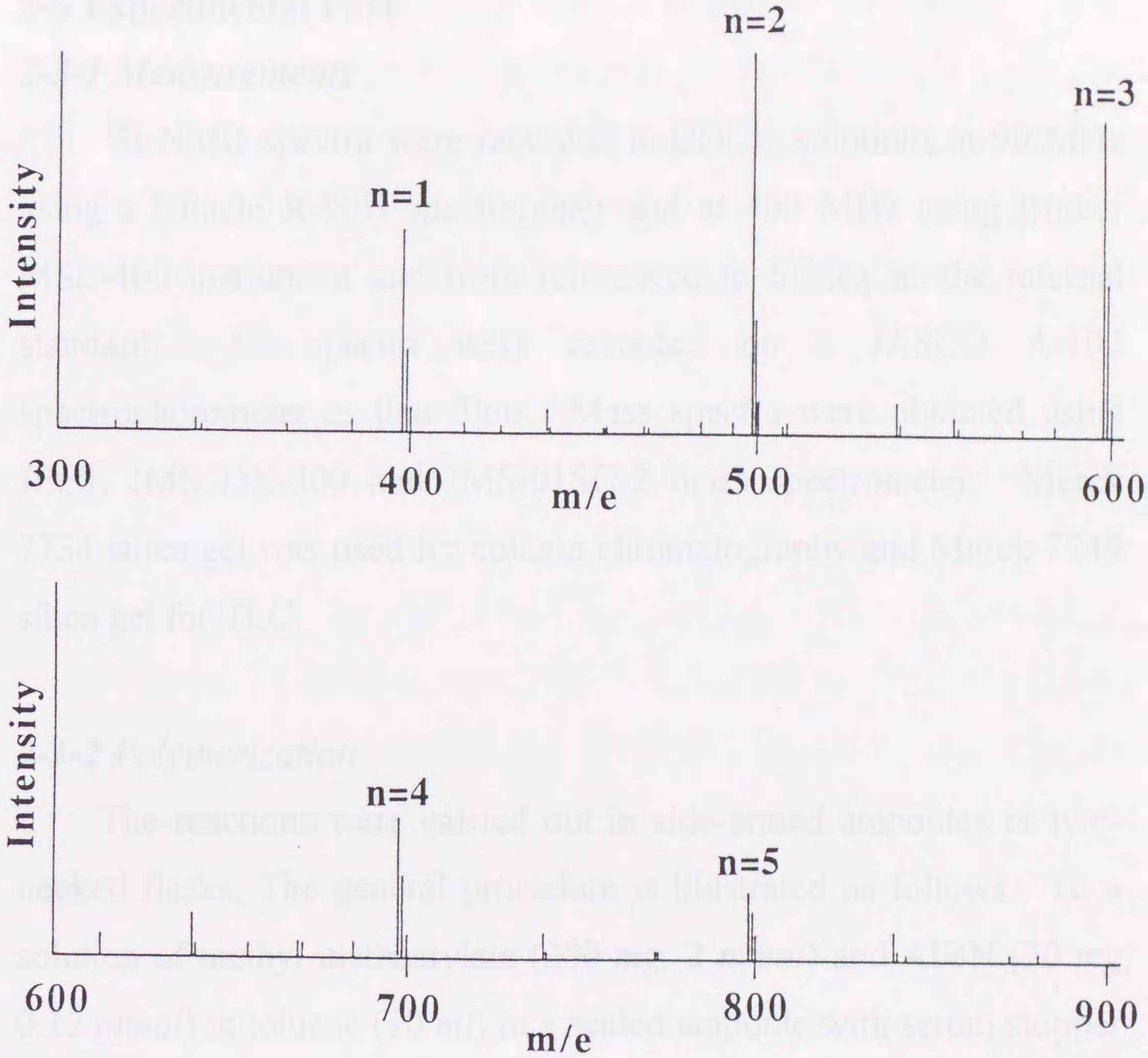
The scheme of the formation of **4** and **5** is similar to that of the formation of **3** (Scheme 4). The cyclization of the third MMA unit decides the configuration in position 6 to form **3** or **4**, and the replacement of the methoxy group with a hydrogen atom or an ethyl group selectes the final products **3** and **4**, or **5**.

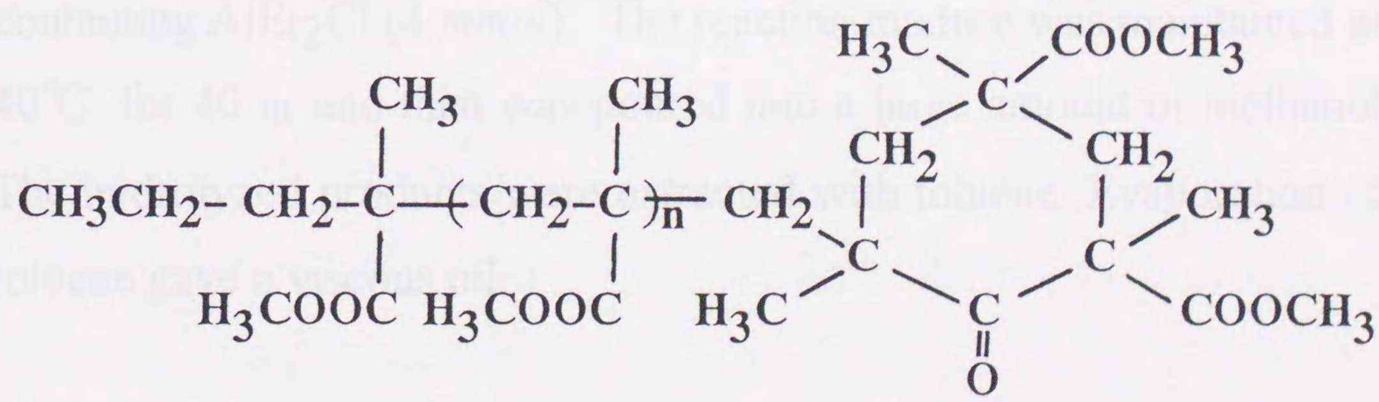
On the basis of the reaction of methyl α-lithioisobutylate with MMA[19], compounds **1** and **2** should be formed by linear trimerization of MMA initiating with hydride ion, followed by a Dieckmann condensation. This trimerization is a minor process in the reaction of MMA with $AlEt_2Cl$ in the presence of AIBN.



3 4 5

Scheme 4





Structure of higher oligomers than the trimer

Figure 8. FD-MS measurements of the oligomer in the presence of $AlEt_2Cl$: [M], 1.0 M ; Al/M molar ratio, 0.5 ; [AIBN], 6 mM ; temp, 40 °C .

2-3 Experimental Part

2-3-1 Measurements

^{1}H NMR spectra were recorded in $CDCl_3$ solutions at 90 MHz using a Hitachi R-90H spectrometer and at 400 MHz using Bruker MSL-400 instrument and were referenced to $SiMe_4$ as the internal standard. IR spectra were recorded on a JASCO A-102 spectrophotometer as thin films. Mass spectra were obtained using JEOL JMS DX-300 and JMS-01SG-2 mass spectrometer. Merck 7734 silica gel was used for column chromatography and Merck 7749 silica gel for TLC.

2-3-2 Polymerization

The reactions were carried out in side-armed ampoules or two-necked flasks. The general procedure is illustrated as follows. To a solution of methyl methacrylate (200 *mg*, 2 *mmol*) and AIBN (20 *mg*, 0.12 *mmol*) in toluene (10 *ml*) in a sealed ampoule with serum stopper cap at the side arm was added a solution of toluene (0.5 *ml*) containing $AlEt_2Cl$ (4 *mmol*). The reaction mixture was maintained at 40℃ for 40 hr and then was poured into a large amount of methanol. The hydrolyzed products were extracted with toluene. Evaporation of toluene gave a viscous oil.

2-3-3 Isolation of oligomers

The oily oligomers were obtained in 98% yields. The oligomers were fractionated using a liquid chromatograph which was attached the Lobar column size B containing Lichroprep RP-8 (Merck Ltd.). Elutions were conducted at ambient temperature with methanol/water (volume ratio 7:3) with a flow rate of 1ml/min. Six fractions were taken as described below. On standing of the fraction 3 for a few days at room temperature, a crystalline compound **3** was isolated.

(a) cis - Dimethyl - 1 , 3 , 3 , 5 - tetramethylcyclohexane - 2 - one - 1 , 5 -dicarboxylate (1)

Yield of isolated pure product: 2.8 %.

IR (film) 1725, 1710, 1450, 1380, 1260, 1160, 1090 cm^{-1}; ^1H NMR (CCl_4) δ=3.7 (3H; s), 3.6 (3H, s), 3.0 (1H; d; *J*=17Hz), 2.5 (1H; d; 17Hz), 1.6 (1H; d; 16Hz), 1.5 (1H; d; 16Hz), 1.3 (3H, s), 1.25 (3H; s), 1.15 (3H; s), 1.1 (3H, s); MS: 270 (M^+; 0.5), 239 (2.5), 214 (19.6), 186 (13.6), 170 (64.8), 151 (3.0), 142 (100), 127 (3.5), 114 (4.2), 83 (3.5), 73 (4.9), 70 (51.3), 69 (7.3). High resolution MS 270.146 (M^+, $C_{14}H_{22}O_5$ requires 270.147).

(b) trans - Dimethyl - 1 , 3 , 3 , 5 - tetramethylcyclohexane - 2- one - 1,5-dicarboxylate (2)

Yield : 5 %.

IR (film) 1725, 1710, 1450, 1380, 1260, 1190, 1160, 1135, 1100 cm^{-1}. ^1H NMR (CCl_4) δ=3.37 (3H; s), 3.69 (3H, s), 2.4 (2H; s), 2.3 (1H; d; *J*=13Hz), 1.7 (1H; d; 13Hz), 1.29 (3H, s), 1.26 (3H; s), 1.10 (3H; s), 0.91 (3H, s). MS: 270 (M^+; 0.5), 214 (4.6), 186 (3.7), 170 (70.0), 151 (3.2), 142 (100), 73 (3.5), 70 (37.8), 69 (3.8).

(c) Methyl 4 , 6 , 7 - trimethyl - 3 - oxo - 7 - propyl - 2 -oxabicyclo [2.2.2]octane-6-endo-carboxylate (3)

Yield : 19 %. m.p. 117-119 ℃.

IR (film) 1775, 1730, 1470, 1450, 1340, 1255, 1145, 1090, 1000, 990, 960 cm^{-1}; ^1H NMR (CCl_4) δ=4.3 (1H; s), 3.7 (3H; s), 2.8 (1H; d; *J*=12Hz), 1.2-1.6 (16H; m), 1.0 (3H; t; *J*=4Hz); MS: 268 (M^+;2.8), 240 (3.6), 209 (4.9), 184 (8.1), 168 (4.9), 165 (4.7), 157 (3.9), 156 (100), 140 (6.0), 128 (16.0), 126 (11.9), 125 (4.6), 124 (6.2), 121 (7.3), 109 (3.7), 99 (4.2), 98 (53.9), 97 (44.9), 69 (31.3). High resolution MS 268.167 (M^+,$C_{15}H_{24}O_4$ requires 268.168). Anal. Calcd for $C_{15}H_{24}O_4$; C 67.12%; H 9.02%. Found C 66.92%; H 8.97%.

(d) Methyl 4 , 6 , 7 - trimethyl - 3 - oxo - 7 - propyl - 2 - oxabicyclo [2.2.2]octane-6-exo-carboxylate (4)

Yield : 12 %.

IR (film) 1760, 1730, 1470, 1450, 1380, 1360, 1280, 1190, 1180, 1160, 1100, 1080, 1020, 1000 cm^{-1}; ^1H NMR (CCl_4) δ=4.3 (1H; d; *J*=8.6Hz) ,3.7 (3H; s), 2.5 (1H; d-d; *J*=14.4Hz; 2Hz), 1.0-1.7 (16H; m), 0.8 (3H; t; *J*=4Hz); MS 268 (M^+;3.7), 249 (3.6), 184 (7.9), 168 (4.1), 156 (100), 140 (4.1), 128 (23.1), 125 (4.4), 124 (6.2), 121 (5.4), 99 (3.2),98 (58.0),97 (43.6), 69 (42.3).

(e) Methyl 1-ethyl-4, 6 , 7 - trimethyl - 3 - oxo - 7 - propyl-2-oxabicyclo [2.2.2]octane-6-exo-carboxylate (5)

Yield : 10 %.

IR (film) 1755, 1725, 1470, 1450, 1380, 1260, 1220, 1200, 1150, 980 cm^{-1}; ^1H NMR (CCl_4) δ=3.6 (3H; s), 2.65 (1H; d-d; *J*=14Hz; 2Hz), 0.7-2.5 (24H; m); MS 296 (M^+;1.3), 212 (22.4), 196 (5.0), 185 (6.3), 184 (94.7), 1685 (27.0), 156 (8.8), 153 (5.3), 152 (47.5), 126 (45.1), 125 (100), 124 (8.6), 98 (22.3), 69 (9.0).

(f) Compound 6

MS 301 ($[M+1]^+$,0.2), 240 (19.5), 200 (5.9), 197 (3.4), 188 (10.6), 156 (3.1), 101 (4.7), 100 (100). High resolution MS 301.198 ($[M+1]^+$, $C_{16}H_{29}O_5$ requires 301.202).

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Chapter 3

OLIGOMERIZATION
OF
ALLYL METHACRYLATE
IN THE PRESENCE OF
ETHYLALUMINUM COMPOUNDS

3-1 Introduction

Allyl methacrylate, an unsymmetrical 1,6-diene, is used in the reaction of the methacryloyl double bond with some participation of allyl bonds in radical polymerization[1,2)]. Cyclopolymerization tendency, though very low under the usual conditions, was highly enhanced with rise in temperature[3)]. Ethylaluminum compounds as complexing agents caused great increase in cyclopolymerization of o-allylphenyl acrylate and methacrylate[4)]. The addition of $SnCl_4$ to allyl methacrylate induced partial cyclopolymerization, but that of $AlEt_{1.5}Cl_{1.5}$ diminished the yield of polymer with increasing Al/M molar ratio[5)]. Such behavior is suggestive of the formation of oligomers together with polymers[6)]. In this chapter, the oligomerization of allyl ester[7)], and mono- and di-substituted allyl esters of methacrylic acid with ethylaluminum compounds will be described together with isolation of its unimer and dimer, and a product arising from Friedel-Crafts type reaction.

$$\begin{array}{l} \quad\quad\;\; CH_3 \\ \quad\quad\;\;\; | \\ CH_2{=}C \\ \quad\quad\;\;\; | \\ \quad\quad\;\; COOCH_2CH{=}CH_2 \end{array}$$

Allyl methacrylate (AMA)

1

3-2 Results and Discussion

3-2-1 Polymerization Behavior of Allyl methacrylate (1)

The oligomerizations of **1** in the presence of ethylaluminum compound and AIBN in toluene were carried out. Spontaneous polymerization of **1**, i. e., in the absence of a radical initiator, occurred in the presence of $AlEt_3$, $AlEt_2Cl$, or $AlEtCl_2$. The addition of the radical initiator caused great increase in the rate of polymerization at 40℃. The rate increased with the Al/M molar ratio and reached a maximum at a ratio of 1.0, as shown in Figures 1 and 2. The molecular weight (Mn) of the products sharply decreased with increasing Al/M molar ratio and gave a constant value at ratio of 1.0 or above. $AlEt_3$ and $AlEt_2Cl$ produced the oligomers with the Mn of 410 and 900 at ratio of 2.0, respectively.

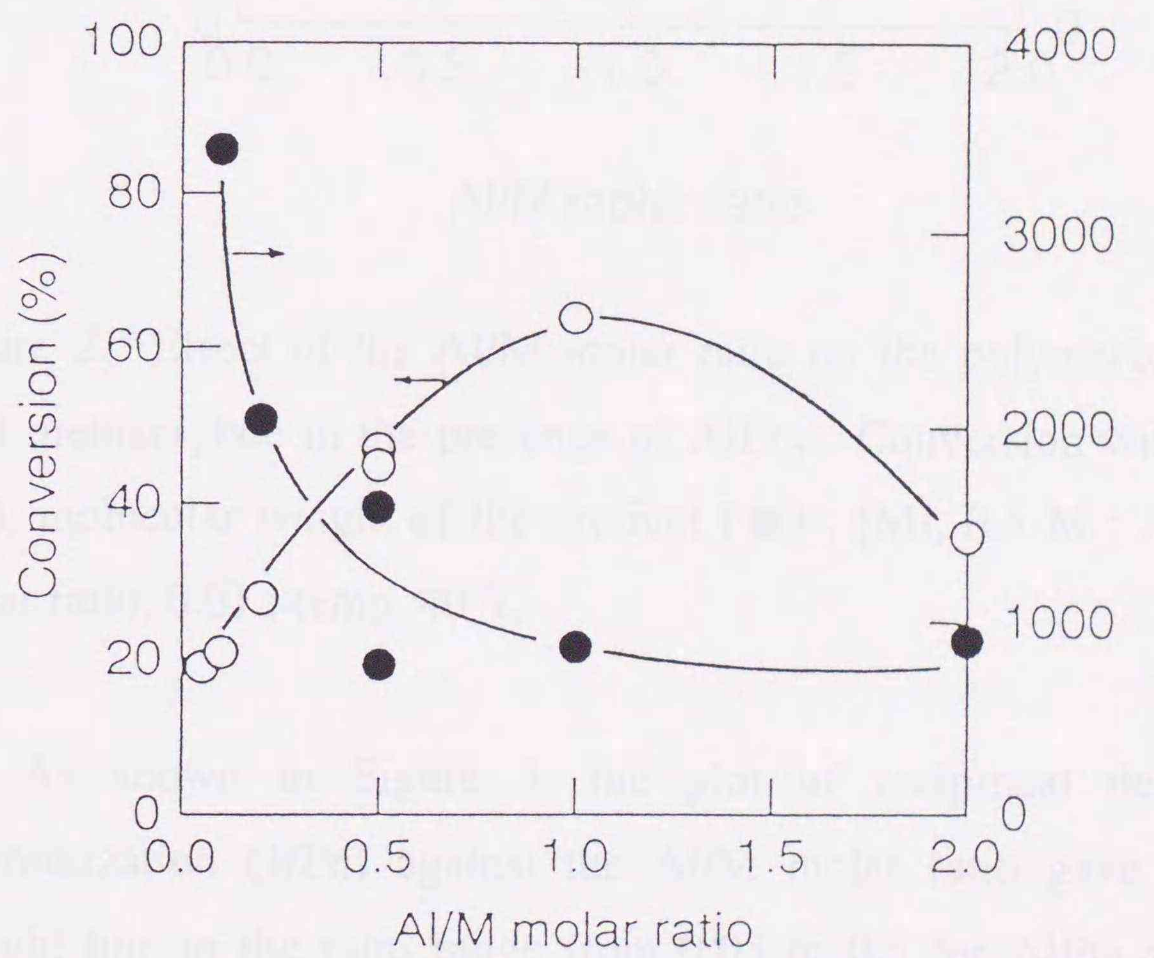


Figure 1. Effect of the Al/M molar ratio on the polymerization of allyll methacrylate in the presence of $AlEt_2Cl$: Conversion within 10h (○); molecular weight of the product (●) ; [M], 0.5 M ; AIBN/M molar ratio, 0.01 ; temp, 40 ℃.

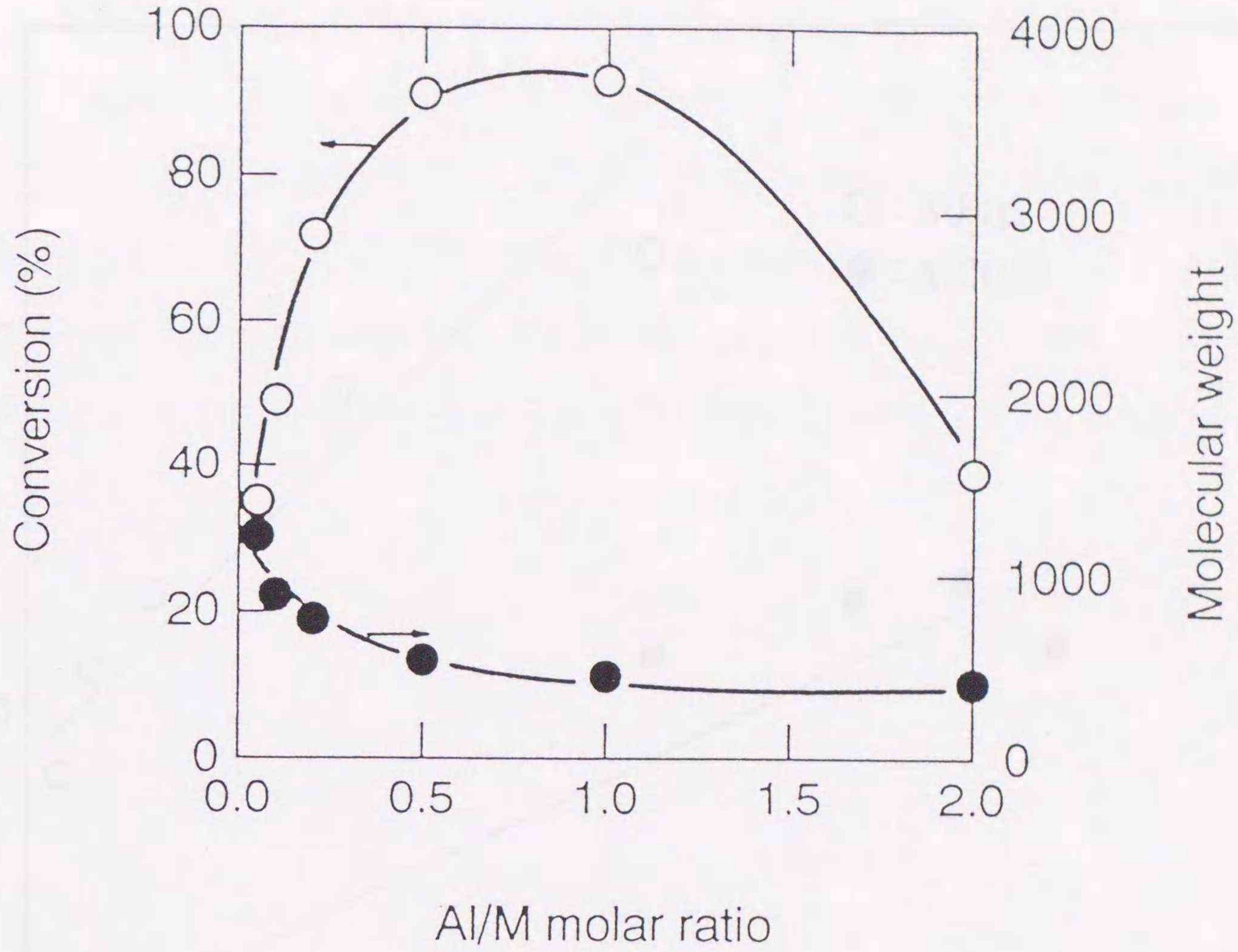


Figure 2. Effect of the Al/M molar ratio on the polymerization of allyl methacrylate in the presence of $AlEt_3$: Conversion within 10h (○); molecular weight of the product (●) ; [M], 0.5 M ; AIBN/M molar ratio, 0.01 ; temp, 40 ℃ .

As shown in Figure 3, the plot of reciprocal degree of polymerization (1/Pn) against the Al/M molar ratio gave a good straight line in the ratio range from 0.05 to 0.5 for $AlEt_3$ and that from 0.1 to 1.0 for $AlEt_2Cl$. The slope was found to be 2.6×10^{-1} for $AlEt_3$, and 1.3×10^{-1} for $AlEt_2Cl$, giving the large transfer constant (C_{tr}). Ethylaluminum compounds were involved with chain transfer in addition to initiation in the polymerization of allyl methacrylate in the same manner as reactions of methyl methacrylate (Chapter 2) and dimethyl methylenesuccinate (Chapter 4).

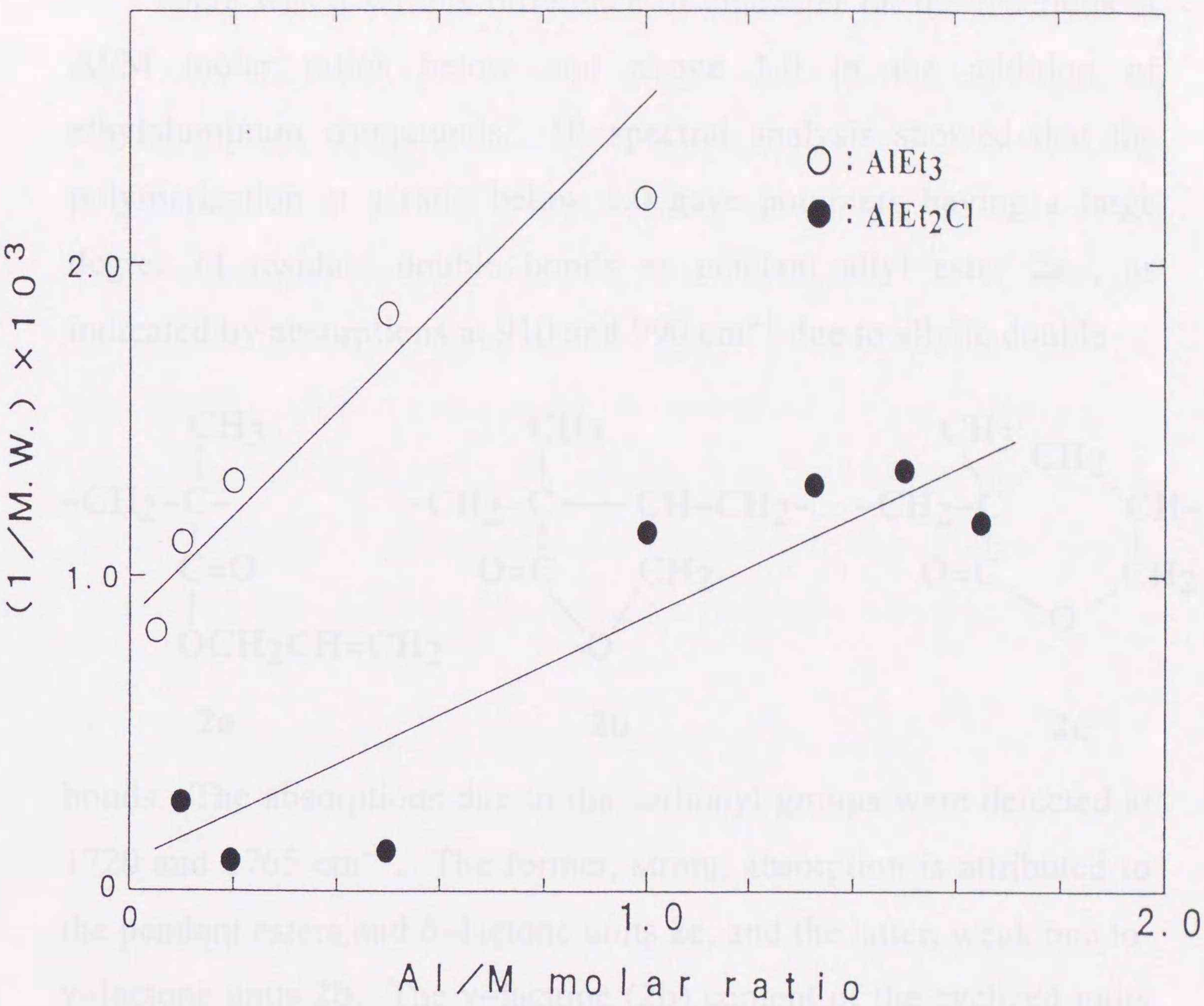
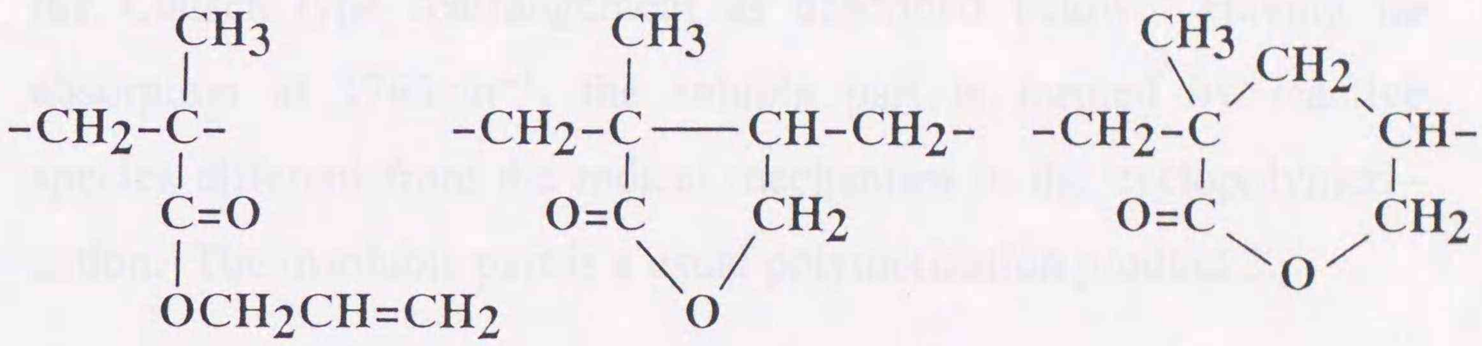


Figure 3. Plot of reciprocal degree of polymerization (1/Pn) against the Al/M molar ratio. (○); in the presence o $AlEt_3$; (●) in the presence of $AlEt_2Cl$.

There was a serious difference of character on the reactions at Al/M molar ratios below and above 1.0 in the addition of ethylaluminum compounds. IR spectral analysis showed that the polymerization at a ratio below 1.0 gave polymers having a large degree of residual double bonds as pendant allyl ester **2a** , as indicated by absorptions at 910 and 990 cm^{-1} due to allylic double



2a **2b** **2c**

bonds. The absorptions due to the carbonyl groups were detected at 1720 and 1765 cm^{-1}. The former, strong absorption is attributed to the pendant esters and δ–lactone units **2c**, and the latter, weak one to γ–lactone units **2b**. The γ–lactone (**2b**) content of the cyclized units was estimated to be 5% for $AlEt_3$ and 0% for $AlEt_2Cl$ at the Al/M molar ratio of 0.5 using the calibration curve presented by Matsumoto *et al*[3]. By ^1H NMR spectroscopy, the content of cyclization ((**2b**+**2c**)/(**2a**+**2b**+**2c**)) was calculated at 23% for $AlEt_3$ and 30% for $AlEt_2Cl$ at an Al/M molar ratio of 0.5. The addition of $AlEt_3$ and $AlEt_2Cl$ to allyl methacrylate caused an increase in cyclopolymerization, because the usual radical polymerization, i.e., in the absence of ethylaluminum compounds, gave the polymer with content of cyclization below 10% under the similar conditions. No cyclized unit, however, was found in the polymers obtained in the presence of $AlEtCl_2$.

The polymers indicated that absorptions newly appeared at 1700 cm^{-1} and alternatively weakened at 1765 cm^{-1} with increasing Al/M molar ratio for $AlEt_3$ and $AlEt_2Cl$. Extraction of the polymers with alkaline solution clarified that the former absorption was only in the soluble part, but the latter one in the insoluble part. The soluble part consists of carboxylic acids likely derived by a mechanism similar to the Claisen type rearrangement as described below. Having no absorption at 1765cm^{-1}, the soluble part is formed by reactive species different from the radical mechanism in the cyclopolymerization. The insoluble part is a usual polymerization product **2**.

3-2-2 Isolation and Structural Analysis of Products.

The addition of $AlEt_3$, $AlEt_2Cl$ and $AlEtCl_2$ at the Al/M molar ratio of 2.0 induced three different reactions characterized by forming predominantly compounds **3**, **4**, and **5**, as gas chromatograms indicated in Figure 4.

In the presence of $AlEt_2Cl$, oily products were obtained in 88% yield, which were fractionated to isolate compound **4a** using a liquid chromatograph on Lichroprep Si-60 (Merck Ltd.) with hexane/ethyl acetate /ethanol (24/21/4.5). But the main fraction was not completely resolved by chromatography. In order to obtain an analytically pure sample the mixture of raw products, therefore, was converted to the methylated derivatives by treating with diazomethane. The corresponding methyl ester **4b** was isolated in 13% yield (based on monomer) by chromatography with hexane/ethanol (vol. ratio 4/3) as eluent. Simple distillation of the methylated oligomers *via* a Kugelrohr apparatus afforded the dimer in

94% purity. Analysis by GLC showed that 23% of **1** was converted to the dimer.

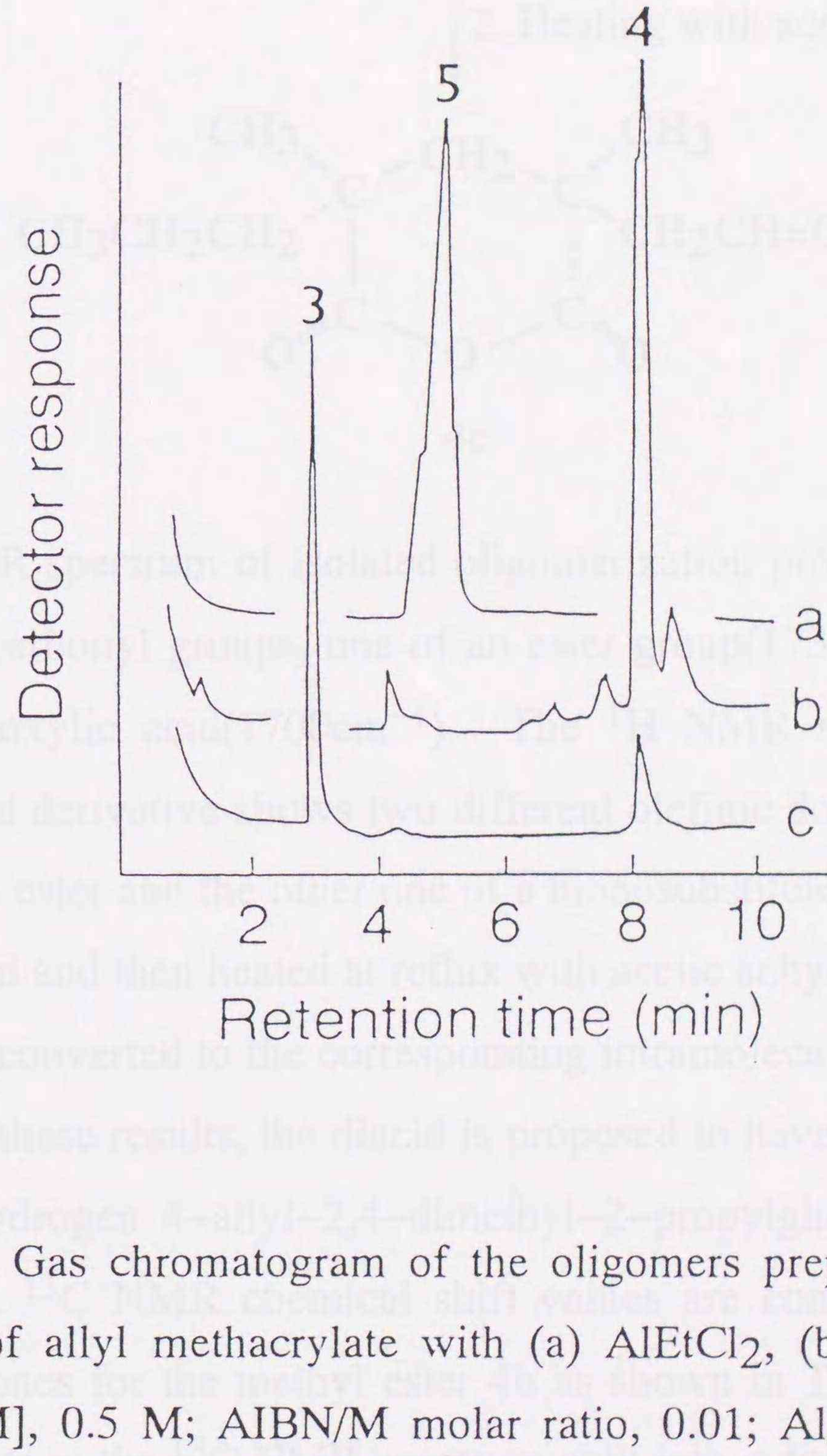
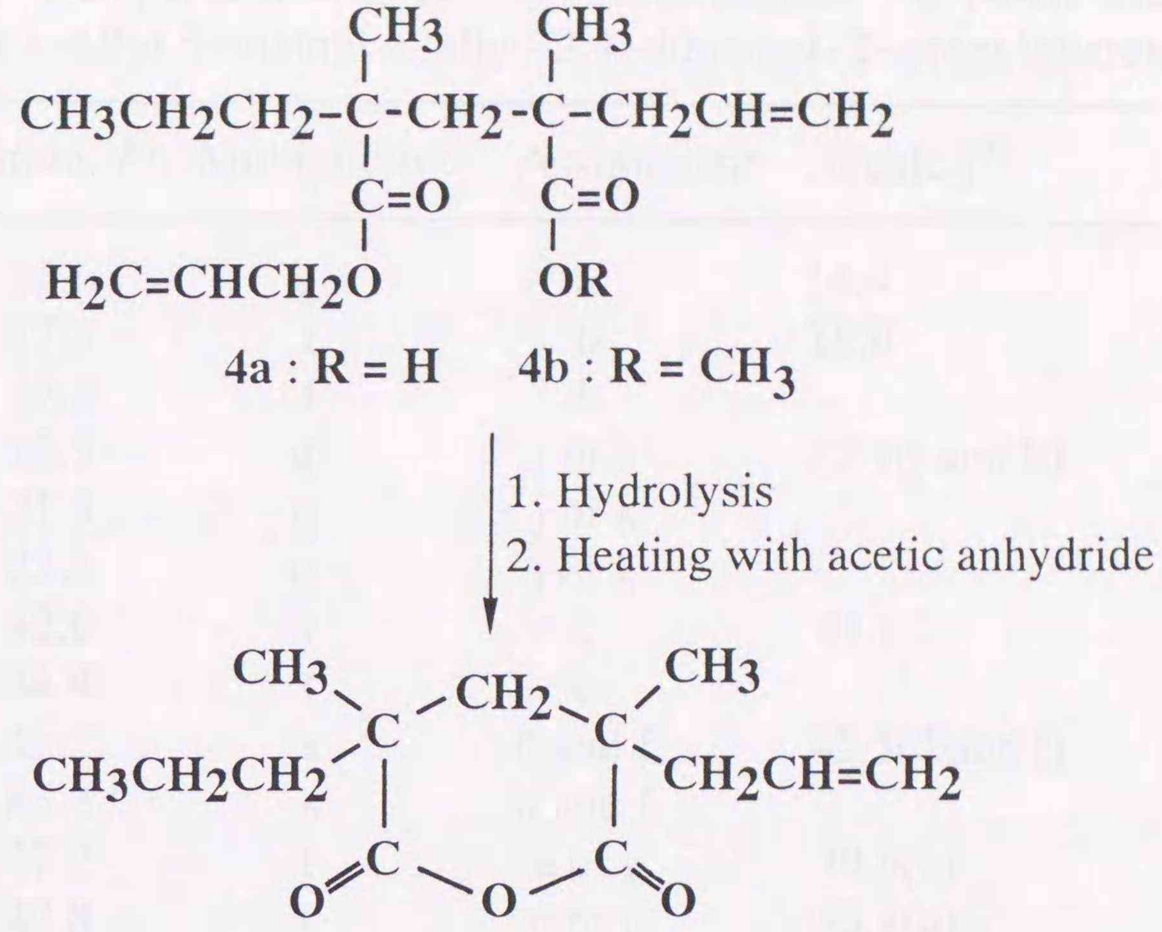


Figure 4. Gas chromatogram of the oligomers prepared from the reactions of allyl methacrylate with (a) $AlEtCl_2$, (b) $AlEt_2Cl$, (c) $AlEt_3$: [M], 0.5 M; AIBN/M molar ratio, 0.01; Al/M molar ratio, 2.0; temp.,40 ℃; time, 10 h. The column was 5 % Thermon–3000 and the temperature was programed at 10 ℃/min from 150 to 250℃.



4a : R = H 4b : R = CH_3

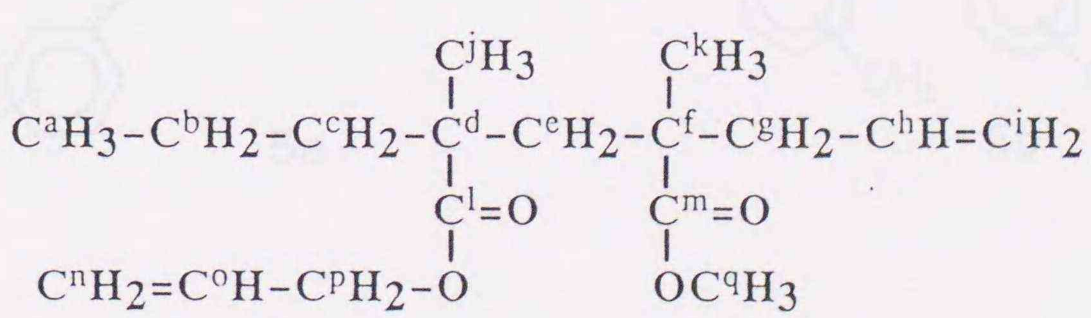
4c

The IR spectrum of isolated oligomerization product shows two different carbonyl groups, one of an ester group(1730cm^{-1}) and one of a carboxylic acid(1700cm^{-1}). The ^{1}H NMR spectrum of the methylated derivative shows two different olefinic double bonds, one of an allyl ester and the other one of a monosubstituted olefin. When hydrolyzed and then heated at reflux with acetic anhydride the methyl ester was converted to the corresponding intramolecular anhydride **4c**. Based on these results, the diacid is proposed to have the structure of 1–allyl hydrogen 4–allyl–2,4–dimethyl–2–propylglutarate **4a**. The calculated ^{13}C NMR chemical shift values are consistent with the assigned ones for the methyl ester **4b** as shown in Table 1. Several components in the ^{13}C NMR spectrum split into a doublet. The GLC of **4a** and **4b** exhibit two peaks of each. These findings indicate that **4a** and **4b** are mixtures of diastereomers.

Table 1. Comparison of observed and calculated ^{13}C NMR chemical shifts for 1-allyl 5-methyl 4-allyl-2,4-dimethyl-2-propylgltarate **4b**[a)]

δ(obs.)[b)]	Multiplicity[c)]	Assignment	δ(calc.)[d)]
14.6	q	a	14.4
17.3	t	b	18.0
17.5	t	b	
18.5	q	j or k	22.1(j and k)
21.5	q	j or k	
22.3	q	j or k	
42.8	t	c	41.6
44.4	t	c	
45.2	s	d and f	45.5(d and f)
45.3	s	d and f	
47.2	t	e or g	39.9(e)
47.8	t	e or g	43.4(g)
48.7	t	e or g	
51.4	q	q	(51.2)[e)]
65.0	t	p	(64.9)[f)]
118.1	t	i and n	(118.0 (n))[f)]
118.5	t	i and n	123.0 (i)
132.3	d	h and/or o	(132.5 (o))[f)]
133.1	d	h and/or o	132.8 (h)
133.9	d	h and/or o	
176.6	s	l and/or m	173.2 (l))[f)]
176.9	s	l and/or m	(174.0 (m))[e)]
177.2	s	l and/or m	

a) In $CDCl_3$ at room temperature.
b) Chemical shift in ppm downfield from tetramethylsilane.
c) Multiplicity in off-resonance spectrum.
d) Chemical shift calculated for **3**.
e) Chemical shift observed for methyl hexanoate.
f) Chemical shift observed for allyl butyrate.



4b

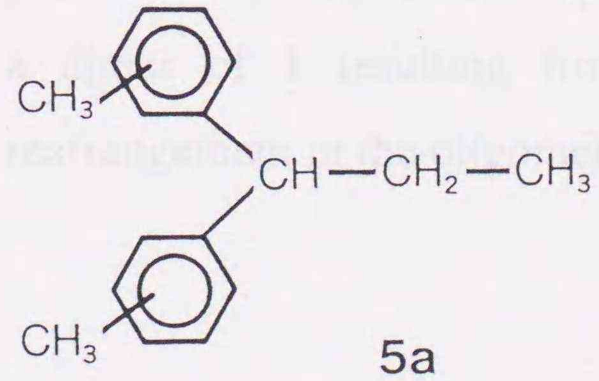
Compound 3 possesses two functional groups of carboxylic acid and allylic double bond, but no ester group, thus being identified as a unimer of allyl methacrylate, 2–methyl–2–propyl–4–pentenoic acid. The analytical data in the experimental section substantiate the

$$CH_3CH_2CH_2\overset{\displaystyle CH_3}{\underset{\displaystyle COOH}{\overset{|}{\underset{|}{C}}}}CH_2CH{=}CH_2$$

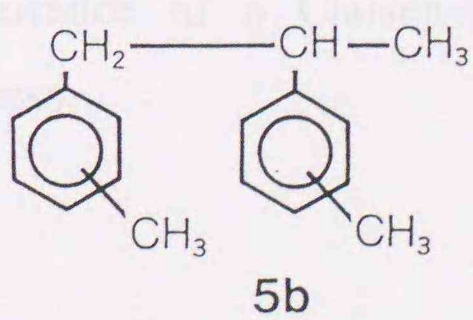
3

assignment. The Claisen type rearrangement, which converted the allyl ester to γ,δ–unsaturated carboxylic acid, resulted in the production of compounds **3** and **4a**.

The IR and the ^1H NMR spectrum of compound **5** exhibited characteristic absorptions of aromatic hydrocarbons capable of recognizing an isomeric mixture of ditolylpropanes. Toluene was used as solvent. The triplet signal at δ=0.85 and doublet one in the range of 1.15 are assigned to the methyl protons in 1,1–and 1,2–ditolylpropanes (**5a** and **5b**), respectively. The relative intensities of all signals indicated in the experimental section are fitted to the 2.3:0.7 mixture of **5a** and **5b**.



5a



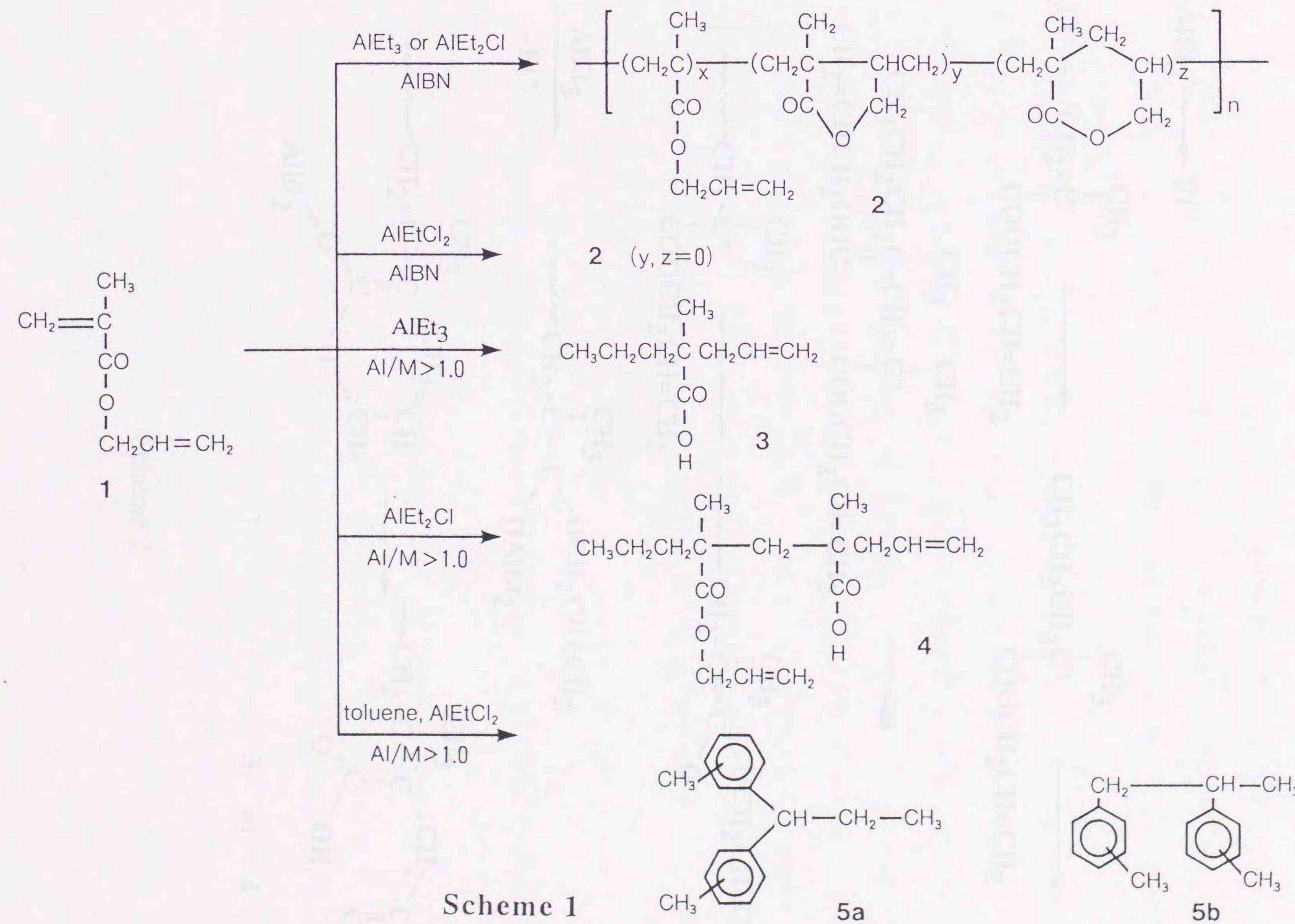
5b

$AlEtCl_2$ may act as a Friedel–Crafts catalyst to utilize allyl methacrylate as an alkylating agent.

3–2–3 Reaction Mechanism

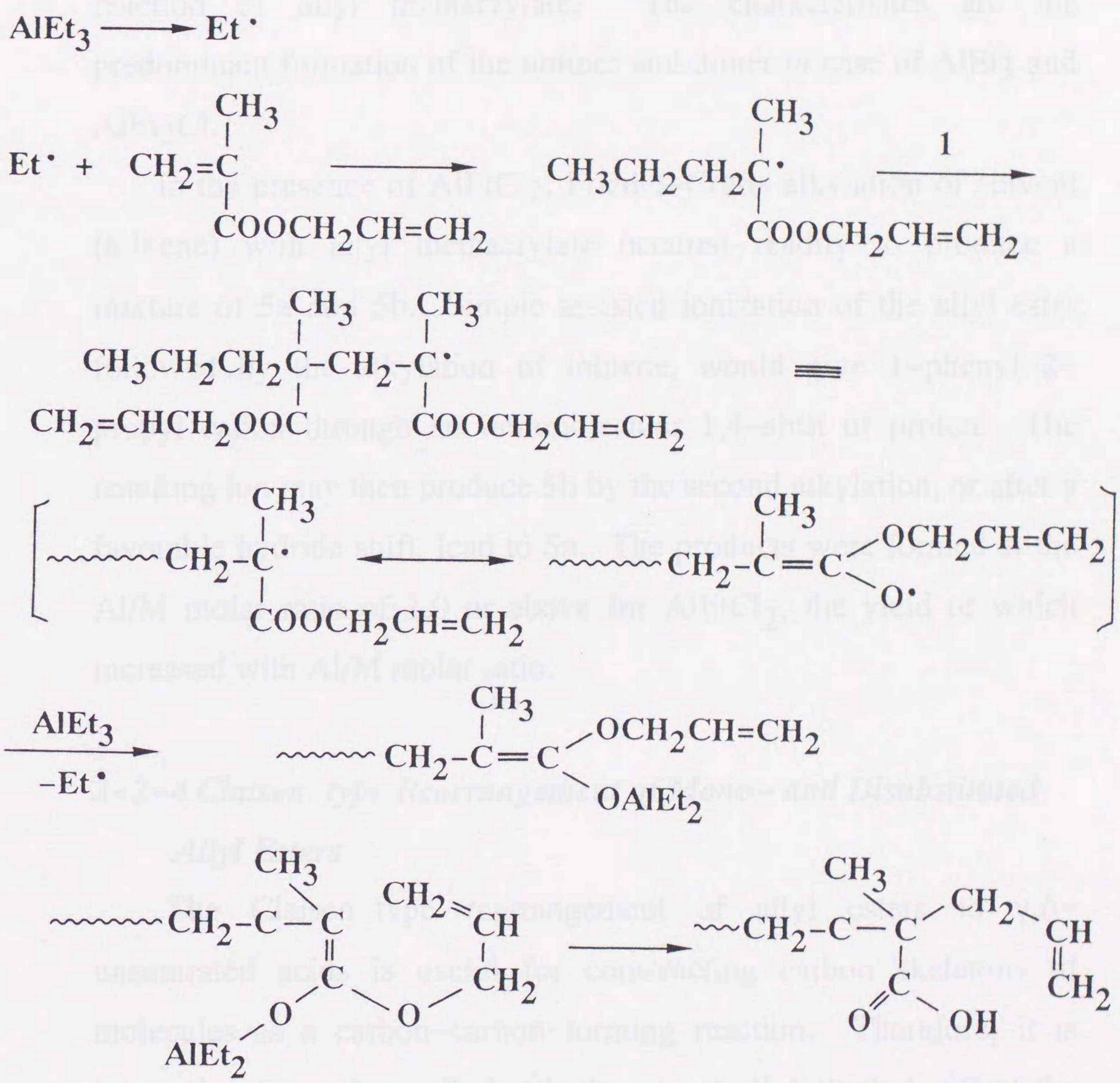
Significant effects of the ethylaluminum compounds upon allyl methacrylate are summarized in Scheme 1. There is essential difference of reactive species between the formations of the lactone ring in compound **2** and of the carboxylic acid in compounds **3** and **4**, because the functional group cannot coexist in a molecule as mentioned above. Cyclopolymerization should be carried out by radical species and Claisen–type rearrangement by nucleophilic species. The reaction of formation of 3 and 4 may be described by Scheme 2. The reaction is initiated by the ethyl radical and the aluminum enolate of unimer or dimer occurred Claisen–type rearrangement. In the presence of $AlEtCl_2$ the polymerization introduced polymer **2** without the cyclized unit by radical species and the Friedel–Crafts alkylation produced compound **5** by an electrophilic species.

Claisen type rearrangements of allyl esters with zinc dust[8)] or lithium isopropylcyclohexylamide[9)] were previously reported. The present study emphasizes especially the productions of a unimer and a dimer of **1** resulting from the occurrence of a Claisen–type rearrangement in the oligomerization process.



1
AlEt3 or AlEt2Cl
AIBN
2
AlEtCl2
AIBN
2 (y, z=0)
AlEt3
Al/M>1.0
3
AlEt2Cl
Al/M>1.0
4
toluene, AlEtCl2
Al/M>1.0
5a
5b

Scheme 1



3 or 4

Scheme 2

In conclusion, differences of Lewis acid strength among ethylaluminum chlorides gave an interesting variety mode in the reaction of allyl methacrylate. The characteristics are the predominant formation of the unimer and dimer in case of $AlEt_3$ and $AlEt_2Cl$.

In the presence of $AlEtCl_2$, Friedel–Crafts alkylation of solvent (toluene) with allyl methacrylate occured readily to produce a mixture of **5a** and **5b**. Simple assisted ionization of the allyl ester, followed by the alkylation of toluene, would give 1–phenyl–2–propyl cation through an intramolecular 1,4–shift of proton. The resulting ion may then produce **5b** by the second alkylation, or after a favorable hydride shift, lead to **5a**. The products were formed at the Al/M molar ratio of 1.0 or above for $AlEtCl_2$, the yield of which increased with Al/M molar ratio.

3–2–4 Claisen type Rearrangement of Mono– and Disubstituted Allyl Esters

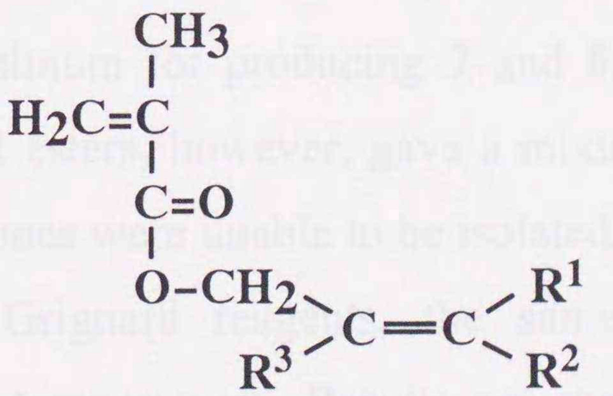
The Claisen type rearrangement of allyl esters to γ,δ–unsaturated acids is useful for constructing carbon skeletons of molecules as a carbon–carbon forming reaction. Therefore, it is interesting to see how alkyl–substituents of allyl alcohols affect the occurrence and the product of this rearrangement. Table 2 shows the results in the reactions of mono– and di–substituted allyl esters of methacrylic acid (**6**) in the presence of $AlEt_3$.

Table 2. Reaction of **6** with triethlalkylaluminum[a)]

Ester	Temp.	Product	Yield[b)]
	(℃)		(%)
6a	80	**7b**	20
6a	40	**8b**	40
6b	80	**7c**	26
6b	40	**8c**	23
6c	80	**7d**	40
6c	40	**8d**	18
6d	80	–	–
6e	80	–	–

a) [**6**] , 0.2 M ; [AIBN] , 1 mM ; $AlEt_3$/**6** molar ratio , 2.0; time, 24 h.

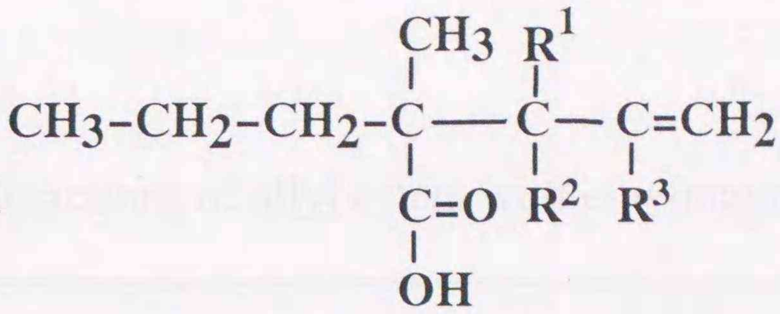
b) Isolated yield. All compounds gave satisfactory ^{1}H NMR and IR spectra.



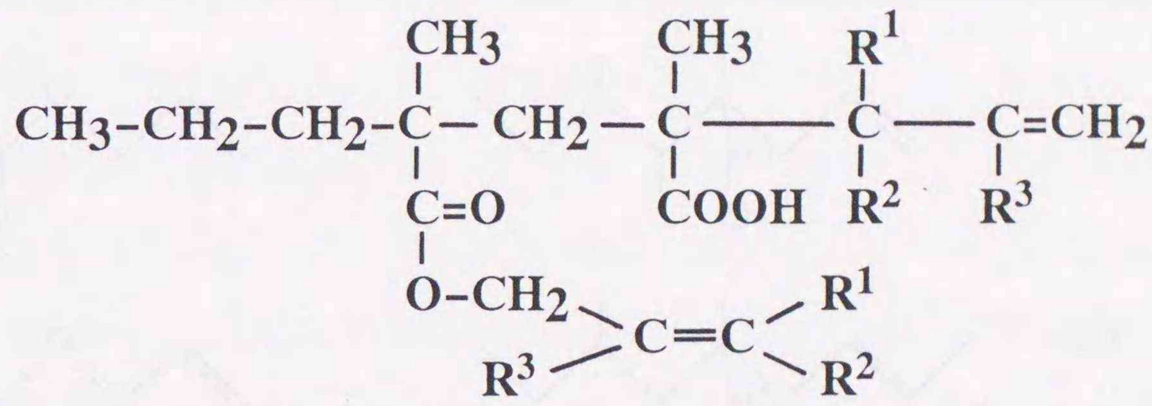
6a: $R^1, R^2 = H$; $R^3 = Me$ **b: $R^1, R^3 = H$; $R^2 = Me$**

c: $R^1, R^3 = H$; $R^2 = n{-}Pr$ **d: $R^3 = H$; $R^1, R^2 = Me$**

e: $R^3 = H$; $R^1 = Me$; $R^2 = -CH_2CH_2CH{=}C(CH_3)_2$



7

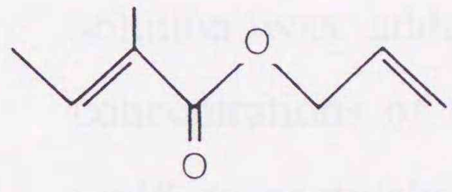
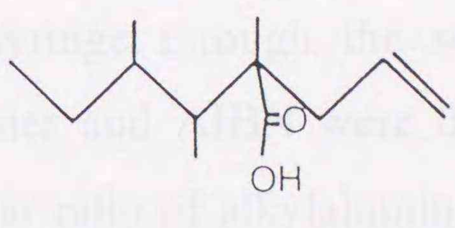
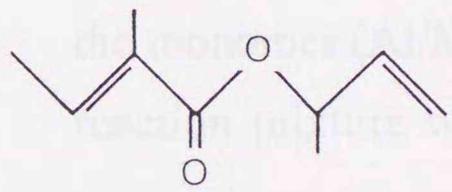
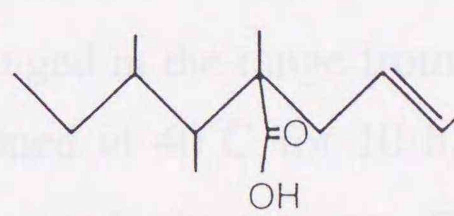
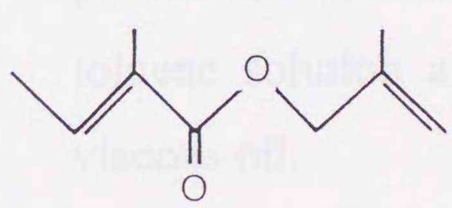
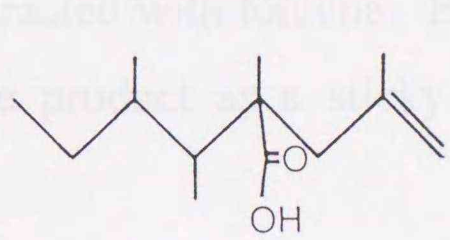
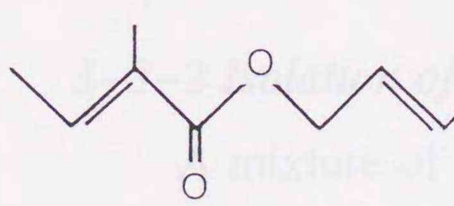
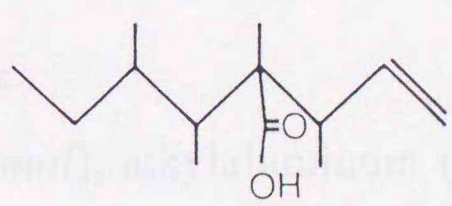
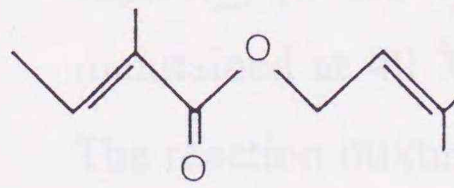
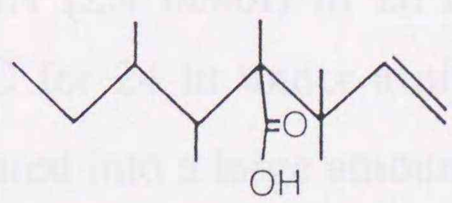
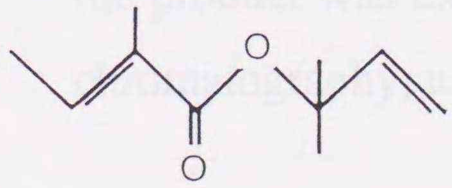
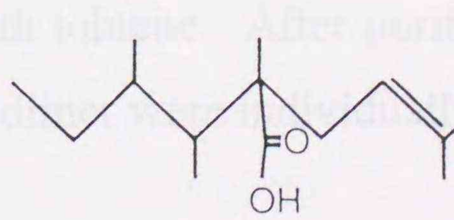


8

In the case of mono–substituted allyl esters **6a–c**, unimer **7** and dimer **8** each was produced in high selectivity by controlling reaction temperature. The conditions at the temperatures of 40 and 80℃ were determined as optimum for producing **7** and **8**, respectively. 3,3–Disubstituted allyl esters, however, gave a mixture of products from which individual ones were unable to be isolated.

By use of Grignard reagents, the same reaction could be performed at low temperature. Results are summarized in Table 3. Reaction of allyl methacrylate with EtMgBr afforded a polymeric product. The presence of large substituent at α–positionis necessitates in this case. Esters of tiglic acid give good yields. Table 3 shows that the yield is affected by the steric hindrance in β–position of product.

Table 3. Reactions of allyl esters with ethylmagnesium bromide

Ester	Product	Yield (%)
		43
		53
		30
		27
		18
		49

[EtMgBr]/[ester] = 4.0 ; solv., ether ; temp., 0°C

3-3 Experimental Part

3-3-1 Polymerization

All reactions were carried out in side-armed ampoules. Monomer, toluene, and AIBN were charged into the ampoules previously equipped with a serum stopper cap at the side arm. The ampoules were evacuated and sealed. The alkylaluminum compound solution was added by a syringe through the serum cap. The concentrations of the monomer and AIBN were 0.5 and 5×10^{-3} *mol/l*, respectively. The molar ratio of alkylaluminum compound to the monomer (Al/M) was changed in the range from 0.05 to 2.0. The reaction mixture was maintained at 40℃ for 10 h, and then it was poured into methanol and extracted with toluene. Evaporation of the toluene solution afforded the product as a sticky semi-solid or a viscous oil.

3-3-2 Isolation of oligomers

A mixture of ester (4 *mmol*), alkylaluminum ($AlEt_3$, $AlEt_2Cl$ or $AlEtCl_2$) (8 *mmol*) and AIBN (2.4 *mmol*) in 20 *ml* of toluene was maintained at 40 ℃ or 80 ℃ for 24 hr under a nitrogen atmosphere. The reaction mixture was poured into a large amount of methanol, and the product was extracted with toluene. After purification by column chromatography, unimer and dimer were individually obtained.

(a) 2-Methyl-2-propyl-4-pentenoic acid (3)

The reaction of the monomer in the presence of $AlEt_3$ at the Al/M molar ratio of 2.0 gave the crude product, which was purified by liquid chromatography on Lichroprep Si-60 (from Merck Ltd.)

with hexane/ethyl acetate/ethanol (vol. ratio 24/21/4.5) to yield a colorless liquid in pure form. Yield : 40%.

IR (NaCl): 2950, 1700, 1645, 1520, 1490, 1450, and 1380 cm^{-1}; ^1H NMR (CCl_4): δ=0.90 (t, *J*=6Hz, 3H), 1.13 (s, 3H), 1.17–1.74 (m, 4H), 2.21 (dd, *J*=14 and 7Hz, 1H), 2.41 (dd, *J*=14 and 7Hz, 1H), 5.08 (d, *J*=12Hz, 2H), 5.60–5,90 (m, 1H), and 12.30 (s, 1H); ^{13}C NMR ($CDCl_3$): δ=14.5 (q), 17.8 (t), 21.1 (q), 41.1 (t), 43.0 (t), 45.9 (s), 118.1 (t), 133.8 (d), and 184.0 (s). Anal. Calcd for $C_9H_{16}O_2$: C, 69.19%; H, 10.32%. Found: C, 69.52%, H, 10.29%. High resolution MS. Calcd for $C_8H_{13}O_2$ ($[M-CH_3]^+$): 141.092. Found: 141.093.

(b) 1–Allyl hydrogen 4–allyl–2,4–dimethyl–2–propyl–glutarate (4a)

The reaction of monomer in the presence of $AlEt_2Cl$ at Al/M molar ratio of 2.0 gave the product in 23% yield.

IR (NaCl): 3070, 2950, 2870, 1730, 1700, 1640, 1470, 1380, 1220, 1150, 980, 920 cm^{-1}; ^1H NMR (CCl_4): δ=0.5–2.7 (m; 17H), 4.55 (d; 2H), 4.7–6.3 (m; 6H), and 10.8 (s; 1H).

(c) 1–Allyl 5–methyl 4–allyl–2,4–dimethyl–2–propylglutarate (4b)

This was obtained from **4a** and diazomethane.Yield:13%

IR (NaCl): 3070, 2950, 2870, 1730, 1640, 1460, 1380, 1220, 1140, 980, 920 cm^{-1}; ^1H NMR (CCl_4):δ=0.6–2.5 (m; 17H), 3.5 (s; 3H), 4.4 (d; 2H), 4.6–5.0 (m; 2H), and 5.0–6.3 (m; 4H). Anal. Calcd for $C_{17}H_{28}O_4$: C 68.89%; H 9.52%. Found: C 68.88%; H 9.53%.

(d) 4,6–Dimethyl–1–nonene–4,6–dicarboxylic anhydride (4c)

IR (NaCl): 3070, 2950, 2870, 1800, 1760, 1640, 1380, 1040, 1010, 920 cm^{-1}; ^{1}H NMR (CCl_4): δ=0.8–2.1 (m; 15H), 2.3 (m; 2H), 5.0–5.3 (m; 2H), and 5.4–6.0 (m; 1H).

(e) Ditolylpropanes (5)

The reaction of monomer in the presence of $AlEtCl_2$ at an Al/M molar ratio of 2.0 gave the crude product, which was purified by distillation *via* Kugelrohr apparatus to yield a mixture of 1,1– and 1,2–ditolylpropane (**5a** and **5b**) as a colorless liquid. Yield: 90%. IR (NaCl): 3040, 2930, 1610, 1500, 1460, and 1380cm^{-1}; ^{1}H NMR (CCl_4): δ=0.85 (t, *J*=7Hz, 0.7H), 1.13 and 1.20 (d × 2, *J*=7Hz, 2.3H), 1.80–2.40 (m; 6.4H), 2.50–3.00 (m, 2.3H), 3.59 (t, *J*=7Hz, 0.3H), 6.60–7.30 (m, 8H). Mass Spectra. Calcd for $C_{17}H_{20}$ (M^+): 224.157. Found: 224.156.

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Chapter 4

REACTION
OF
ESTERS, DIESTER, AND γ-KETOESTERS
WITH
ALKYLALUMINUM COMPOUNDS

4-1 Introduction

Secondary alcohol are generally prepared by the action of Grignard reagents on aldehydes or by the reduction of ketones. Aldehydes and ketones , however, are more difficult to synthesize in comparison with esters. It is well known that esters are reduced to primary alcohols by triisobutylaluminum, diethylaluminum hydride[1,2] or lithium aluminum hydride, and are converted to tertiary alcohols by the action of Grignard reagents. Comines *et a*l. have described one-step synthesis of aromatic secondary alcohols by the reaction of esters with $LiBH_4$-RMgX[3]. However, only a little attention was given to the reaction of esters with trialkylaluminums[4]. Pasynkiewicz *et al.*[5] have investigated the reaction of $AlEt_3$ with *p*-substituted ethyl benzoate from which aldehydes and ketones resulted. Preparation of tertiary alcohols by the action of triethylaluminum on esters have been shown in a patent.[6]

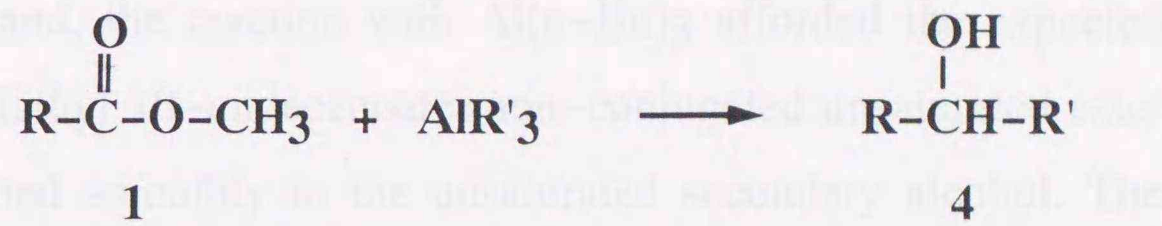
In previous chapters it was described that alkylaluminum compounds cause dimerization , reduction , alkylation , and rearrangement of acrylic esters. The reactions of ordinary aliphatic esters with alkylaluminums become of interest as the next subject. In this chapter, one step conversion of unconjugated esters **1** to secondary alcohols and the reaction of alkylaluminum compounds with dimethyl methylenesuccinate **2** and γ-ketoesters **3** will be described.

$R\text{-}COOCH_3$ (**1**) $CH_2=C(CH_2COOCH_3)(COOCH_3)$ (**2**) $R\text{-}C(=O)\text{-}CH_2CH_2COOCH_3$ (**3**)

4–2 Results and Discussion

4–2–1 Reaction of Aliphatic Esters

The reaction of aliphatic esters **1** with AlR'_3 (R' = n–Pr , n–Bu) gives selectively secondary alcohols **4** (Scheme 1). Results are summarized in Table 1.



1 **4**

Scheme 1

Table 1. Synthesis of secondary alcohols **4** from the reaction of esters **1** with trialkylaluminums[a)]

R	Yield of **4** (%)[b)] Al(n–Pr)$_3$	Al(n–Bu)$_3$
$CH_3(CH_2)_3$–	0	44
$(CH_3)_2CH$–	0	14
$CH_3CH_2(CH_3)CH$–	0	39
$CH_3(CH_2)_4$–	17	51
$CH_3(CH_2)_5$–	31	49
$CH_3(CH_2)_6$–	39	53
$CH_3(CH_2)_7$–	44	50
$CH_3(CH_2)_8$–	50	44
$CH_2{=}CH(CH_2)_8$–	76	52
$CH_3(CH_2)_{10}$–	42	56

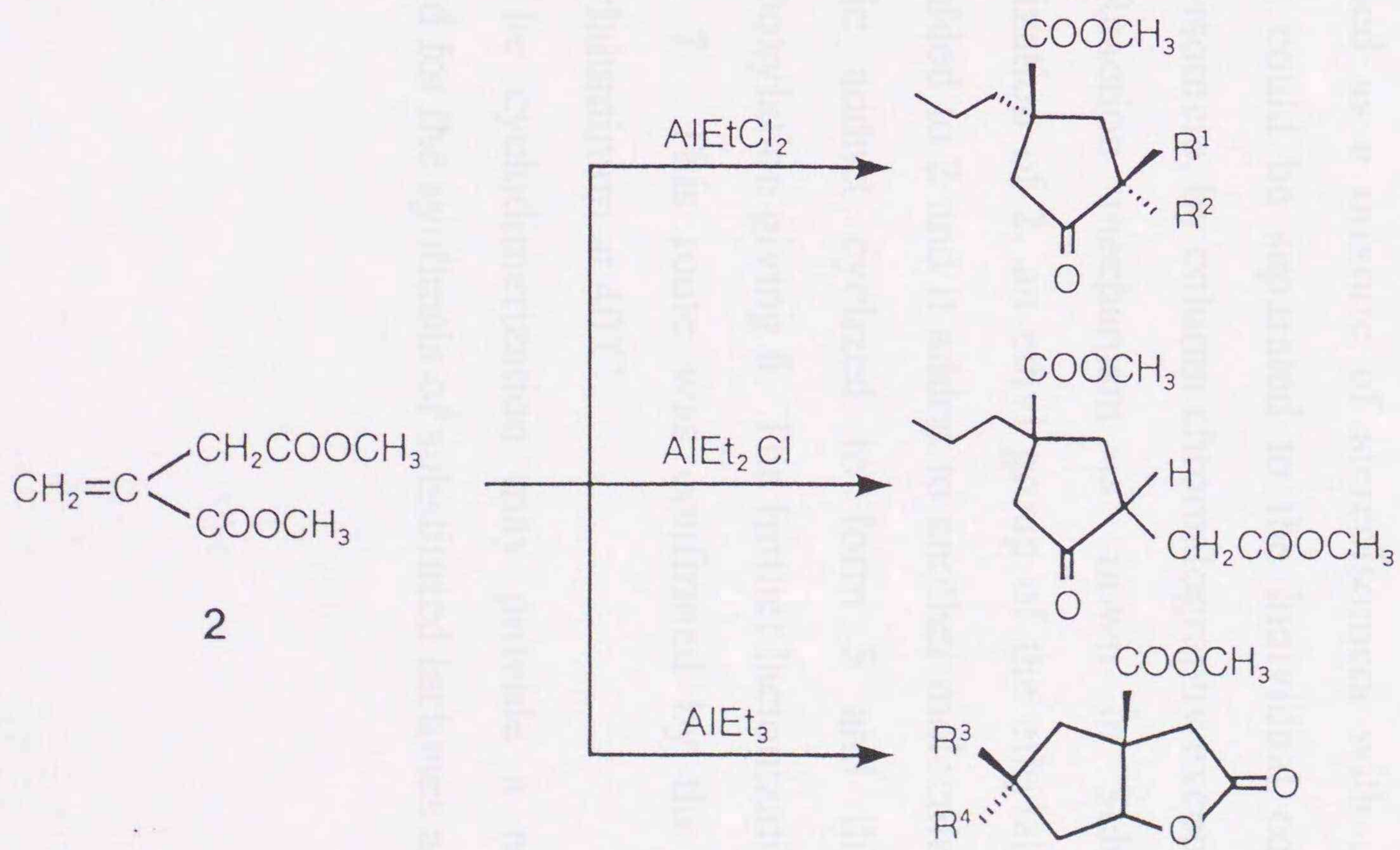
a) [Al]/[Ester]=1.2; solvent, toluene; temp.,90 °C; time, 3 h.

b) Yields were determined by GLC.

This reaction formed secondary alcohols **4** without the formation of tertiary alcohols. The yields of **4** were increased with increasing number of carbon atoms in the alkyl groups of the substrates **1**. None of the product were obtained from the reaction of methyl valerates (R = n–Bu, i–Bu, and sec–Bu) with $Al(n\text{-}Pr)_3$. On the other hand, the reaction with $Al(n\text{-}Bu)_3$ afforded the expected product. Methyl 10–undecenoate, non–conjugated unsaturated ester, was converted smoothly to the unsaturated secondary alcohol. The method is useful for the preparation of secondary alcohols with an alkyl group, which originated the trialkylaluminum.

4–2–2 Reaction of Dimethyl Methylenesuccinate 2

The reaction of dimethyl methylenesuccinate **2** with ethyl–aluminums gave various products according to the reaction conditions (Scheme 2). Result are summarized in Table 2. The reaction of **2** with $AlEtCl_2$ gave methyl 1,4–dimethylcarbonyl–2–oxo – 4 – propyl – 1 – cyclopentaneacetate **5**. The reaction of $AlEt_2Cl$ with **2** was best at 80 ℃ to give methyl 4–methoxy–carbonyl –2 – oxo – 4 – propyl – 1–cyclopentane acetate **6**. The formation of dimethyl 3–oxo–7–propyl–2–oxabicyclo [2.2.0]octane–5,7–dicarboxylate **7** was observed when $AlEt_3$ was used at 40 ℃ for 25 hr..



	R^1	R^2
5a	CH_2COOCH_3	$COOCH_3$
5b	$COOCH_3$	CH_2COOCH_3
6		

	R^3	R^4
7a	$COOCH_3$	n-C_3H_7
7b	n-C_3H_7	$COOCH_3$

Scheme 2

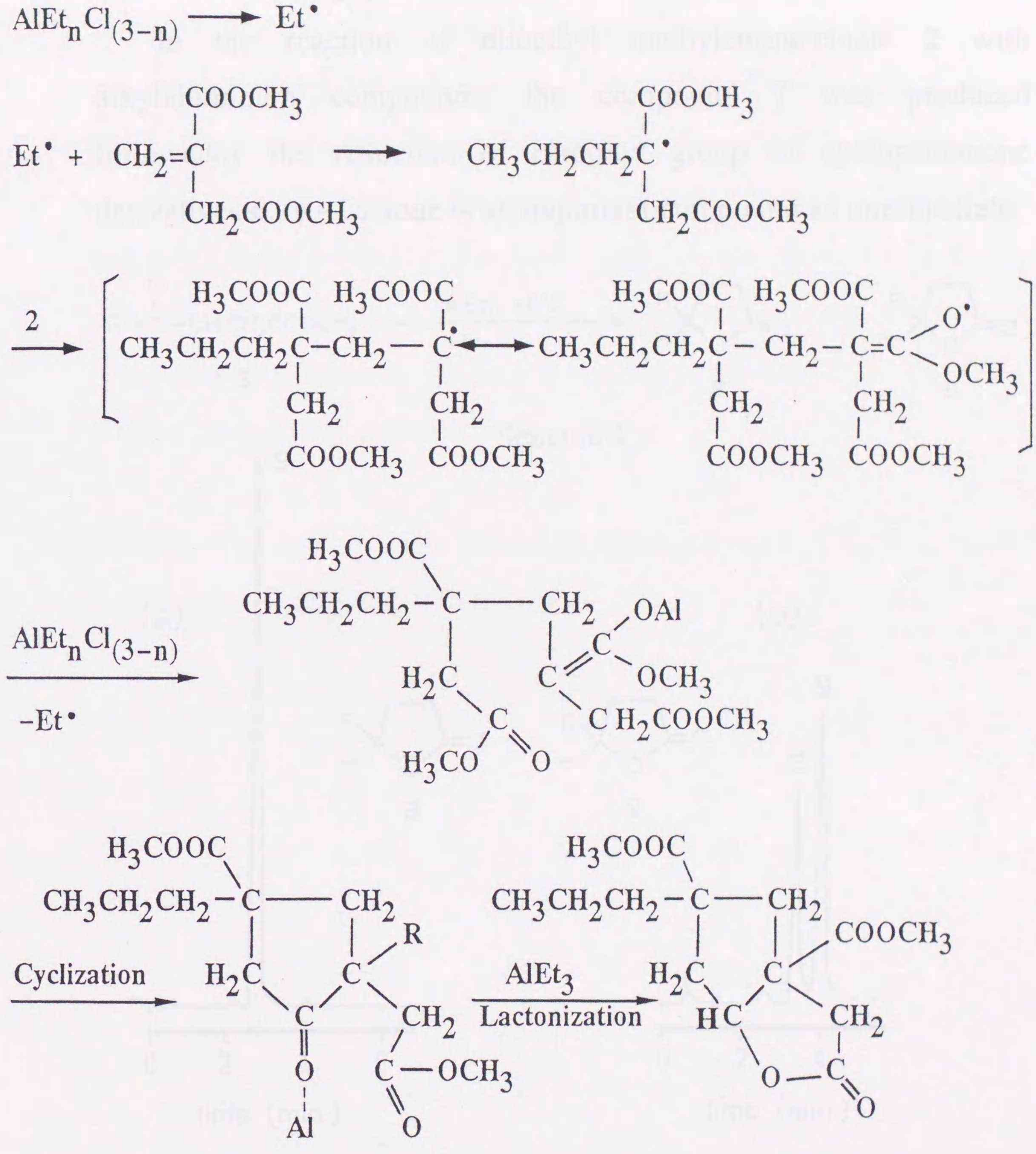
Table 2. Cyclodimerization of dimethyl methylenesuccinate **2** with alkylaluminums.

Aluminum Compound	Al / **2** (molar ratio)	Product	Yield (%)
$AlEtCl_2$	2.0	**5**	21
$AlEt_2Cl$	2.0	**6**	31
$AlEt_3$	1.0	**7**	34

Although the yields were uniformly low, the cyclodimer content in the distillable products was beyond 75 % and containing one product in high selectivity. Each of the cyclodimers **5**, **6**, and **7** was obtained as a mixture of stereoisomers with a ratio of about 1:1, which could be separated to the individual components, cis– and trans–isomers, by column chromatography except for **6**.

Reaction mechanism is shown in Scheme 3. For the dimerization of **2**, an ethyl group of the ethylaluminum compounds was added to **2** and it added to another molecule of **2**. The resulting dimeric adduct cyclized to form **5** and then took place the decarboxylation giving **6**. The further lactonization of **5** proceeded to afford **7**. This route was confirmed by the reaction of **5** with triethylaluminum at 40℃.

The cyclodimerization may provide a new and convenient method for the synthesis of substituted lactones and cyclic ketones.



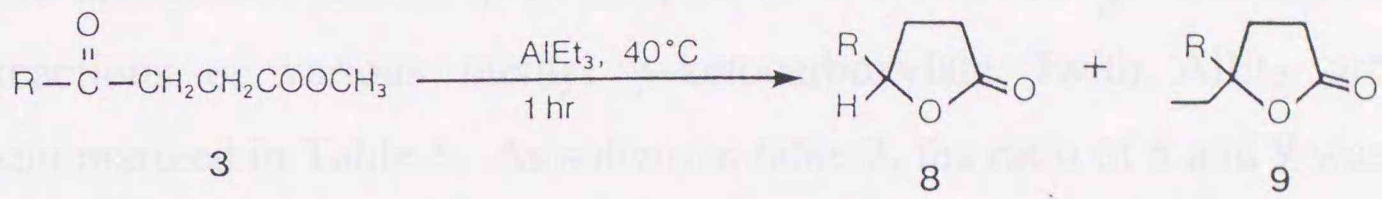
5 : R = −COOCH$_3$ 5 or 6 7

6 : R = H

Scheme 3

4-2-3 Reaction of γ-Ketoesters 3

In the reaction of dimethyl methylenesuccinate 2 with alkylaluminum compounds, the compound 7 was produced followedby the reduction of carbonyl group of cyclopentanone derivatives 6. γ -Lactone is an important compound as intermediate



Scheme 4

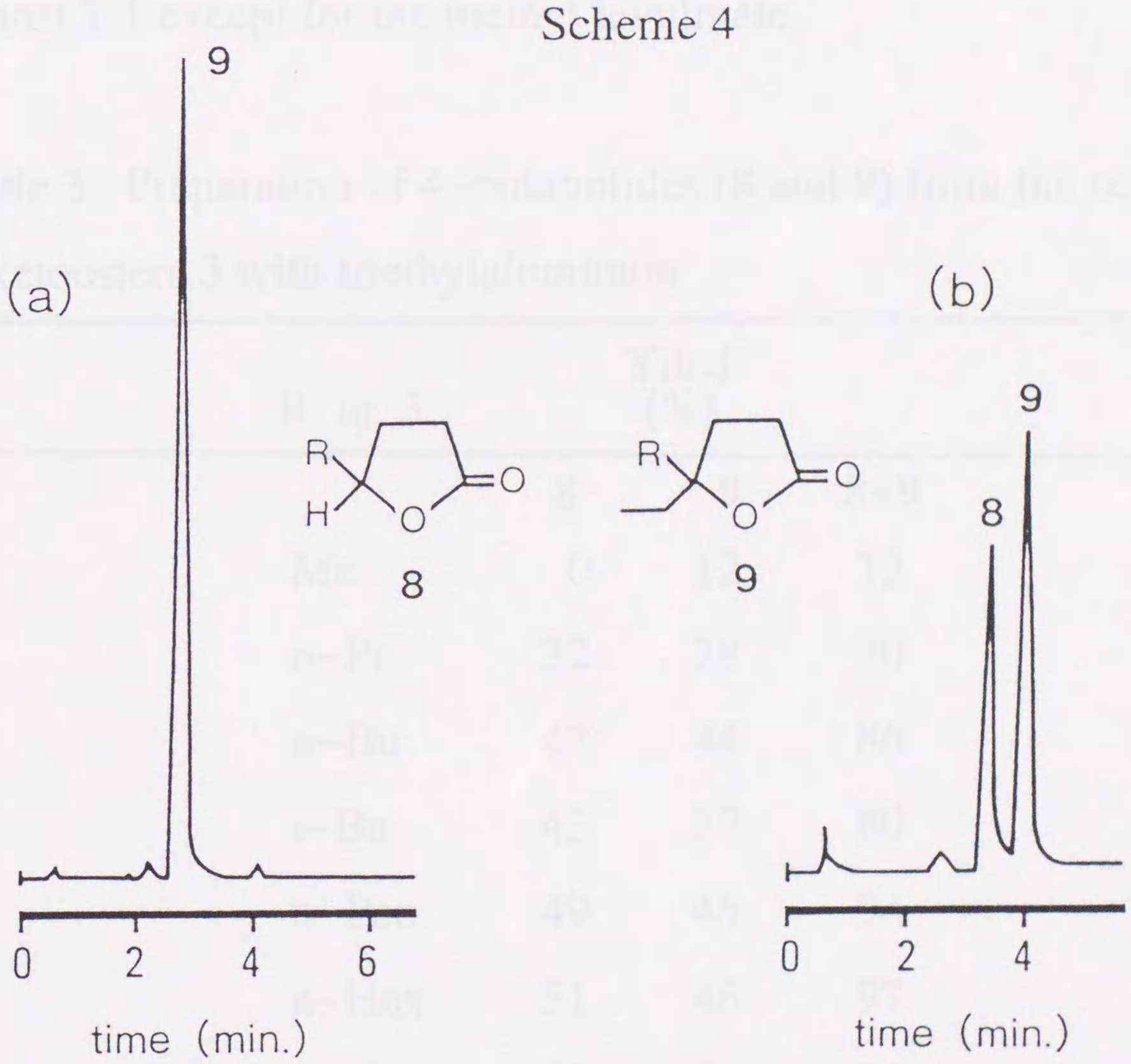


Figure 1. Gas chromatogram of reaction products prepared from the reactions of triethyaluminum with (a) methyl levulinate. (b) methyl γ -ketoheptanoate:[M], 0.2M; $AlEt_3$/M molar ratio, 2.0; time, 1 h; temp, 40 ℃ .

in the perfume and medicine syntheses[7]. Thus, the synthesis of γ-lactone was examined by the reaction of the γ-ketocarboxylic acid methyl esters **3** with triethylaluminum. As a result, 4–butanolid (γ–lactone) derivatives (**8** and **9**) were obtained selectively. The gaschromatogram of reaction product of methyl levulinate with triethylaluminum showed only one perk as shown in Figure 1–(a).

On the other hand, two compounds, **8** and **9**, were observed in the reaction of methyl γ–ketoheptanoate **3** with $AlEt_3$. Results of reactions of various methyl γ–ketocarboxylate 7with $AlEt_3$ are summarized in Table 3. As sohwn in table 3, the ratio of **8** and **9** was almost 1:1 except for the methyl levulinate.

Table 3. Preparation of 4–butanolides (**8** and **9**) from the reaction of γ–ketoesters **3** with triethylaluminum

R in **3**	Yiled (%)		
	8	**9**	**8+9**
Me	0	12	12
n–Pr	32	38	70
n–Bu	42	44	86
i–Bu	43	37	80
n–Pen	49	45	94
n–Hex	51	46	97
n–Hep	50	42	92
n–Non	48	44	92

Only one absorption was observed at $1770cm^{-1}$ in IR measurement of the mixture. Mass spectrum of the former peak was identical with γ–heptanolactone **8**. Mass spectrum of the latter peak was similar to that of 4–ethyl–4–methyl–4–butanolide **9**. Therefore, the compound is 4–ethyl–4–prolyl–4–butanolid.

It is presumed that the results is influenced by the bulkiness of substituent. There is a tendency for the yields to a rise with increasing bulkiness of **R** in **3**. These compounds were produced by the addition of $AlEt_3$ to carbonyl carbon in ketones. Various 4–butanolide derivatives can be synthesized by the combination of the alkyl group of **3** and the alkyl group of trialkylaluminums.

4-3 Experimental Part

In a typical procedure for the reactions of aliphatic esters with AlR_3, a solution of **1** (2 *mmol*) in toluene (10 *ml*) containing AlR'_3 (2.4 *mmol*) was maintained at 90 ℃ for 3 h under a nitrogen atmosphere with occasional shaking. After quenching with a large amount of methanol, products were extracted with ether. Evaporation of ether gave the product.

The reaction of dimethyl methylenesuccinate (**2**) is as follows. A mixture of dimethyl methylenesuccinate (633*mg*, 4 *mm*ol), $AlEtCl_2$ (8 *mmol*) and AIBN (20 *mg*, 0.12 *mmol*) in 20 *ml* of toluene was maintained at 40 ℃ for 25 hr under a nitrogen atmosphere. The reaction mixture was poured into a large amount of methanol and the product was extracted with toluene. After the purification by column chromatography, cis−**4a** and trans−**4b** were isolated.

The reaction of γ−ketoesters are as follows: A mixture of γ−ketoesters (4 *mmol*) and $AlEt_3$ (8 *mmol*) in 20 *ml* of toluene was maintained at 40 ℃ for 1 hr under a nitrogen atmosphere. The reaction mixture was poured into a large amount of methanol and the product was extracted with toluene. Then the toluene was distilled off and the product was obtained.

(a) Methyl 1 , 4 − dimethylcarbonyl − 2 − oxo − 4 − propyl − 1 − cyclopentaneacetate (5)

5a : IR (film) 1720 cm^{-1} br.s ; ^{1}H−NMR (C_5D_5N) δ= 3.71,3.68, and 3.60 (each 3H, s),3.44 (1H, d, *J*=18Hz), 3.22 (1H, d, *J*=18Hz), 3.09 (1H, d, *J*=15Hz), 2.98 (1H, d, *J*=15Hz), 2.91 (1H, d, J=18Hz), 2.68 (1H, d, *J*=18Hz), 1.83 (2H, m), 1.27 (2H, sex., *J*=7.5Hz), 0.84

(3H, t, J=7.5Hz); ^{13}C–NMR ($CDCl_3$) δ=209.8, 176.6, 171.1, 170.4, and 58.2 (each s), 53.2, 52.4, and 52.0 (each q), 47.8 (s), 46.9, 42.0, 41.8, 38.5, and 19.0 (each t), 14.3 (q). Exact MS calcd. for $C_{15}H_{22}O_7$ 314.137, found 314.137; according to the ^{1}H–NMR spectrum, **5a** was assigned to *cis*–configuration on the basis of the near equivalence of methylene proton in position **3** and **5**.

5b: IR and mass spectra are identified as **5a**.
^{1}H–NMR ($CDCl_3$) δ=3.73, 3.68, and 3.65 (each 3H, s), 3.33 (1H, d, J=19Hz), 3.22 (1H, d, J=14Hz), 2.95 (2H, s), 2.41 (1H, d, J=19Hz), 2.09 (1H, d, J=14Hz), 1.4–2.0 (2H, m), 1.24 (2H, m), 0.91 (3H, t, J=7.5Hz); ^{13}C–NMR ($CDCl_3$) δ=211.3, 176.0, 171.0, 170.1, and 57.8 (each s), 52.8, 52.3, and 52.0 (each q), 48.8 (s), 46.1, 43.7, 42.8, 38.7, and 19.1 (each t), 14.2 (q).

(b) Methyl 4 – methoxycarbonyl – 2 – oxo – 4 – propyl – 1 – cyclopentaneacetate (6)

6a and **6b**: IR (film) 1730 cm^{-1} br s; ^{1}H–NMR ($CDCl_3$) δ =3.73, 3.72, 3.71, and 3.70 (total 6H, each s), 1.1–3.2 (11H, m), 0.91 (3H, t, J=7Hz); ^{13}C–NMR ($CDCl_3$) **6a**: δ=216.2, 176.4, and 172.1 (each s), 52.4 and 51.8 (each q), 49.4 (s), 46.8 (d), 44.1 (t), 42.0, 39.0, 33.5, and 19.1 (each t), 14.3 (q); **6b**: 216.2, 176.3, and 172.1 (each s), 52.4 and 51.8 (each q), 48.1 (s), 46.3 (d), 43.3, 39.7, 37.4, 34.1, and 18.6 (each t), 14.3 (q). Exact MS calcd for $C_{13}H_{20}O_5$ 256.131. Found 256.130.

(c) Dimethyl 3 – oxo – 7 – propyl – 2 – oxabicyclo [2.2.0] octane – 5 ,7–dicarboxylate (7)

7a: IR (film) 1780 and 1725 cm^{-1} br, s; ^{1}H–NMR ($CDCl_3$) δ =5.19 (1H, dd, *J*=6.5 and 4.5 Hz), 3.74 and 3.69 (each 3H,s), 3.13 (1H, d, *J*=15Hz), 3.07 (1H, d, *J*=19Hz), 2.94 (1H, dd, *J*=15 and 8Hz), 2.69 (1H, d, *J*=19Hz), 1.40–2.00 (3H), 1.20 (2H, m), 0.89 (3H, t, *J*=7.5Hz); ^{13}C–NMR ($CDCl_3$) δ=176.1, 174.3 and 173. 2 (each s), 87.2 (d), 55.4 and 54.8 (each t), 14.3 (q). Exact MS Calcd for $C_{14}H_{20}O_6$ 284.126. Found 284.125.

7b:IR and mass spectra are identified as **7a.**

^{1}H–NMR ($CDCl_3$) δ=4.99 (1H, d, *J*=4.5Hz), 3.80 and 3.71 (each 3H, s), 3.23 (1H, d, *J*=19Hz), 2.82 (1H, d, *J*=19Hz), 2.76 (1H, d, *J*=14Hz), 2.16 (1H, dd, *J*=14 and 3 Hz), 1.34–2.10 (3H), 1.21 (2H, m), 0.90 (3H, t, *J*=7.5Hz); ^{13}C–NMR ($CDCl_3$) δ=176.2, 174.7, and 174.1 (each s), 87.3 (d), 55.6 and 55.0 (each s), 53.1 and 52.4 (each q), 45.4, 44.0, 42.1, 39.7, and 19.3 (each t), 14.3 (q). Because of exclusive formation by the reaction of **2a** with triethylaluminum, **7b** was assigned to *cis*–confiruration.

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Chapter 5

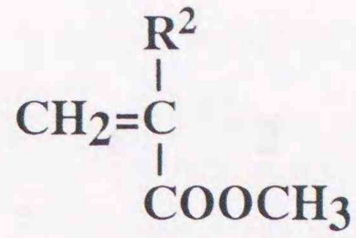
SELECTIVE DIMERIZATION
OF
α–ALKYL SUBSTITUTED ACRYLATES
WITH
GRIGNARD REAGENTS

5-1 Introduction

In the previous chapters it was clarified that the oligomerization of acrylate delivatives, such as methyl methacrylate, allyl methacrylate, and dimethyl methylenesuccinate, were initiated by organoaluminum compounds whose diversity acting as Lewis acid and nucleophile is used satisfactorily in a series of reactions. Unlike Grignard reagents, however, only a limited kind of organoaluminums is accessible. Lebedeva *et al.*[1] and Owens *et al.*[2] have reported the formation of linear dimers in the reaction of methyl acrylate and methacrylate with Grignard reagents. This reaction occurred with a combination of 1,4– and 1,2–addition giving various products along with the linear dimers. Kanemasa *et al.*[3,4] have reported that 2–(trimethylsilyl)– acrylate reacts with Grignard reagents to lead the chemo– and diastereoselective dimerization.

In this chapter, author wishes to describe the reaction of a series of acrylates **2a–f** with Grignard reagents **1a–f**, which leads selectively to the formation of 1:2 adducts **4**, together with results on the diastereoselectivity in the dimerization and on the subsequent reaction of 1:2 adduct anion **3** in situ with some electrophiles[5] such as aldehyde, carbon dioxide, bromine, acetyl chloride, ethylene oxide, and acrylate itself.

	1a : R^1 = Et	**1d : R^1 = n–Bu**
R^1–MgBr	**1b : R^1 = n–Pr**	**1e : R^1 = i–Bu**
	1c : R^1 = i–Pr	**1f : R^1 = t–Bu**
1		



2a : R^2 = Me

2b : R^2 = Et

2c : R^2 = n–Pr

2d : R^2 = i–Pr

2e : R^2 = n–Bu

2f : R^2 = i–Bu

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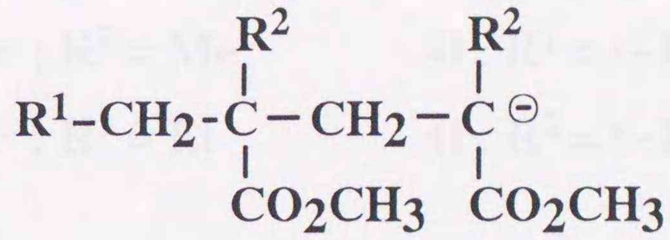

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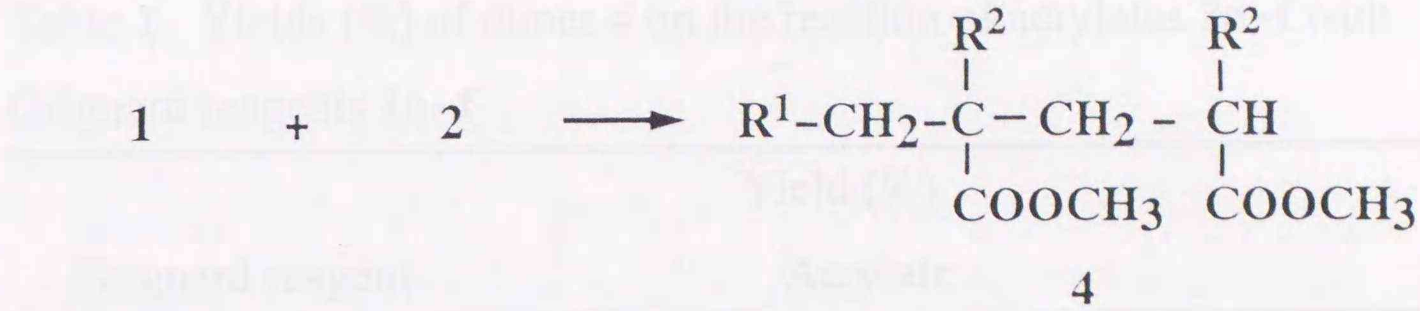
3a : R^1 = Et ; R^2 = Me	**3f : R^1 = i–Pr ; R^2 = n–Pr**
3b : R^1 = Et ; R^2 = Et	**3g : R^1 = i–Pr ; R^2 = i–Pr**
3c : R^1 = Et ; R^2 = i–Pr	**3h : R^1 = t–Bu ; R^2 = Me**
3d : R^1 = i–Pr ; R^2 = Me	**3i : R^1 = t–Bu ; R^2 = Et**
3e : R^1 = i–Pr ; R^2 = Et	**3j : R^1 = t–Bu ; R^2 = i–Pr**

5–2 Results and Discussion

5–2–1 Dimerization of Acrylates with Grignard Reagents

Methyl α–ethylacrylate **2b** was converted exclusively to a 1:2 adduct (glutarate **4b**) by successive 1,4–addition with ethylmagnesium bromide **1a** above a **1a** / **2b** molar ratio of 1.0 (Scheme 1), whereas predominantly to a cyclic 1:3 adduct (4–oxo cyclohexanedi–carboxylate **7a**) below this ratio (Figure 1).



4a : R^1 = Et ; R^2 = Me	4f : R^1 = i–Pr ; R^2 = n–Pr
4b : R^1 = Et ; R^2 = Et	4g : R^1 = i–Pr ; R^2 = i–Pr
4c : R^1 = Et ; R^2 = i–Pr	4h : R^1 = t–Bu ; R^2 = Me
4d : R^1 = i–Pr ; R^2 = Me	4i : R^1 = t–Bu ; R^2 = Et
4e : R^1 = i–Pr ; R^2 = Et	4j : R^1 = t–Bu ; R^2 = i–Pr

Scheme 1

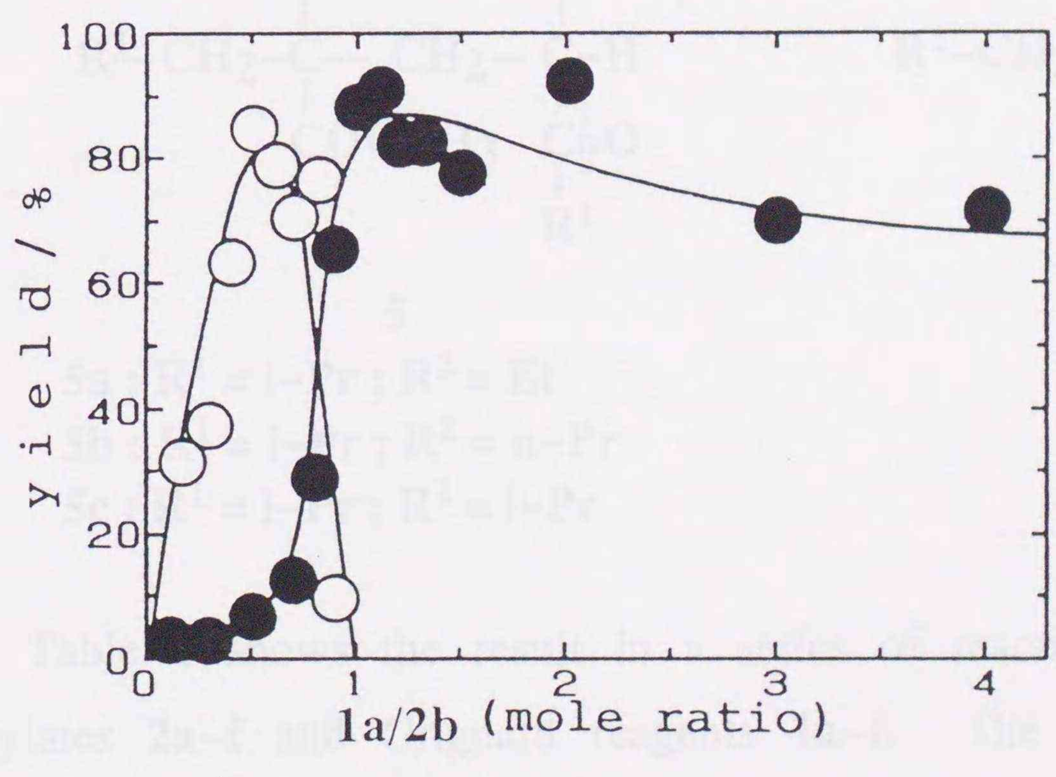
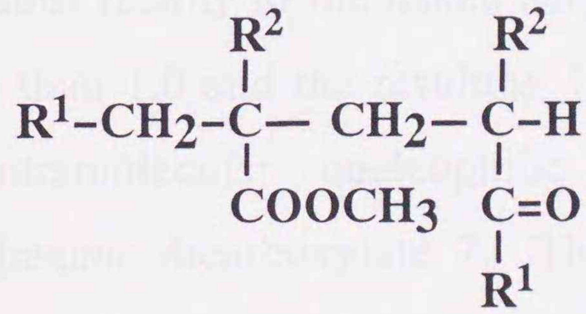


Figure 1. Formation of 2:1 and 3:1 adducts in the reaction of ester **2b** with Grignard reagent **1a** in ether at 0 ℃. (●) 2:1 adduct **4b**; (○) 3:1 adduct **7a**.

Table 1. Yields (%) of dimer **4** on the reaction of acrylates **2a–f** with Grignard reagents **1a–f**

Grignard reagent	Yield (%) Acrylate					
	2a	**2b**	**2c**	**2d**	**2e**	**2f**
1a	48	93	98	70	98	85
1b	47	92	96	68	95	85
1c	58	71	53	34	63	11
1d	35	80	88	58	92	94
1e	21	63	65	80	87	98
1f	51	98	64	32	77	16

Reaction conditions; solvent, ether; time, 1 h; temp., 0 ℃; **1**:**2** = 2:1 (molar ratio).



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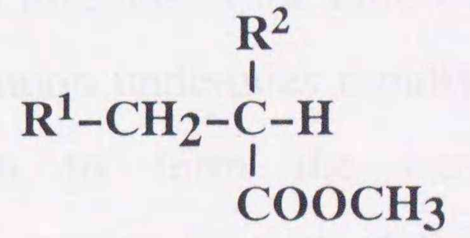

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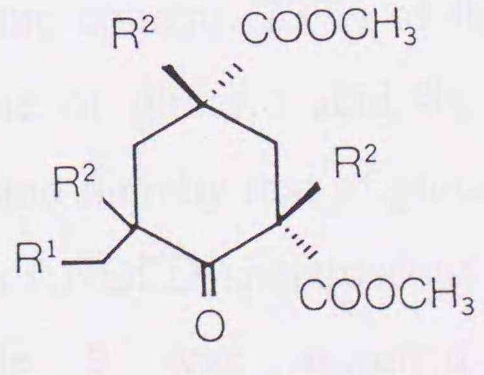
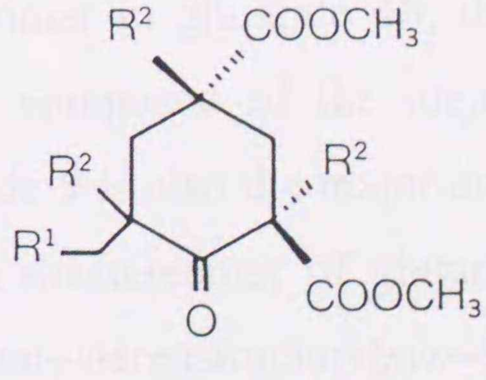
5a : R^1 = i–Pr ; R^2 = Et
5b : R^1 = i–Pr ; R^2 = n–Pr
5c : R^1 = i–Pr ; R^2 = i–Pr

Table 1 shows the result in a series of reactions between acrylates **2a–f** and Grignard reagents **1a–f**. The reactions of acrylates **2b**, **2c**, and **2e** with Grignard reagents **1a** , **1b** , and **1d** afforded the glutarates **4** in satisfactory yields. Having a tendency to form higher oligomers, acrylate **2a** methyl methacrylate gave the corresponding glutarate in low yield. Grignard reagent **1c** subsequently underwent 1,2-addition with the produced glutarates to give ketoesters **5a–c** along with unchanged glutarates. The combination of both highly hindered compounds, acrylates **2d** and **2f**, and Grignard reagents **1c** and **1f** led to form 1:1 adducts **6** rather than 1:2 adducts.

The 1:2 adduct anion **3** is a long-lived intermediate, which is well stabilized by chelation with a counter ion and presumably by the assistance of another molecule of the Grignard. The acrylate complexed with the Grignard, being less reactive than the naked one, is unable to react with the stabilized anion, and thus, after quenching with water the 1:2 adduct (glutarate **4**) was obtained exclusively at the **1** / **2** ratio of 1.0 or above. However, the stabilized anion may adds readily to the naked acrylate which presents at the ratio of lower than 1.0 and the resulting 1:3 adduct anion undergoes rapidly an intramolecular nucleophilic cyclization to form the oxo cyclohexane dicarboxylate **7**. Thereby, how excess amount of the naked acrylate might be, the oligomeric products of larger than the 1:3 adduct are unable to be formed.



cis–7

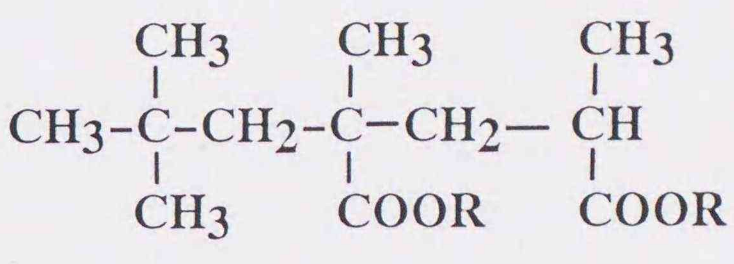


trans–7

7a : R^1 = Et ; R^2 = Et **7b : : R^1 = t–Bu ; R^2 = Et**

5-2-2 Diastereoselectivity of 1:2 Adducts

The stereochemistry of the glutarate consisting of a mixture of diastereomers , *syn* - and *anti* - isomers , is noteworthy. The configuration of the glutarates was established according to physical and ^{1}H NMR data of the glutaric acid **8a** and the anhydride **9**



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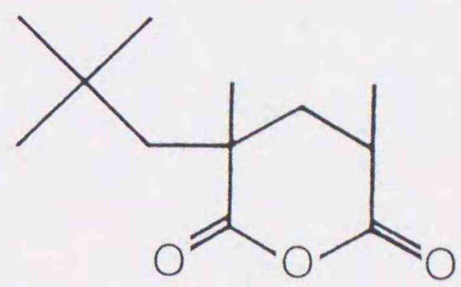
8a : R = H , **8b** : R = CH_3



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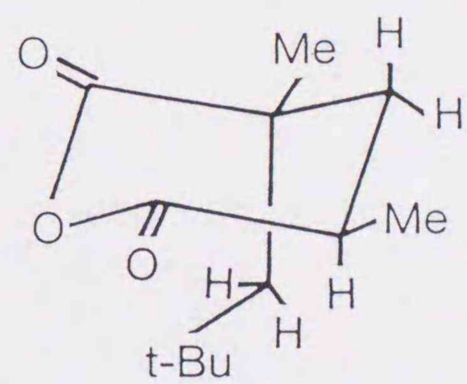
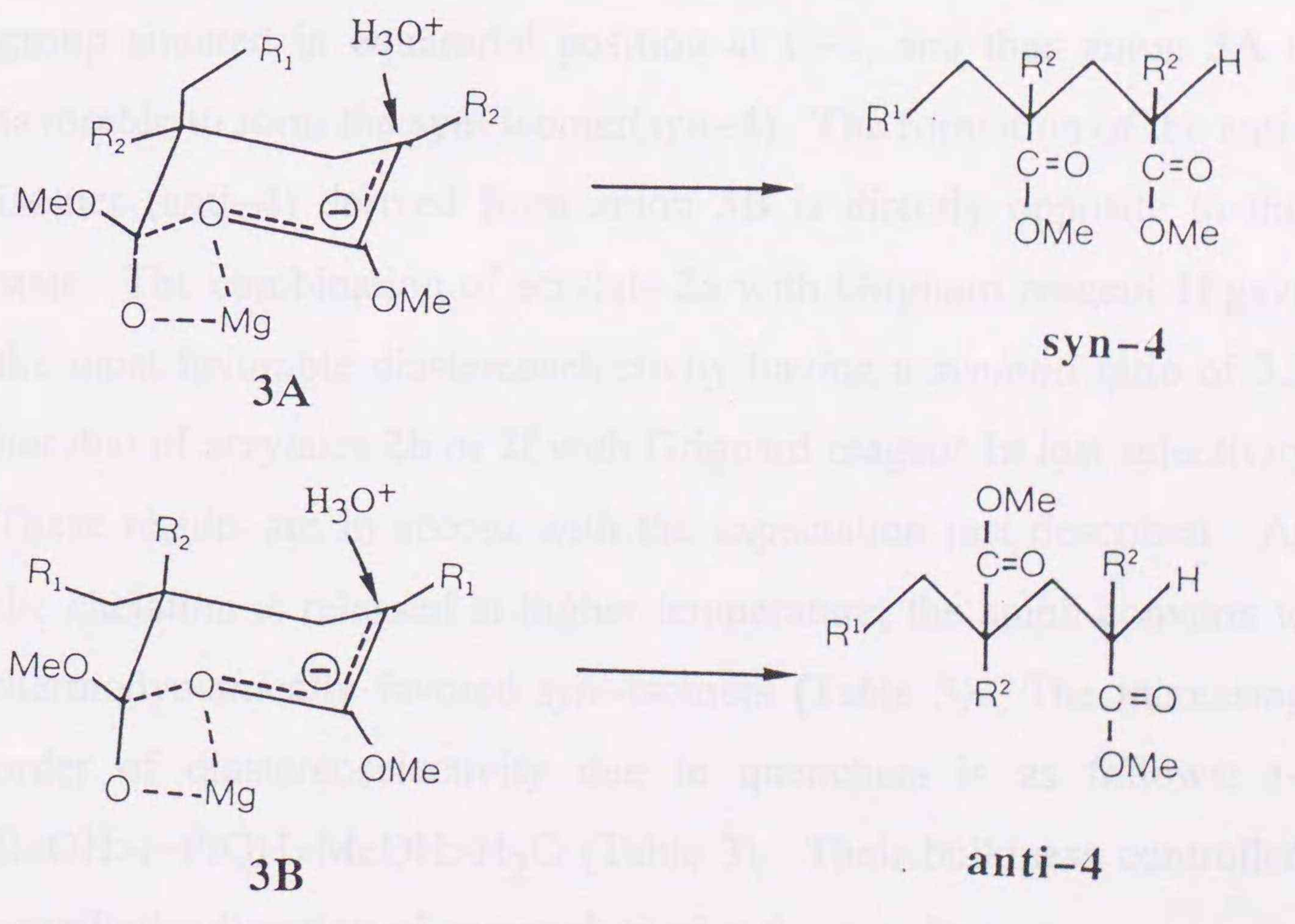


syn-**9**

derived from glutarate **4h**. Both of the acid and the anhydride were crystallized from hexane. Because the isolated yield (28%) was beyond the content (23%) of the minor isomer in glutarate **4h**, the crystalline of glutaric acid **8a** should be composed of the major isomer, and thereby that of glutaric anhydride **9** is also the major one. By use of NOED spectroscopy, the major diastereomer of glutaric anhydride **9** was assigned to a *syn*-stereostructure(*syn*-**9**). Irradiation of the axial proton at C-3 caused an enhancement of the equatorial proton at C-2 and one of methylene protons in the neopentyl group at C-1, thus revealing their *syn*-relationship. The result deduces the conclusion that the major isomer of glutarate **4h** also has a *syn*–stereostructure. On the basis of this stereochemistry, the *syn*/*anti* ratio of diastereomers, that is, the diastereoselectivity for the glutarates was determined by the ^{1}H NMR measurement in the presence of a shift reagent, $Eu(dpm)_3$. Every glutarate contains greater amounts of *syn*–isomer rather than *anti*–one (Table 2).

The diastereoselectivity appears to be controlled by the differences in bulkiness between two alkyl groups on the acrylate and the Grignard. Highly isotactic poly(metyl methacrylate) is usually formed by stereoregulating mechanism involving interactions of the incoming monomer, the chain end, and the penultimate group with the counterion[6,7]. Judging from their considerations, as shown in Scheme 2, it can be presumed that 1:2 adduct anions **3A** and **3B** are stabilized by an intramolecular chelation.



Scheme 2

Table 2. Yields (%) and diastereoselectivities of 2:1 adducts **4**[a)]

Grignard reagent	Acrylate[b)]					
	2a	**2b**	**2c**	**2d**	**2e**	**2f**
1a	48(2.2)	93(1.0)	98	70(1.0)	98	85
1b	47	92	96	68	95	85
1c	58(2.3)	71(2.4)	53	34(2.5)	63	11
1d	35	80	88	58	92	94
1e	21	63	65	80	87	98
1f	51(3.3)	98	64	32(2.0)	77	16

a) Grignard **1** /Acrylate **2** molar ratio, 2.0; temp., 0℃; solvent, ether.
b) Yield based on the acrylate is determined by GLC. Selectivity characterized by the ratio of *syn/anti* isomers is indicated in parenthesis.

Since the R^2 group is more bulky than the R^1CH_2 group, the R^2 group situated in equatorial position at C–1, and thus anion **3A** is favorable to form the syn–isomer(syn–**4**). The formation of the anti–isomer (anti–**4**) derived from anion **3B** is directly opposite to this state. The combination of acrylate **2a** with Grignard reagent **1f** gave the most favorable diastereoselectivity having a *syn/anti* ratio of 3.3, but that of acrylates **2b** or **2f** with Grignard reagent **1a** lost selectivity. These results are in accord with the expectation just described. As the chelation is released at higher temperature, the anion converts to thermodynamically favored *syn*–isomers (Table 3). The increasing order of diastereoselectivity due to quenchers is as follows: t–BuOH>i–PrOH>MeOH>H_2O (Table 3). Their bulkiness controlled exactly the direction of approach to give the *syn*–isomer.

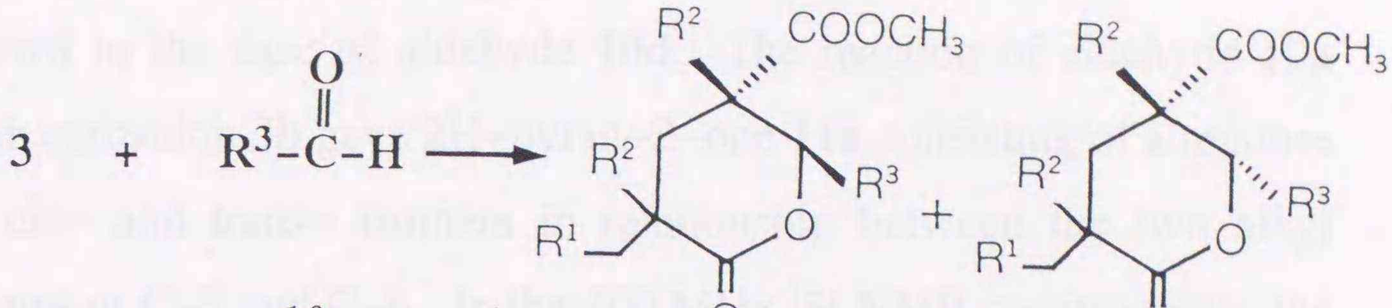
Table 3. Influence of quenchers on dimerization of **2d** with **1a**[a)]

Entry	Quencher	Solvent	Temp. ℃	Yield[b)] %	DS[c)]
1	H_2O	ether	r.t	19	3.1
2	H_2O	ether	0	46	2.4
3	H_2O	ether	−78	55	2.2
4	H_2O	THF	0	43	−
5	H_2O	toluene	0	15	2.6
6	MeOH	ether	0	−	2.6
7	i−PrOH	ether	0	−	3.2
8	t−BuOH	ether	0	−	3.6

a) **1a**/**2d** molar ratio, 2.0.
b) Yield based on the acrylate **2d** was determined by GLC.
c) Diastereoselectivity is characterized by the ratio of *syn*/*anti* isomers.

5−2−3 Reactions of Several Electrophiles with the 1:2 Adduct Anion 3

The 1:2 adduct anion **3** is still sufficiently reactive to attack electrophiles such as aldehydes, carbon dioxide, bromine, acetyl chloride, ethylene oxide, and acrylates themselves. Attack of the anions on aldehydes **10a−e** gave 2H − pyran− 2 − ones **11a−f** in satisfactory yields (Scheme 3). Results are summarized in Table 4.



10 **cis-11** **trans-11**

10a : R^3 = Et **11a** : $R^1 = R^2$ = Et ; R^3 = Et
10b : R^3 = Octyl **11b** : $R^1 = R^2$ = Et ; R^3 = Octyl
10c : $R^3 = -\!<$ **11c** : $R^1 = R^2$ = Et ; $R^3 = -\!<$
10d : R^3 = t–Bu **11d** : $R^1 = R^2$ = Et ; R^3 = t–Bu
10e : R^3 = vinyl **11e** : $R^1 = R^2$ = Et ; R^3 = vinyl
11f : R^1 = t–Bu ; R^2 = Et ; R^3 = Et

Scheme 3

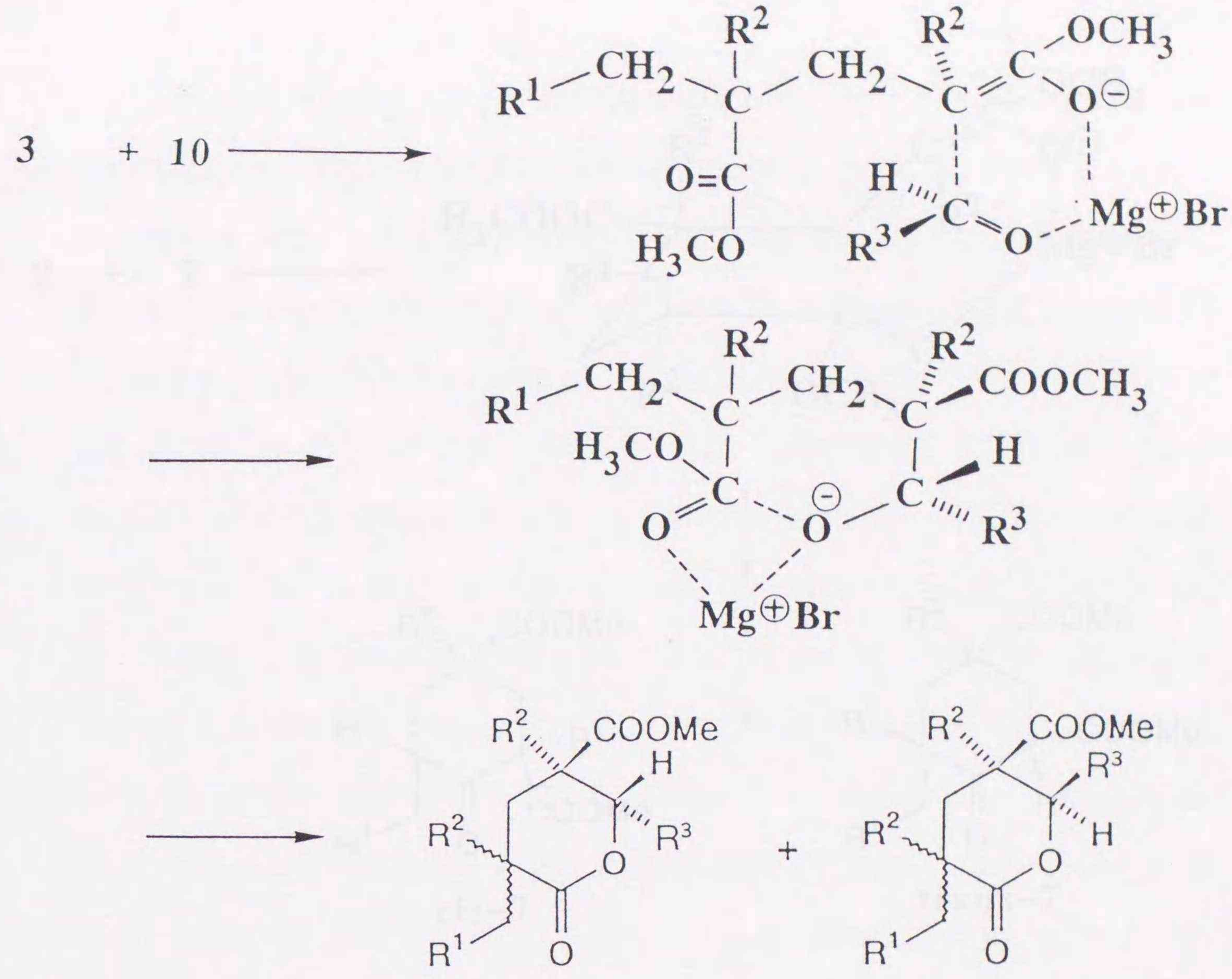
Table 4. Reaction of 2:1 adduct anions **3** with aldehydes[a)]

Anion	Aldehyde	Solvent	Temp. ℃	Product	Yield[b)] %	DS[c)]
3b	**10a**	ether	r.t.	**11a**	77	2.3
3b	**10a**	ether	0	**11a**	82	1.9
3b	**10a**	ether	–78	**11a**	80	1.4
3b	**10a**	THF	r.t	–	0	–
3b	**10a**	toluene	r.t	–	0	–
3b	**10b**	ether	r.t.	**11b**	55	2.3
3b	**10c**	ether	r.t.	**11c**	52	>10
3b	**10d**	ether	r.t.	**11d**	25	>10
3b	**10d**	ether	r.t.	**11d**	56[d)]	>10
3b	**10e**	ether	r.t	**11e**	58	1.4
3i[e)]	**10a**	ether	r.t.	**11f**	22	4.5

a) [Aldehyde]/[Adduct ion] molar ratio, 1.0. b) Isolated yield based on the acrylate. c) Diastereoselectivity (cis/trans). d) Yield was obtained after addition of 3 mole % of $SnCl_4$. e) [Aldehyde]/[Adduct ion] molar ratio, 2.0.

The addition of $SnCl_4$ caused a moderate increase in yields as shown in the case of aldehyde **10d**. The reaction of aldehyde **10a** with carbanion **3b** gave 2H–pyran–2–one **11a** consisting of a mixture of cis– and trans– isomers in relationship between the two alkyl groups at C–5 and C–6. In the 400 MHz ^{1}H NMR spectroscopy, the isolated isomers showed a distinct difference in chemical shifts of the 4– and 6–protons [the major isomer: δH 1.48 and 2.24 (4–H), and 4.16 (6–H); the minor isomer: δH 1.86 and 2.19 (4–H), and 4.56 (6–H)]. In the six–membered 2H–pyran–2–one two conformers in the cis–isomer, each of which has a proton and an ethyl group, and an ethyl and a carbomethoxy group, respectively, in the axial positions at C–6 and C–5, differ in their free energy, whereas those in the trans–one, each of which has two ethyl groups, and a proton and a carbomethoxy group, respectively, have a similar extent of free energy. On the basis of the comparisons between chemical shift and conformation, it seems reasonable to conclude that the major diastereomer has a cis–stereostructure and the minor diastereomer an anti–one. In this general way the cis/trans ratio of products was determined by the ^{1}H NMR measurement. Compounds **11c** and **11d** obtained from bulky aldehydes **10c** and **10d** were isolated as a almost single diastereomer consisting of cis–stereostructure.

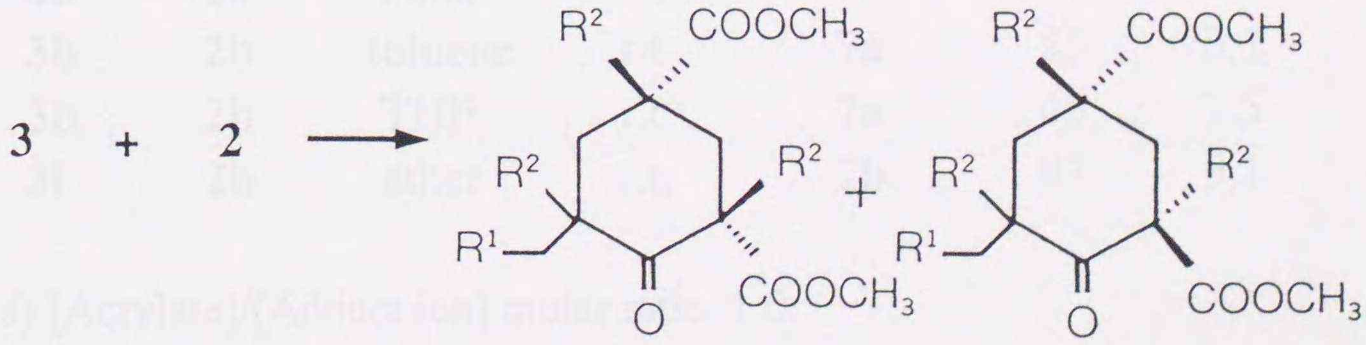
Depicted as Scheme 4, the approach of aldehyde to 1:2 adduct anion **3** occurs from the innerface of the anion through chelation of the carbonyl group with the counter ion. At this time, the sterically favorable cis–configuration is formed.



cis-11 trans-11

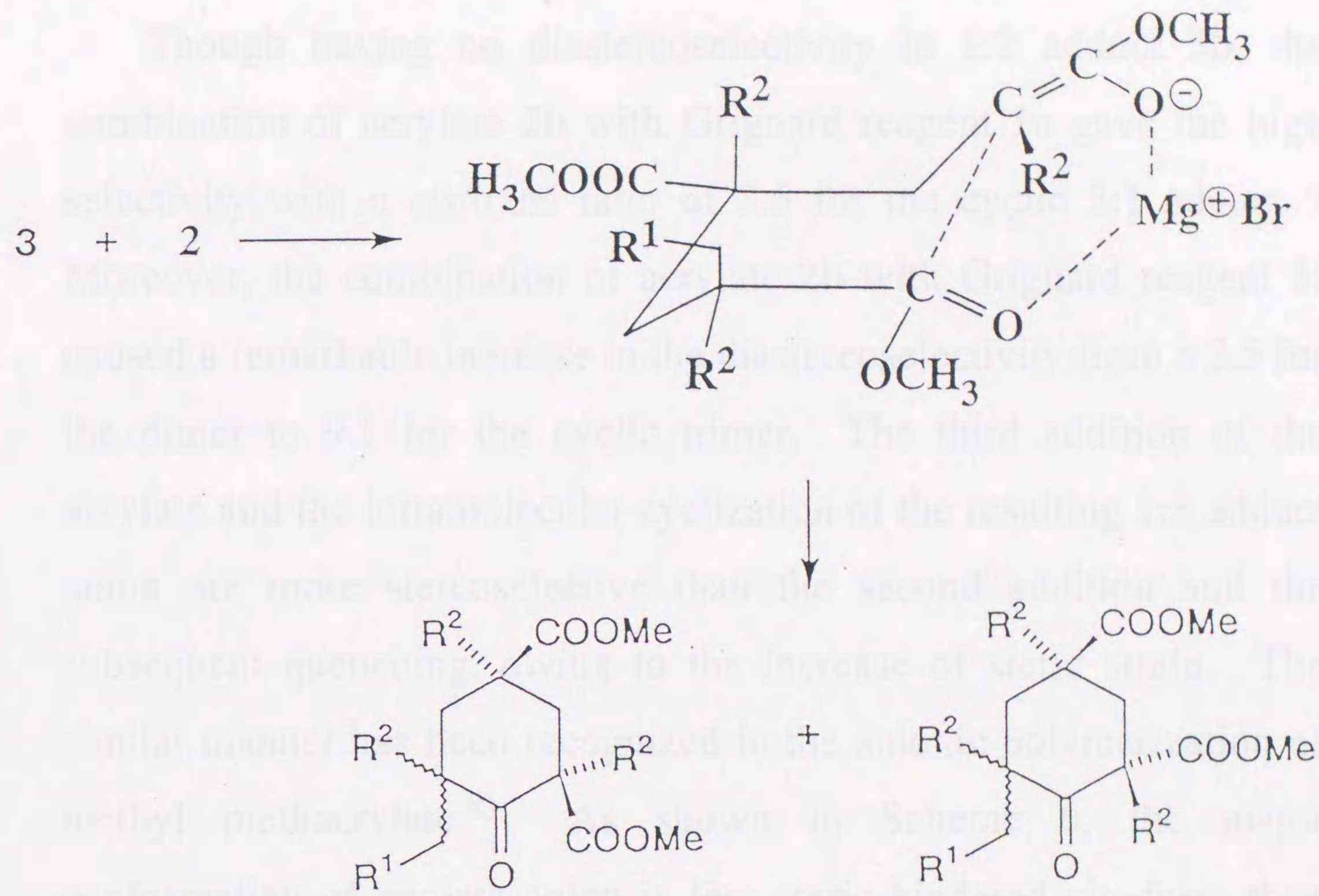
Scheme 4

The addition of another molecule of acrylate **2b** to 1:2 adduct anions **3b** and **3i** gave the cyclic 1:3 adducts **7a** and **7b** (Scheme 5) in the very same manner as the reaction at the **1/2** ratio below 1.0 (Scheme 6). Results are summarized in Table 5.



cis-7 trans-7

Scheme 5



cis-7 trans-7

Scheme 6

Table 5. Reaction of 2:1 adduct anions 3 with acrylates[a)]

Anion	Acrylate	Solvent	Temp. ℃	Product	Yield[b)] %	DS[c)]
3b	**2b**	ether	r.t.	**7a**	97	3.5
3b	**2b**	ether	0	**7a**	90	2.7
3b	**2b**	ether	−78	**7a**	67	1.4
3b	**2b**	toluene	r.t	**7a**	55	3.1
3b	**2b**	THF	r.t	**7a**	45	1.5
3i	**2b**	ether	r.t.	**7b**	93	9.1

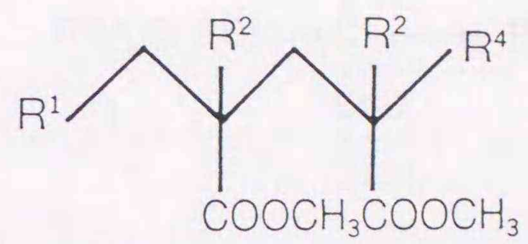
a) [Acrylate]/[Adduct ion] molar ratio, 1.0.

b) Yield was determined by GLC.

c) Diastereoselectivity (cis/trans).

Though having no diastereoselectivity in 1:2 adduct **3b**, the combination of acrylate **2b** with Grignard reagent **1a** gave the high selectivity with a *cis*/trans ratio of 3.5 for the cyclic 3:1 adduct **7**. Moreover, the combination of acrylate **2b** with Grignard reagent **1f** caused a remarkable increase in the diastereoselectivity from a 2.5 for the dimer to 9.1 for the cyclic trimer. The third addition of the acrylate and the intramolecular cyclization of the resulting 1:3 adduct anion are more stereoselective than the second addition and the subsequent quenching, owing to the increase of steric strain. The similar manner has been recognized in the anionic polymerization of methyl methacrylate.[8)] As shown in Scheme 6, the major conformation of enolate anion is less steric hindered cis–form than trans–form for the transition state. The bulkiness of R^3 affects the conformation of third unit by 1,3–diaxial interaction. In all the reactions of the 1:2 adduct anion, increasing temperature tends to increase diastereoselectivity. As the chelation is released at higher temperature, the thermodynamically stable cis–isomers is preferred. The effect of solvents need to be further investigated for having a thorough grasp of the nature.

As an electrophile, bromine and acetyl chloride showed a moderate reactivity affording **12b** and **12c** ,respectively. On the ohter hand, carbon dioxide and ethylene oxide gave the corresponding products **12a** and **13** in poor yields. Acrylonitrile also produced a



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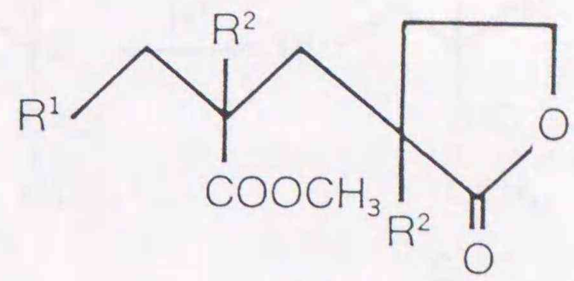

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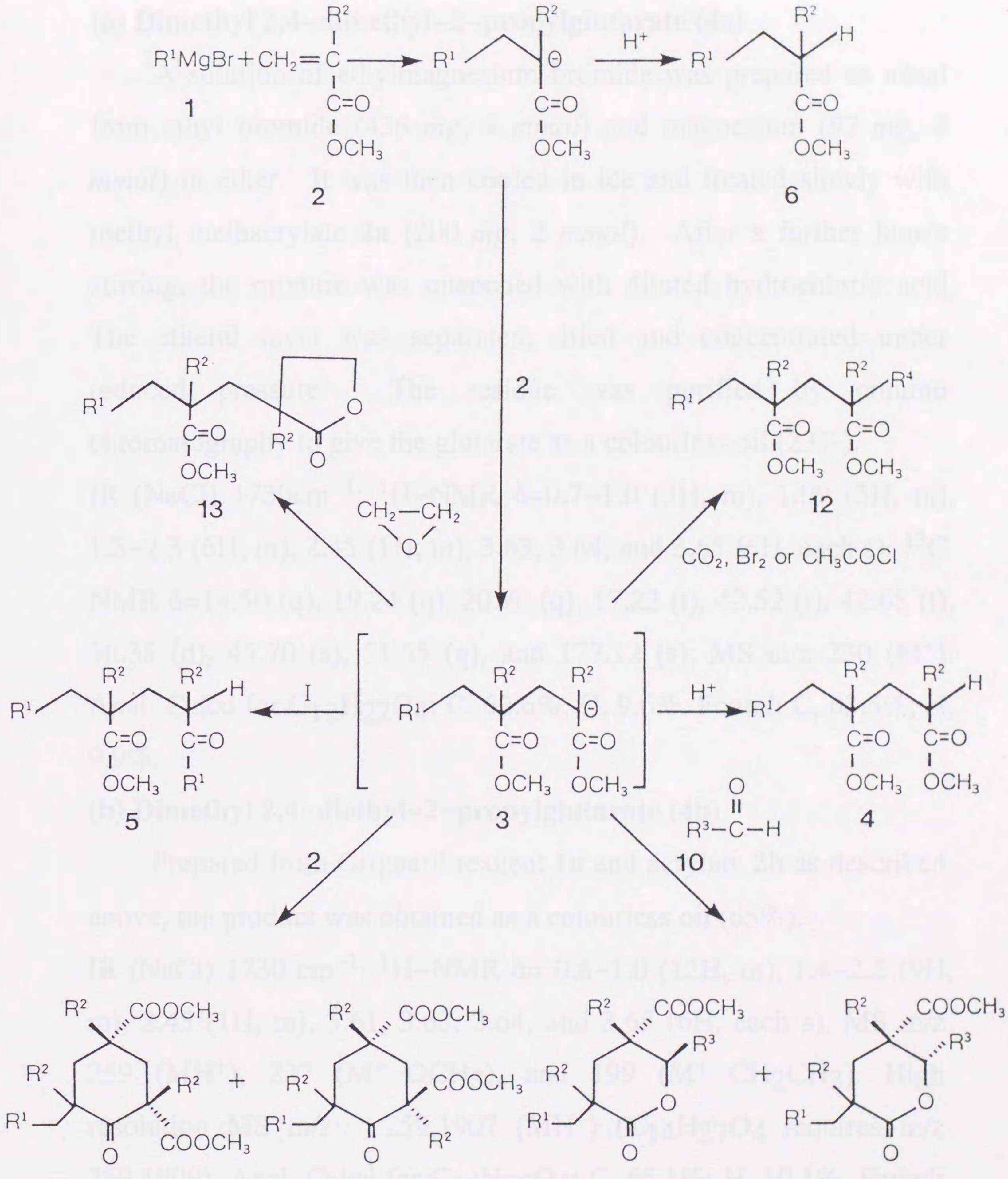
12a : R^4 = HOOC– 12b : R^4 = Br 12c : R^4 = $CH_3\overset{\overset{O}{\|}}{C}$–

Table 6. Reaction of 2:1 adduct anions **3** with electrophiles[a)]

Anion	Electrophile	Solvent	Temp. ℃	Product	Yield[b)] %
3b	CO_2	ether	r.t.	**12a**	22
3b	Br_2	ether	r.t.	**12b**	50
3b	acetyl chloride	ether	r.t.	**12c**	40
3b	ethylene oxide	ether	r.t	**13**	12

a) [Electrophile]/[Adduct ion] molar ratio, 1.0.
b) Isolated yield.

The reaction process are summerized in Scheme 7. The reaction of anionic dimer **3** with various electrophiles is a useful method for introducing another functional group to the dimer. The case using aldehydes as substrates corresponds to a variation of the Stobb condensation. The oligomerization is capable of extending three or four carbon atoms in one–pot by a mild and convenient procedure to prepare regiospecifically a variety of derivatives from the acrylates, cyclopentanones, ketoesters, etc.


R¹MgBr + CH₂=C
1
2
H⁺
6
13
12
CO₂, Br₂ or CH₃COCl
I
5
3
4
10
cis-7
trans-7
cis-11
trans-11

Scheme 7

5-3 Experimental

(a) Dimethyl 2,4-dimethyl-2-propylglutarate (4a)

A solution of ethylmagnesium bromide was prepared as usual from ethyl bromide (436 *mg*, 4 *mmol*) and magnesium (97 *mg*, 4 *mmol*) in ether. It was then cooled in ice and treated slowly with methyl methacrylate **2a** (200 *mg*, 2 *mmol*). After a further hour's stirring, the mixture was quenched with diluted hydrochloric acid. The etheral layer was separated, dried and concentrated under reduced pressure. The residue was purified by column chromatography to give the glutarate as a colourless oil (23%).

IR (NaCl) 1730cm^{-1}; ^{1}H-NMR δ=0.7–1.0 (3H, m), 1.09 (3H, m), 1.3–2.3 (6H, m), 2.45 (1H, m), 3.63, 3.64, and 3.65 (6H, each s); ^{13}C NMR δ=14.50 (q), 19.24 (q), 20.70 (q), 17.22 (t), 42.52 (t), 42.68 (t), 36.35 (d), 45.70 (s), 51.55 (q), and 177.12 (s); MS m/z 230 (M^+). Anal. Calcd for $C_{12}H_{22}O_4$: C, 62.6%; H, 9.6%. Found: C, 63.5%; H, 9.9%.

(b) Dimethyl 2,4-diethyl-2-propylglutarate (4b)

Prepared from Grignard reagent **1a** and acrylate **2b** as described above, the product was obtained as a colourless oil (65%).

IR (NaCl) 1730 cm^{-1}; ^{1}H-NMR δ= 0.6–1.0 (12H, m), 1.4–2.2 (9H, m), 2.45 (1H, m), 3.61, 3.63, 3.64, and 3.65 (6H, each s). MS m/z 259 (MH^+), 227 (M^+–OCH_3), and 199 (M^+–CH_2CH_3). High resolution MS m/z 259.1907 (MH^+) ($C_{14}H_{27}O_4$ requires m/z 259.1909). Anal. Calcd for $C_{14}H_{26}O_4$: C, 65.1%; H, 10.1%. Found: C, 64.8%; H, 10.1%.

(c) Dimethyl 2, 4-diisopropyl-2-propyl glutarate (4c)

Prepared from Grignard reagent **1a** and acrylate **2b** as described above, the product was obtained as a colourless oil (46%).

IR (NaCl) 1730 cm^{-1}; ^1H–NMR δ= 0.7–1.0 (15H, m), 1.1–2.1 (8H, m), 2.3 (1H, m), 3.57, 3.61, and 3.62 (6H, each s); MS: m/z 286 (M^+), 271 (M^+–CH_3), and 227 (M^+–CO_2CH_3). Anal. Calcd for $C_{16}H_{30}O_4$: C, 67.1%; H, 10.6%. Found: C, 67.2%; H, 10.6%.

(d) Dimethyl 2–isobutyl–2, 4, –dimethyl–glutarate (4d)

Prepared from Grignard reagent **1c** and acrylate **2a** as described above, the product was obtained as a 2.3:1 mixture of 2,4–syn and anti– isomers.

IR (NaCl) 1730 cm^{-1}; ^1H–NMR δ= (400MHz)[for the 2,4–*anti*–isomer] 0.80 (3H, d, *J* 6.3 Hz), 0.87 (3H, d, *J* 6.4 Hz), 1.15 (3H, d, *J* 7.1 Hz), 1.16 (3H, s), 1.33 (1H, dd, *J* 8.6 Hz and 3.2 Hz), 1.39 (1H, dd, *J* 14.3 Hz and 3.3 Hz), 1.64 (1H, dd and 1H, m), 2.26 (1H, dd, *J* 14.3 Hz and 9.1 Hz), 2.53 (1H, m), 3.62 and 3.64 (6H, each s); [for the 2, 4–*syn*–isomer] 0.79 (3H, d, J 6.4 Hz), 0.87 (3H, d, *J* 6.4 Hz), 1.10 (3H, s), 1.12 (3H, d, *J* 7.1 Hz), 1.34 (1H, dd, *J* 13.2 Hz and 4.2 Hz), 1.65 (1H, dd and 1H, m)1.73 (1H, dd, *J* 14.2 Hz and 3.7 Hz), 1.96 (1H, dd, *J* 14.2 Hz and 8.3 Hz), 2.45 (1H, m)3.64 and 3.66 (6H, each s). Anal. Calcd for $C_{13}H_{24}O_4$: C, 63.9%; H, 9.9%. Found: C, 63.8%; H, 9.95%.

(e) Dimethyl 2,4–diethyl–2–isobutyl glutarate (4e)

Prepared from Grignard reagent **1c** and acrylate **2a**, the product was obtained as a colourless oil (46 %).

IR (NaCl) 1730 cm^{-1}; ^1H–NMR δ= 0.6–1.0 (12H, m), 1.4–2.2 (9H, m), 2.45 (1H, m), 3.61, 3.63, 3.64, and 3.65 (6H, each s). MS m/z

273 (MH^+), 257 (M^+–CH_3), 241 (M^+–OCH_3), 213 (M^+–CO_2CH_3), and 153 (M^+–2 CO_2CH_3). High resolution MS m/z 273.2113 (MH^+) ($C_{15}H_{29}O_4$ reqires m/z 273.2006). Anal. Calcd for $C_{15}H_{28}O_4$:C, 66.1%; H, 10.4%. Found: C, 65.0%; H, 10.3%.

(f) Dimethyl 2–isobutyl–2,4–dipropyl glutarate (4f)

Prepared from Grignard reagent **1c** and acrylate **2c** as described above, the product was obtained as a colourless oil.

IR (NaCl) 1730 cm^{-1}; ^1H–NMR: δ=0.7–1.1 (12H, m), 1.1–1.8 (11H, m), 1.9–2.2 (2H, m), 2.25 (1H, m), and 3.62 (6H, s). Anal. Calcd for $C_{17}H_{32}O_4$: C, 68.0%; H, 10.7%. Found: C, 67.9; H, 10.95%.

(g)Dimethyl 2–isobutyl–2,4–diisopropyl glutarate (4g)

Prepared from Grignard reagent **1c** and acrylate **2d** as described above, the product was obtained as a colourless oil.

IR (NaCl) 1730 cm^{-1}; ^1H–NMR δ=0.7–1.1 (18H, m), 1.1–1.8 (11H, m), 1.1–2.2 (7H, m), 2.3 (1H, m), 3.58, 3.60, 3.63, and 3.64 (6H, each s). Anal. Calcd for $C_{17}H_{32}O_4$: C, 68.0%; H, 10.7%. Found: C, 68.1%; H, 10.8%.

(h) Dimethyl 2,4–dimethyl–2–neopentyl glutarate (4h)

Prepared from Grignard reagent **1f** and acrylate **2a** as described above, the product was obtained as a colourless oil (33%).

IR (NaCl) 1730 cm^{-1}; ^1H–NMR δ= 0.92 (9H, s), 1.0–1.3 (6H, s and d), 1.4–2.2 (4H, m), 2.45 (1H, m), and 3.67 (6H, s). Anal. Calcd for $C_{14}H_{26}O_4$: C, 65.1%; H, 10.1%. Found: C, 65.6%; H, 10.4%.

(i) Dimethyl 2,4–diethyl–2–neopentyl glutarate (4i)

Prepared from Grignard reagent **1f** and acrylate **2b**, the product was obtained as a colourless oil (70%).

IR (NaCl) 1730cm^{-1}; ^{1}H–NMR δ= 0.89 (15H, m), 1.1–2.2 (8H, m), 2.45 (1H, m), 3.63, 3.67, and 3.68 (6H, each s). Anal. Calcd for $C_{16}H_{30}O_4$: C, 67.1%; H, 10.6%. Found: C, 67.8%; H, 10.6%.

(j) Dimethyl 2,4–diisopropyl–2–neopentyl glutarate (4j)

Prepared from Grignard reagent **1d** and acrylate **2d** as described above, the product was obtained as a colourless oil.

IR (NaCl) 1730 cm^{-1}; ^{1}H–NMR δ= 0.89 (6H, d, *J* 6.9 Hz), 0.92 (3H, d, *J* 7.0 Hz), 0.93 (9H, s), 0.96 (3H, d, *J* 6.9 Hz), 1.52 (1H, d, *J* 14.7 Hz), 1.78 (1H, dd, *J* 15.0 and 1.6 Hz), 1.90 (1H, m), 2.14 (1H, dd, *J* 14.8 and 8.8 Hz), 2.16 (1H, m), 2.67 (1H, ddd, *J* 1.7 ,8.8, and 14.2 Hz), 3.60, and 3.65 (6H, each s). Anal. Calcd for $C_{18}H_{34}O_4$: C, 68.75%; H, 10.9%. Found: C, 68.8%; H, 11.0.

(k) Methyl 2,4–diisopropyl–5–oxo–2–propylheptanoate (5a)

Produced by the reaction of acrylate **2d** with Grignard reagent **1a**, a 4.9:1 mixture of glutarate **4c** and ketoester **5a** was separated to each component by TLC. The ketoester was obtained as a colourless oil.

IR (NaCl) 1710 and 1720 cm^{-1}; ^{1}H–NMR δ= 0.7–1.1 (18H, m), 1.1–2.2 (14H, m), 2.80 (1H, m), and 3.72 (3H, s). MS m/z 284 (M^+) and 253 (M^+–OCH_3).

(l) Methyl 2, 4–diethyl–2–isobutyl–6–methyl–5–oxoheptanoate (5b)

Produced by the reaction of acrylate **2b** with Grignard reagent **1c**, a 1.3:1 mixture of glutarate **4e** and ketoester **5b** was separated to each component by TLC. The ketoester was obtained as a colourless oil.

IR (NaCl) 1710 and 1730 cm^{-1}; ^1H–NMR δ= 0.6–1.1 (18H, m), 1.1–2.2 (10H, m), 2.70 (1H, m), and 3.70 (3H, s). MS m/z 284 (M^+), 269 (M^+–CH_3), 253 (M^+–OCH_3), and 241 (M^+–CH $(CH_3)_2$).

(m) Methyl 2– isobutyl–6–methyl–2 , 4–dipropyl–5–oxoheptanoate (5c)

Produced by the reaction of acrylate **2c** with Grignard reagent **1c**, a 1.7:1 mixture of glutarate **4f** and ketoester **5c** was separated to each component by TLC. The ketoester was obtained as a colourless oil.

IR 1710 and 1730 cm^{-1}; ^1H–NMR δ= 0.7–1.1 (18H, m), 1.1–2.1 (14H, m), 2.75 (1H, m), and 3.68 (3H, s). MS m/z 312 (M^+)and 297 (M^+–CH_3).

(n) Tetrahydro–3 , 5 , 6–triethyl– 5–methoxycarbonyl–3–propyl–2H–pyran–2–one (8a)

A solution of 1:2 adduct anion **3b** prepared from Grignard reagent **1a** (4 *mmol*) and acrylate **2b** (2 *mmol*) was treated slowly with aldehyde **10a** (2 *mmol*). After the reaction for 1h at 0℃ the mixture was quenched with diluted hydrochloric acid. By removal of the solvent from the etheral solution, the product was obtained as a 2.3:1 mixture of 5, 6–*syn*– and *anti*– dialkyl isomers of 2H–pyran–2–one **11a**, which was separated to each isomer by TLC. IR (NaCl)

1730cm^{-1}; ^{1}H-NMR δ= (400MHz)[5, 6-*syn* diethyl isomer] 0.86–0.97 (9H, m), 1.05 (3H, t, *J* 7.3 Hz), 1.48 (1H, d, *J* 14.4Hz), 1.55–2.05 (10H, m), 2.24 (1H, d, *J* 14.4Hz), 3.69 and 3.73 (3H, each s), and 4.16 (1H, m); [5, 6-*anti* diethyl isomer] 0.84–1.00 (12H, m), 1.24–1.82 (10H, m), 1.86 (1H, d, *J* 14.7Hz), 2.19 (1H, d, *J* 14.7Hz), 3.74 and 3.75 (3H, each s), and 4.56 (1H, m). MS m/z 280 (M^+). Anal. Calcd for $C_{16}H_{28}O_4$: C, 67.6%; H, 9.9%. Found: C, 67.7%; H, 10.3%.

(o) Tetrahydro-3, 5-diethyl-5-methoxycarbonyl-6-octyl-3-propyl-2H-pyran-2-one (11b)

Prepared from 1:2 adduct anion **3b** and aldehyde **10b** as described above, the product was obtained as a 3.2:1 mixture of 5,6-*syn*- and *anti*- dialkyl isomers of 2H-pyran-2-one **11b.**
IR (NaCl) 1730cm^{-1}; ^{1}H-NMR δ= 0.8–1.1 (12H, m), 1.1–2.4 (24H, m), 3.70, 3.73 (3H, each s), and 4.25 and 4.65 (1H, each m). Anal. Calcd for $C_{23}H_{40}O_4$: C, 71.3%; H, 11.4%. Found: C, 71.8%; H, 11.5%.

(p) Tetrahydro - 3 , 5 - diethyl - 6 - (1 - ethylpropyl) - 5 - methoxycarbonyl-3-propyl-2H-pyran-2-one (11c)

Prepared from 1:2 aduct anion **3b** and the aldehyde **10c** as described above, the 5, 6-*syn* dialkyl isomer of 2H-pyran-2-one **11c** was almost exclusively obtained as a colourless oil.
IR (NaCl) 1730cm^{-1}; ^{1}H-NMR δ= 0.7–1.1 (15H, m), 1.1–2.3 (15H, m), 3.68 (3H, s), and 4.30 (1H, d). Anal. Calcd for $C_{19}H_{34}O_4$: C, 69.9%; H, 10.5%. Found: C, 67.7%; H, 10.4%. ;;

(q) **Tetrahydro-6-tert-butyl-3 , 5-diethyl-5-methoxycarbonyl-3-propyl-2H-pyran-2-one (11d)**

Prepared from the 1:2 adduct anion **3b** and the aldehyde **10d** as described above, the 5, 6-*syn*- dialkyl isomer of 2H-pyran-2-one **11d** was almost exclusively obtained as a colourless oil. IR (NaCl) 1730cm^{-1}; ^{1}H-NMR δ= 0.70-1.0 (9H, m), 1.05 (9H, s), 1.2-2.5 (8H, m), 3.64 (3H, s), and 4.00 (1H, d).

(r) **Tetrahydro-3, 5-diethyl-5-methoxycarbonyl-3-propyl-6-vinyl-2H-pyran-2-one (11e)**

Prepared from 1:2 adduct anoin **3b** and the aldehyde **10e** as described above, the product was obtained as a 1.4:1 mixture of 5, 6-*syn* and *anti*-dialkyl isomers of 2H-pyran-2-one **11e**.
IR (NaCl) 1730cm^{-1}; ^{1}H-NMR δ= 0.7-1.1 (9H, m), 1.1-2.4 (8H, m), 3.72 and 3.77 (3H, each s), 4.68 (1H, d , *J* 8Hz), 5.3-5.5 (2H, m), and 5.7-6.2 (1H, m). MS m/z 282 (M^+). Anal. Calcd for $C_{16}H_{26}O_4$: C, 68.1%; H, 9.3%. Found: C, 64.5%; H, 9.9%.);

(s) **Dimethyl 1 , 3 , 5-triethyl-4-oxo-5-propyl-1 , 3-cyclohexane-dicarboxylate (7a)**

A solution of 1:2 adduct anion **3b** prepared from Grignard reagent **1a** (2 *mmol*) and acrylate **2b** (2 *mmol*) was treated further with acrylate **2b** (2 *mmol*) at 0℃. After 1h, the mixture was quenched with diluted hydrochloric acid. By removal of the solvent from the etheral solution, the product was obtained as a 3.5:1 mixture of 1, 3-*syn* and *anti*- dialkyl isomers of 1, 3-cyclohexanedicarboxylate **7a** which was separated to each component by TLC.

1,3-*syn*-diethyl isomer] IR (NaCl) 1710 and 1730cm^{-1}; ^{1}H-NMR δ = 0.7-1.0 (12H, m), 1.2-2.1 (12H, m), 2.38 (1H, d, *J* 16Hz), 3.00 (1H, d, *J* 16Hz), 3.60 (3H, s), and 3.70 (3H, s); [1, 3-anti- diethyl isomer]0.6-1.1 (12H, m), 1.1-2.3 (12H, m), 2.42 (2H, s), 3.65 (6H, s). MS m/z 340 (M^+), 309 (M^+-OCH_3), and 281 (M^+-CO_2CH_3). Anal. Calcd for $C_{16}H_{32}O_5$: C, 67.0%; H, 9.5%. Found: C, 66.7%; H, 9.65%.

(t) Trimethyl 1, 3-diethyl-1, 1, 3-hexanetricarboxylate (12b)

To a solution of 1:2 adduct anion **3b** (2 *mmol*) was added dry ice (2 *mmol*) at 0℃. The mixture was stirred for 1h, and the etheral solution was separated and then treated with diazomethane. The solvent was evaporated, and the residue was subjected to column chromatography to give the title compound **12b** (22%).

IR (NaCl) 1730 cm^{-1}; ^{1}H-NMR δ= 0.6-1.0 (9H, m), 2.32 (2H, s), 3.60 (3H, s), and 3.68 (6H, s). MS m/z 316 (M^+). Anal. Calcd for $C_{16}H_{28}O_6$: C, 60.7%; H, 8.9%. Found: C, 60.8%, H, 8.9%.

(u) Dimethyl 2-bromo-2, 4-diethyl-4-propylglutarate (12c)

To a solution of 1:2 adduct anion **3b** (2 *mmol*) was slowly added an etheral solution of bromine (2 *mmol*) at 0℃. The mixture was stirred for 1h and the etheral solution was separated. The solvent was evaporated off, and the residue was subjected to column chromatography to give the title compounmd **12c** (50%).

IR (NaCl) 1730cm^{-1}; ^{1}H-NMR δ= 0.6-1.1 (9H, m), 1.1-2.4 (8H, m), 2.49 (1H, s), 2.51 (1H, s), 3.57 (3H, s), and 3.67 (3H, s). MS m/z

336 (M^+) and 338 ($[M+2]^+$). Anal. Calcd for $C_{14}H_{25}O_4Br$: C, 49.9%; H, 7.5%; Br, 23.7%. Found: C, 51.5%; H, 7.85%; Br, 20.6%.

(v) Dimethyl 2-acetyl-2, 4-diethyl-4-propylglutarate (12d)

A solution of 1:2 adduct anion **3b** (2 *mmol*) was treated with an etheral solution of acetyl chloride (2 *mmol*) as described above. The etheral solution was separated and the solvent was evaporated off. The residure was subjected to column chromatography to give the title compounmd **12d** (40%).

IR (NaCl) 1710 and 1730cm^{-1}; ^{1}H-NMR δ= 0.5–1.0 (9H, m), 1.0–2.0 (1H, s), 2.16 (1H, s), 2.17 (1H, s), 3.54 (3H, s) and 3.62 (3H, s). MS m/z 300 (M^+). Anal. Calcd for $C_{16}H_{28}O_5$: C, 63.95%; H, 9.4%. Found: C, 63.5%; H, 9.6%.

(w) 3-Ethyl-3- (2-ethyl-2-methoxycarbonyl) pentyl-4-butanolide (13)

A solution of 1:2 adduct anion **3b** (2 *mmol*) was treated with an etheral solution of ethylene oxide (2 *mmol*) was separated and the solvent was evaporated. The residue was subjected to column chromatography to give the title compound **13** (12%).

IR 1725 and 1765cm^{-1}; ^{1}H-NMR δ= 0.6–1.1 (9H, m), 1.1–2.3 (12H, m), 3.66 (3H, s), and 4.1–4.3 (2H, m). MS m/z 276 (M^+). Anal. Calcd for $C_{15}H_{26}O_4$: C, 66.6%; H, 9.7%. Found: C, 65.5%; H, 9.8%.

(x) 2, 6-dimethyl-2-neopentylglutaric anhydride (9)

Glutaric acid **8a** (0.35 g, 1.52 *mmol*) was heated with acetic anhydride (10 *ml*) under reflux for 5h. After evaporation, recrystallization of remainder from hexane gave the glutaric anhydride **9** (68%) as a white crystalline solid, m.p. 96–98℃. IR (KBr) 1790 and 1750 cm^{-1}; ^1H–NMR δ= (400 MHz) 1.01 (9H, s, $(CH_3)_3C$, 1.37 (3H, d, *J* 7Hz, CH_3–3), 1.45 (3H, s, CH_3–1), 1.49 (1H, d, *J* 15Hz, CH_2–1), 1.55 (1H, dd, *J* 12 and 14Hz, 2a–H), 1.74 (1H, d, *J* 15 Hz, CH_2–1), 1.99 (1H, dd, *J* 7, 14, 2e–H), and 2.97 (1H, dq, *J* 7 and 12 Hz, 3–H). Anal. Calcd for $C_{12}H_{20}O_3$: C, 67.9%, H, 9.5%. Found: C, 67.95%; H, 9.6%.

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Chapter 6

SUMMARY AND CONCLUSIONS

The followings were clarified by this study.

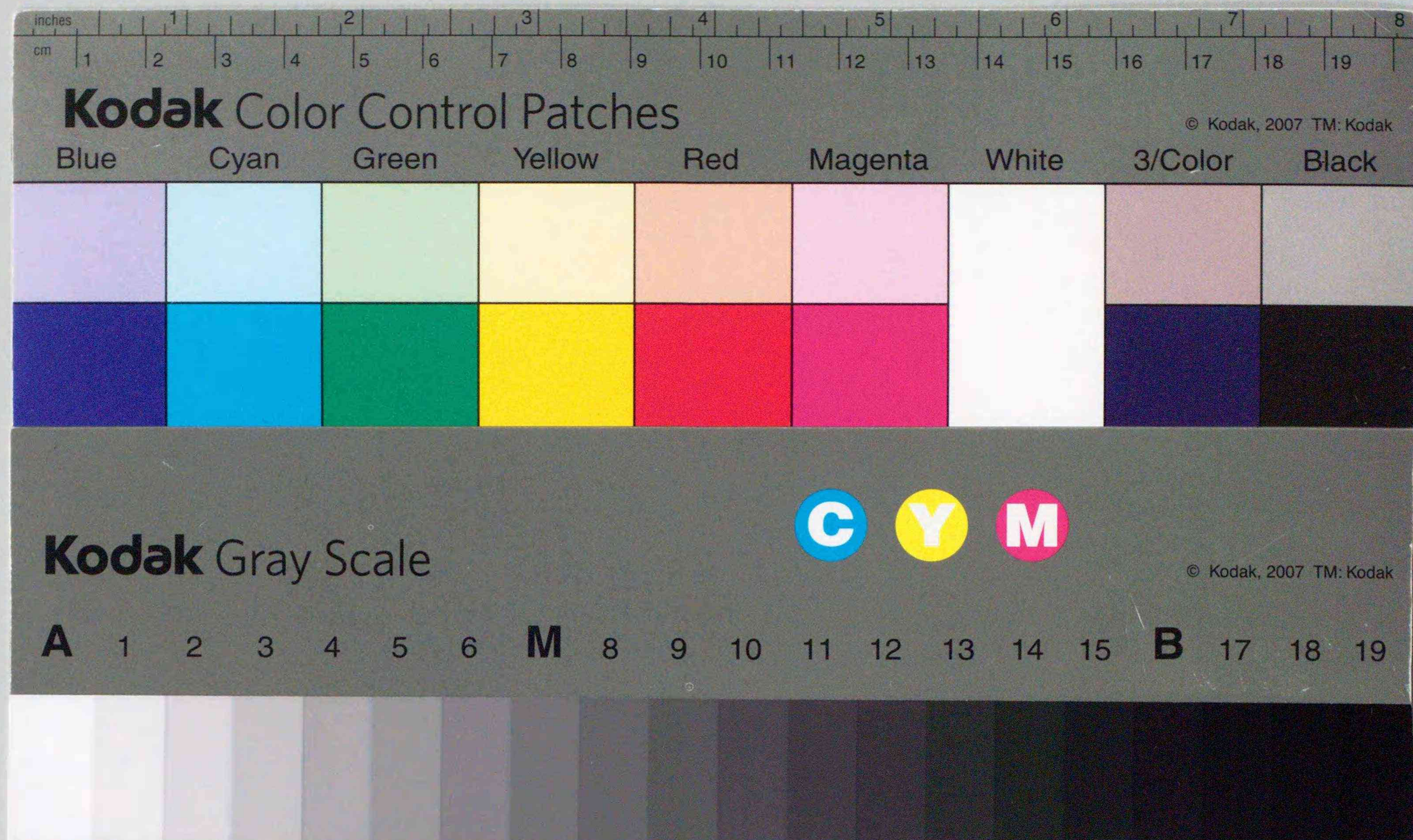
Radical oligomerization of methyl methacrylate in the presence of ethylaluminum compound was initiated with ethyl radical and the resulting oligomer had a cyclic structure in the terminal end. Trimer consisting of the bicyclic lactone structure was produced selectively in the range of high Al/monomer molar ratio. Ethylaluminum compounds acted as initiator and terminator.

The reaction of allyl methacrylate with ethylaluminum compounds caused the addition of ethyl radical to β–carbon of methacrylate at the first step, and followed by Claisen type rearrangement of allyl group at a relatively low temperature, producing γ,δ–unsaturated acids. In case of using ethylaluminum dichloride, Friedel–Crafts type alkylation of toluene (as solvent) with methacrylate took place readily.

The reaction of dimethyl methylenesuccinate gave one of cyclopentanone derivatives. Chemoselectively was depending on the Lewes acidity and alkylating ability of ethylaluminums. The reaction of γ–ketoester with trialkylaluminum produced the 4–butanolide derivatives. Unlike Grignard reagents, trialkylaluminum reacted with esters to produce *sec*–alcohols excludingly.

A stable dimeric anion was formed in the reaction of α–substituted acrylates with Grignard reagent, which has an ability to react with various electrophiles such as such as aldehyde, carbon dioxide, bromine, acetyl chloride, ethylene oxide, and acrylate itself *in situ,* affording γ–lactone, triester, α–bromoester, γ– ketoester, δ–lactone, and cyclohexanone derivatives, respectively. The intermediate anions were stabilized by cordination with aluminum compounds or the Grignard reagents through the carbonyl group.

The reaction conditions are comparatively mild and the acrylates were selectively converted into desired compounds. Consequently, present study demonstrated that the oligomerization of acrylates with organoaluminums and organomagnesium compounds are very useful for organic synthesis.



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