

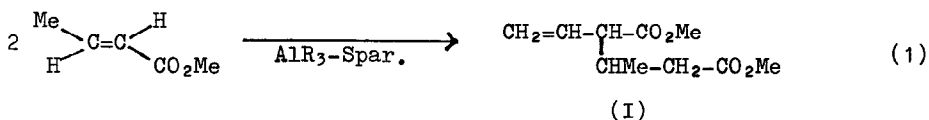
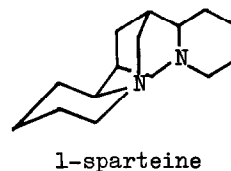
A SELECTIVE DIMERIZATION REACTION OF METHYL CROTONATE
BY ALUMINUM ALKYL-SPARTEINE COMPLEX*

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We have previously reported that the complex of aluminum alkyl with Lewis base, such as α, α' -dipyridyl or triphenylphosphine, polymerizes acrylonitrile and methyl methacrylate, which are not polymerized anionically by aluminum alkyl alone.¹⁾

Here we report a new type of isomerized dimerization of methyl crotonate, as shown in Eq. (1), in the presence of an equimolar or a catalytic amount of the aluminum alkyl-sparteine complex.

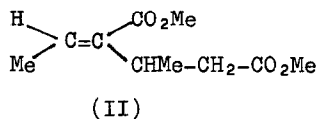


Methyl crotonate was added to a mixture of aluminum alkyl and sparteine solutions. After a given time the mixture was poured into water containing a small amount of hydrochloric acid. The ether extract of the reaction product was distilled, giving at 90-110°C/10 mmHg dimers of methyl crotonate, i.e. dimer (I) and, if any, (II) and (III).

The isolated dimers (I) and (II) were identified to be dimethyl 2-methylpent-4-ene-1,3-dicarboxylate and dimethyl 2-methylpent-cis-3-ene-1,3-dicarboxylate, respectively, by NMR, IR, mass spectrum and elementary analysis. Although

* This is Part II in the series "Organometallic Compound with Lewis Base". Part I, see ref. 1).

several attempts to isolate (III) by g.l.c. were unsuccessful, from the NMR spectrum it is indicated that (III) is not a trans-isomer of (II) but might be a diastereomer of (I).



Dimer (I): NMR (in CCl_4); τ 4.05-4.47 (m, 1H, $\text{CH}_2=\text{CH}-$), τ 4.79-5.07 (m, 2H, $\text{CH}_2=\text{CH}-$), τ 6.38 (s, 3H, CO_2CH_3), τ 6.42 (s, 3H, CO_2CH_3), τ 6.99-7.35 (m, 1H, $\text{CH}_2=\text{CH}-\overset{|}{\text{C}}-$), τ 7.47-8.19 (m, 3H, $-\overset{|}{\text{C}}(\text{CH}_3)-\text{CH}_2-$), τ 9.11 (d, 3H, $\text{CH}_3-\overset{|}{\text{C}}-$). Principal IR bands (cm^{-1}) (liquid film); 1745 vs ($\nu_{\text{C}=\text{O}}$), 1645 w ($\nu_{\text{C}=\text{C}}$), 930 ($\delta_{\text{C-H}}$ of $-\text{CH}=\text{CH}_2$). Molecular weight by mass spectrometry; 197 (calcd. 200). Anal. Calcd. for (I): C, 60.0; H, 8.0. Found: C, 59.7; H, 8.0.

Dimer (II)*: NMR (in CCl_4); τ 3.30 (q, 1H, $\text{H}-\overset{|}{\text{C}}=\text{C}$), τ 6.34 (s, 3H, $\text{C}=\text{C}-\text{CO}_2\text{CH}_3$), τ 6.42 (s, 3H, $-\text{CH}_2\text{CO}_2\text{CH}_3$), τ 6.59-6.95 (m, 1H, $\text{CH}_3-\overset{|}{\text{C}}-$), τ 7.19-7.67 (m (ABX type), 2H, $-\text{CH}_2-\text{CO}_2\text{CH}_3$), τ 8.14 (d, 3H, $\text{CH}_3-\text{C}=\text{C}$), τ 8.83 (d, 3H, $\text{CH}_3-\overset{|}{\text{C}}-$). Principal IR bands (cm^{-1}) (liquid film); 1745, 1720 vs ($\nu_{\text{C}=\text{O}}$), 1645 w ($\nu_{\text{C}=\text{C}}$). Molecular weight by mass spectrometry; 200 (calcd. 200). Anal. Calcd. for (II): C, 60.0; H, 8.0. Found: C, 59.9; H, 8.1.

Results of the reaction of methyl crotonate with AlR_3 -sparteine complex are shown in Table 1. In the equimolar reaction of methyl crotonate with the AlR_3 -sparteine complex, (I) and (II) as well as a small amount of (III) were produced when R was an isobutyl group. On the other hand, the reaction was shown to be exclusively selective when R was an ethyl or methyl group, and (I) was the sole reaction product. When excess methyl crotonate was added, the dimerization reaction proceeded catalytically. It is notable in this case that only (I) was produced regardless of the structure of the R group.

As shown in Table 2, the thus obtained dimer of methyl crotonate showed optical activity. This asymmetric synthesis is direct evidence that dimerization reaction occurred on the AlR_3 -sparteine complex under the influence of the chiral ligand sparteine.

* These NMR data of (II) agree with those reported for the cis isomer in the cis-trans mixture.²⁾

Table 1 Dimerization of Methyl Crotonate by AlR_3 -Sparteine Complex^{a)}

No.	R	AlR_3 -Spar. (mmol)	MCr ^{b)} (mmol)	Solvent ^{c)} (ml)	Temp. (°C)	Time (hr)	Yield ^{d)} (%)	Comp. of Product (%) ^{e)}		
								I	II	III ^{f)}
1	Me	33	33	Pent. 40	30	15	ca. 15	100	trace	0
2	Et	33	33	Bz. 40	30	15	ca. 15	100	trace	0
3	iBu	33	33	Pent. 40	30	20	ca. 20	11	73	16
4	iBu	33	33	Bz. 40	30	15	ca. 15	54	34	12
5	Me	33	330	Bz. 55	50	1	129	100	trace	0
6	Et	33	330	Bz. 55	50	1	195	100	trace	0
7	Et	33	330	Bz. 55	30	4	274	100	trace	0
8	iBu	33	330	Bz. 55	50	1	176	100	trace	0

a) Spar./ AlR_3 =1 b) MCr: Methyl crotonate

c) Bz.: Benzene, Pent.: n-Pentane

d) Yield of dimer vs. AlR_3 -Spar. complex

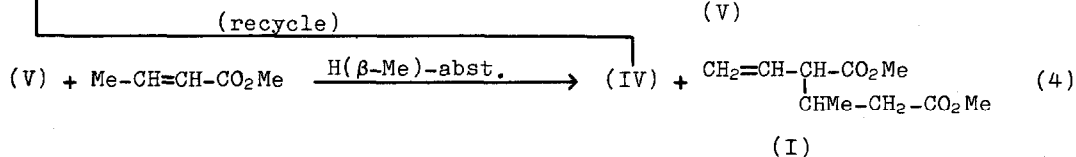
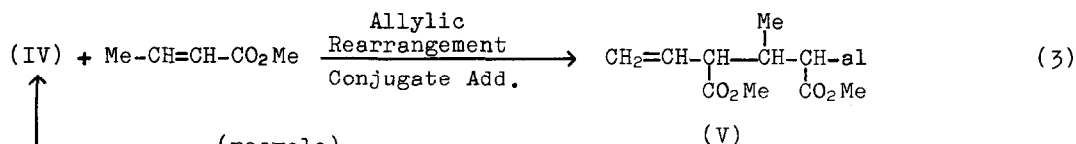
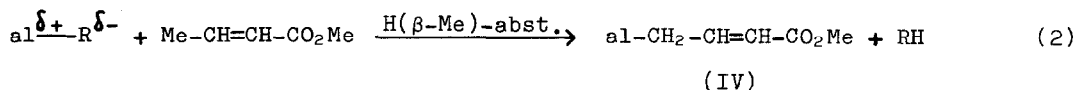
e) Composition was determined by g.l.c.

f) Unidentified, but not the trans isomer of (II)Table 2 Specific Rotation of Dimers of Methyl Crotonate
Obtained by AlR_3 -Sparteine Complex

Dimer (No. ^{a)})	C (g/dl) ^{b)}	$[\alpha]_D^{r.t.}$
I (1)	2.158	+ 1.30
I (2)	1.005	+ 1.15
II (3)	0.745	+ 3.49
I (7)	1.629	+ 0.68
cf. Sparteine	0.780	- 5.13

a) See Table 1. b) Solvent: benzene

From these results, the most probable mechanism of the specific dimerization of methyl crotonate to (I) is considered to be as follows:



Saegusa et al. reported the dimerization of methyl crotonate to (II) and its trans-isomer by the Cu_2O -isocyanide system.^{2,3)} They considered that these products were obtained through an isomerization reaction of the assumed intermediate (I), though they did not actually isolate (I) from their reaction system. In our case, however, (I) is the only product when AlR_3 -sparteine complex is used as catalyst, and the trans-isomer of (II) has not been produced at all. Thus, a high selectivity of almost 100 % to produce the isomerized dimer (I), a new type of dimer, is characteristic of the AlR_3 -sparteine complex catalyst.

From the facts that AlR_3 by itself did not dimerize methyl crotonate and that the dimer of methyl crotonate obtained by AlR_3 -sparteine complex showed optical activity, it is concluded here again¹⁾ that the coordination of sparteine to AlR_3 not only activates the aluminum-carbon bond but also affords a chiral structure to the environment around the aluminum species.

References

- 1) M. Ikeda, T. Hirano and T. Tsuruta, Makromol. Chem., 150, 127 (1971).
- 2) T. Saegusa, Y. Ito, S. Kobayashi and S. Tomita, Chem. Commun., 1968, 273.
- 3) T. Saegusa, Y. Ito, S. Tomita and H. Kinoshita, J. Org. Chem., 35, 670 (1970).