Reactions of Metal Alkyl – Active Methylene Chelate Compounds with α,β-Unsaturated Carbonyl Compounds

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The method of the preparation of zinc (or aluminum) alkyl - active methylene chelate compounds was studied. The chelate compounds were identified mainly by NMR, IR, and component analysis. Zinc alkyl - active methylene chelate compounds were found to cause a Michael-type addition reaction with α,β-unsaturated esters or nitriles. Aluminum alkyl - active methylene chelate compounds exhibited lower reactivities than the zinc chelate compounds toward α,β-unsaturated carbonyl compounds. Kinetic studies of the addition reaction revealed that the reaction proceeded according to a first-order rate law with respect to both the metal compound and the α,β-unsaturated carbonyl compound. The effects of substituents on the metal atom as well as on the chelate ring were also studied. The intercorrelation among the chemical shift of the methine proton of the chelate ring, σ_p of the subsituents and the reactivity of metal alkyl - active methylene chelate compounds suggested that the rate of the addition reaction was governed mainly by the stability of the chelate ring.

In previous papers,[1-5] a series of studies of the reaction modes of metal alkyls, such as *n*-BuLi, *n*-BuMgBr, *n*-Bu_2Zn, and *n*-Bu_3Al, with α,β-unsaturated carbonyl compounds was reported. The reactivities of both metal alkyls and α,β-unsaturated carbonyl compounds were quantitatively determined. These studies were undertaken in order to elucidate the initiation mechanism in the anionic polymerization of α,β-unsaturated carbonyl compounds. In the course of our studies, we noticed some characteristic chemical behavior of the metal alkyl - active methylene compound system; this promoted us to study in more detail the structure and the reactivity of the metal alkyl - active methylene compound system in the reaction with α,β-unsaturated carbonyl compounds, and to compare them with those of simple metal alkyls in the reaction.

This paper will be concerned with studies of the method of the preparation of chelate compounds from the metal alkyls and active methylene compounds and of their structure identification, mainly by the use of nuclear magnetic resonance spectra (NMR) and infrared spectra (IR). The results of kinetic studies of the reactions between the metal alkyl-active methylene chelate compound and the α,β-unsaturated carbonyl compound are also included in this paper. Dimethyl malonate was mainly used as the active methylene component.

Experimental

Reagents. Benzene, *p*-cymene, and *n*-hexane were distilled over sodium wire.[6] Tetrahydrofuran was distilled after refluxing over potassium hydroxide, and again distilled over sodium wire.[6] Dimethyl malonate, dimethyl methylmalonate, dimethyl chloromalonate, ethyl acetoacetate, methyl cyanoacetate, and malononitrile were distilled after refluxing over calcium hydride. Methanol was dehydrated by magnesium methoxide.[6] Diethylamine was distilled after refluxing over potassium hydroxide and distilled again over calcium hydride.[6] *n*-Butyl mercaptan was distilled over calcium hydride.[6] Methyl isopropenyl ketone (MIPK) and methyl propenyl ketone (MNPK) were synthesized from the corresponding ketones and aldehydes[7,8] respectively. Commercial methyl acrylate (MA), methyl methacrylate (MMA), methyl crotonate (MCr), acrylonitrile (AN), and crotononitrile (CrN) were distilled over calcium hydride. Commercial methyl vinyl ketone (MVK) was dried by means of a molecular sieve and distilled. Methacrylonitrile (MAN) was synthesized according to the literature.[9] Di-*n*-butylzinc and triethylindium were synthesized according to the literature.[10,11] *n*-Butylzinc chloride was synthesized by Noltes' method[12] and was purified by recrystallization from *n*-hexane. Commercial triethylaluminum, triisobutylaluminum, and diethylaluminum chloride were distilled under reduced pressure.

Preparation of Metal Alkyl - Active Methylene Chelate Compounds. *n*-Butyl(dimethyl malonato)zinc was prepared by a hydrogen-abstraction reaction between *n*-Bu_2Zn and dimethyl malonate in the molar ratio of 1 : 1, in benzene and at room temperature. After the solvent had been dried up, *n*-butyl(dimethyl malonato)zinc was obtained in the form of a white solid. Diethyl(dimethyl malonato)aluminum was prepared from Et_3Al and dimethyl malonate in a malor ratio of 1 : 1, in benzene and at room temperature. It was distilled under reduced pressure after distilling off the solvent. Colorless liquid; bp 53°C/0.15 mmHg. Other metal alkyl - active methylene chelate compounds were prepared in a similar way. The preparation method is tabulated in Table 1.

The abbreviations of the names of the metal alkyl - active methylene chelate compounds are as follows:

n-Butyl(dimethyl malonato)zinc: *n*-BuZnDMM, (Dimethyl malonato)zinc chloride: ClZnDMM, (Dimethyl malonato)-

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TABLE 1. PREPARATIVE METHOD OF METAL ALKYL-ACTIVE METHYLENE CHELATE COMPOUNDS[a)]

Compound	Compound		Reaction temp.	State of product
	A	B		
n-BuZnDMM[b)]	n-Bu_2Zn	$CH_2(CO_2Me)_2$	r.t.	Colorless solid
ClZnDMM[b)]	n-BuZnCl	$CH_2(CO_2Me)_2$	r.t.	Colorless solid
MeOZnDMM[b)]	n-BuZnOMe	$CH_2(CO_2Me)_2$	40°C	Colorless solid
n-BuSZnDMM[b),c)]	n-BuZnSBu	$CH_2(CO_2Me)_2$	40°C	Colorless solid
$Et_2NZnDMM$[b)]	n-BuZnDMM	Et_2NH	60°C	Solid
n-BuZnDMMM[b)]	n-Bu_2Zn	$CH_3CH(CO_2Me)_2$	r.t.	Colorless solid
n-BuZnDMCM[b)]	n-Bu_2Zn	$ClCH(CO_2Me)_2$	r.t.	Colorless solid
n-BuZnEAA	n-Bu_2Zn	$CH_3COCH_2CO_2Et$	r.t.	Glassy state
Et_2AlDMM	Et_3Al	$CH_2(CO_2Me)_2$	r.t.	bp 53°C/0.15 mmHg
EtClAlDMM	Et_2AlCl	$CH_2(CO_2Me)_2$	r.t.	bp 70°C/0.20 mmHg
EtMeOAlDMM	Et_2AlDMM	MeOH	r.t.	Glassy state
i-$BuEt_2NAlDMM$	i-Bu_2AlNEt_2	$CH_2(CO_2Me)_2$	60°C	—
$Et_2AlDMMM$	Et_3Al	$CH_3CH(CO_2Me)_2$	r.t.	bp 66°C/0.30 mmHg
$Et_2AlDMCM$	Et_3Al	$ClCH(CO_2Me)_2$	r.t.	mp *ca.* 30°C, bp 83°C/0.40 mmHg
Et_2AlMCA	Et_3Al	$CNCH_2CO_2Me$	r.t.	Glassy state
EtClAlMCA	Et_2AlCl	$CNCH_2CO_2Me$	r.t.	Glassy state
Et_2AlEAA	Et_3Al	$CH_3COCH_2CO_2Et$	r.t.	bp 45°C/0.20 mmHg
Et_2InDMM	Et_3In	$CH_2(CO_2Me)_2$	r.t.	Colorless solid

a) All reactions were carried out by adding B into a benzene solution of A.

b) All zinc alkyl-active methylene chelate compounds were purified by washing with n-hexane or recrystallization from n-hexane.

c) n-BuZnSBu was prepared from n-Bu_2Zn and n-BuSH in benzene.

TABLE 2. COMPONENT ANALYSIS OF ZINC ALKYL-ACTIVE METHYLENE CHELATE COMPOUNDS

Compound	n-Bu	Cl	MeO	Et_2N	n-BuS	Zn	DMM	DMMM	DMCM	EAA
n-BuZnDMM	0.97	—	—	—	—	1.00	1.02	—	—	—
ClZnDMM	—	a)	—	—	—	1.00	1.00	—	—	—
MeOZnDMM	—	—	1.01	—	—	1.00	0.97	—	—	—
n-BuSZnDMM	—	—	—	—	0.98	1.00	0.99	—	—	—
$Et_2NZnDMM$	—	—	—	0.96	—	1.00	1.00	—	—	—
n-BuZnDMMM	1.02	—	—	—	—	1.00	—	0.98	—	—
n-BuZnDMCM	0.98	—	—	—	—	1.00	—	—	0.97	—
n-BuZnEAA	0.99	—	—	—	—	1.00	—	—	—	1.01

a) Chlorine was not determined.

TABLE 3. COMPONENT ANALYSIS OF ALUMINUM ALKYL-ACTIVE METHYLENE CHELATE COMPOUNDS

Compound	Et	Cl	MeO	Al	DMM	DMMM	DMCM	EAA
Et_2AlDMM	2.02	—	—	1.00	1.00	—	—	—
EtClAlDMM	1.00	a)	—	1.00	1.02	—	—	—
EtMeOAlDMM	1.02	—	0.98	1.00	0.96	—	—	—
$Et_2AlDMMM$	1.98	—	—	1.00	—	0.99	—	—
$Et_2AlDMCM$	2.00	—	—	1.00	—	—	1.00	—
Et_2AlEAA	2.01	—	—	1.00	—	—	—	1.02

a) Chlorine was not determined.

TABLE 4. DEGREE OF ASSOCIATION OF ZINC ALKYL-ACTIVE METHYLENE CHELATE COMPOUNDS

Compound	Concn. (mol/l)	Degree of association
n-BuZnDMM	0.188	2
MeOZnDMM	0.206	4—6
$Et_2NZnDMM$	0.250	1
n-BuZnDMMM	0.300	1—2
n-BuZnDMCM	0.305	1—2
n-BuZnEAA	0.206	2

TABLE 5. DEGREE OF ASSOCIATION OF ALUMINUM ALKYL-ACTIVE METHYLENE CHELATE COMPOUNDS

Chelate compound	Concn. (mol/l)	Degree of association
Et_2AlDMM	0.105	1
EtMeOAlDMM	0.197	1
EtClAlDMM	0.164	1
$Et_2AlDMCM$	0.175	1
$Et_2AlDMMM$	0.180	1
Et_2AlEAA	0.193	1

TABLE 6. NMR DATA OF METAL ALKYL - ACTIVE METHYLENE CHELATE COMPOUNDS

Compound	No. of peak	Assignment	Chemical shift[a]	Area ratio
Dimethyl malonate	1	$-CO_2CH_3$	6.65	6
	2	$\overset{\diagup}{\underset{\diagdown}{C}}H_2$	6.89	2
Dimethyl chloromalonate	3	$-CO_2CH_3$	6.72	6
	4	$Cl-\overset{\diagup}{\underset{\diagdown}{C}}H$	5.40	1
Dimethyl methylmalonate	5	CO_2CH_3	6.63	6
	6	$-\overset{\diagup}{\underset{\diagdown}{C}}H$	6.84	1
	7	$CH_3-\overset{\diagup}{\underset{\diagdown}{C}}-$	8.80	3
Methyl cyanoacetate	8	$-CO_2CH_3$	6.69	3
	9	$CN-CH_2$	7.23	2
Ethyl acetoacetate	10	$-OCH_2-$	6.09	2
	11	$-CH_2-$	6.97	2
	12	$CH_3\underset{\overset{\|}{O}}{C}-$	8.21	3
	13	CH_3	9.03	3
n-BuZnDMM	1	$M\overset{\diagup\!\!\diagup}{\underset{\diagdown\!\!\diagdown}{C}}H$	5.57	1
	2	$-CO_2CH_3$	6.67	6
	3	$-CH_2-CH_2-$	—	4
	4	CH_3	8.90	3
	5	$M-CH_2-$	9.22	2
ClZnDMM[b]	6	$M\overset{\diagup\!\!\diagup}{\underset{\diagdown\!\!\diagdown}{C}}H$	5.27	1
	7	$-CO_2CH_3$	6.52	6
MeOZnDMM	8	$M\overset{\diagup\!\!\diagup}{\underset{\diagdown\!\!\diagdown}{C}}H$	5.19	1
	9	CH_3O	6.04	3
	10	$-CO_2CH_3$	6.54	6
$Et_2NZnDMM$	11	$M\overset{\diagup\!\!\diagup}{\underset{\diagdown\!\!\diagdown}{C}}H$	5.26	1
	12	$-CO_2CH_3$	6.54	6
	13	CH_2-N	7.80	4
	14	CH_3	9.17	6
n-BuZnDMCM	1	$-CO_2CH_3$	6.59	6
	2	$-CH_2-CH_2-$	—	4
	3	CH_3	8.93	3
	4	$M-CH_2-$	9.42	2
n-BuZnDMMM	5	$-CO_2CH_3$	6.51	6
	6	$CH_3-\overset{\diagup\!\!\diagup}{\underset{\diagdown\!\!\diagdown}{C}}M$	8.01	3
	7	$-CH_2-CH_2-$	—	4
	8	CH_3	8.96	3
	9	$M-CH_2-$	9.27	2
n-BuZnEAA	10	$M\overset{\diagup\!\!\diagup}{\underset{\diagdown\!\!\diagdown}{C}}H$	5.05	1
	11	$-OCH_2$	6.08	2
n-BuZnEAA	12	$CH_3-\underset{\overset{\|}{O}}{C}-$	8.02	3
	13	$-CH_2CH_2$	—	4
	14	CH_3	8.95	3
	15	$OCH_2C\underline{H}_3$	8.98	3
	16	$M-CH_2-$	9.34	2
Et_2AlDMM	1	$M\overset{\diagup\!\!\diagup}{\underset{\diagdown\!\!\diagdown}{C}}H$	5.36	1
	2	$-CO_2CH_3$	6.81	6
	3	CH_3	8.67	6
	4	$M-CH_2$	9.70	4
EtClAlDMM	5	$M\overset{\diagup\!\!\diagup}{\underset{\diagdown\!\!\diagdown}{C}}H$	5.47	1
	6	$-CO_2CH_3$	6.92	6
	7	CH_3	8.70	3
	8	$M-CH_2$	9.60	2
EtMeOAlDMM	9	$M\overset{\diagup\!\!\diagup}{\underset{\diagdown\!\!\diagdown}{C}}H$	5.18	1
	10	CH_3O	6.48	3
	11	$-CO_2CH_3$	6.64	6
	12	CH_3	8.60	3
	13	$M-CH_2-$	9.70	2
i-$BuEt_2NAlDMM$	14	$M\overset{\diagup\!\!\diagup}{\underset{\diagdown\!\!\diagdown}{C}}H$	5.08	1
	15	CO_2CH_3	6.58	6
	16	$N-CH_2$	7.35	4
	17	$-\overset{|}{\underset{|}{C}}H$	—	1
	18	CH_3	8.92	6
	19	$N-CH_2-C\underline{H}_3$	9.15	6
	20	$M-CH_2$	9.76	2
$Et_2AlDMCM$	1	$-CO_2CH_3$	6.80	6
	2	CH_3	8.72	6
	3	$M-CH_2$	9.80	4
$Et_2AlDMMM$	4	$-CO_2CH_3$	6.78	6
	5	CH_3-CM	8.23	3
	6	CH_3	8.63	6
	7	$M-CH_2$	9.57	4
Et_2AlEAA	8	$M\overset{\diagup\!\!\diagup}{\underset{\diagdown\!\!\diagdown}{C}}H$	5.18	1
	9	$-\underset{\overset{\|}{O}}{C}-O-CH_2$	6.20	2
	10	$CH_3\underset{\overset{\|}{O}}{C}$	8.37	3
	11	$M-CH_2-CH_3$	8.63	6
	12	$-\underset{\overset{\|}{O}}{C}-O-CH_2-C\underline{H}_3$	9.13	3
	13	$M-CH_2$	9.68	4

a) τ-value, tetramethylsilane as internal standard.

b) Mixed solvent (THF: Benzene = 1 : 1) was used.

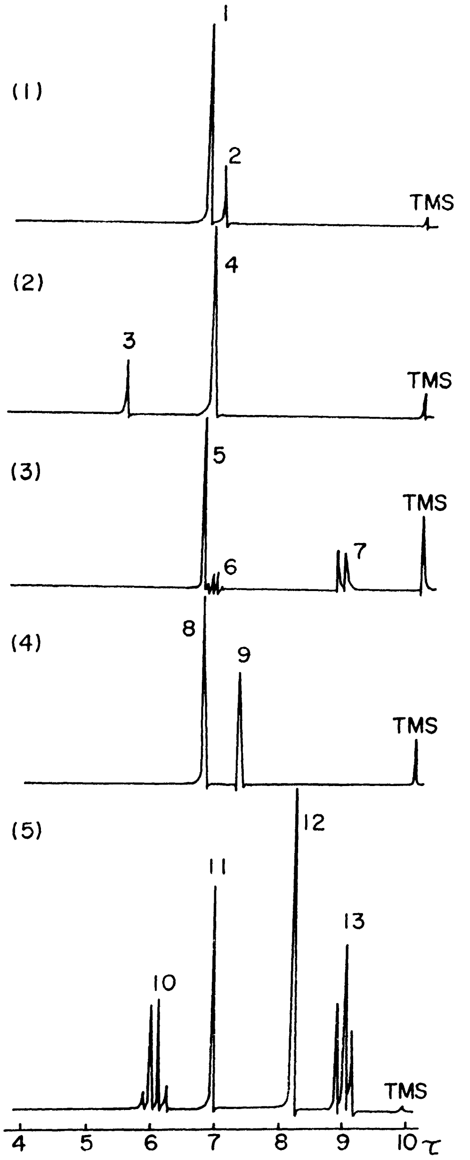


Fig. 1. NMR spectra of active methylene compounds (in benzene).
(1) Dimethyl malonate (2) Dimethyl chloromalonate
(3) Dimethyl methylmalonate (4) Methyl cyanoacetate
(5) Ethyl acetoacetate

zinc methoxide: MeOZnDMM, (Dimethyl malonato)zinc butylmercaptide: n-BuSZnDMM, (Dimethyl malonato)zinc diethylamide: $Et_2NZnDMM$, n-Butyl(dimethyl methylmalonato)zinc: n-BuZnDMMM, n-Butyl(dimethyl chloromalonato)zinc: n-BuZnDMCM, n-Butyl(ethyl acetoacetato)zinc: n-BuZnEAA, Diethyl(dimethyl malonato)aluminum: Et_2AlDMM, Ethyl-(dimethyl malonato)aluminum chloride: EtClAlDMM, Ethyl-(dimethyl malonato)aluminum methoxide: EtMeOAlDMM, Isobutyl(dimethyl malonato)aluminum diethylamide: i-$BuEt_2NAlDMM$, Diethyl(dimethyl methylmalonato)aluminum: $Et_2AlDMMM$, Diethyl(dimethyl chloromalonato)aluminum: $Et_2AlDMCM$, Diethyl(methyl cyanoacetato)aluminum: Et_2AlMCA, Ethyl(methyl cyanoacetato)aliminum chloride: EtClAlMCA, Diethyl(ethyl acetoacetato)aluminum: Et_2AlEAA, Diethyl(dimethyl malonato)indium: Et_2InDMM.

Analyses of Metal Alkyl-Active Methylene Chelate Compounds. The analyses of the metal alkyl-active methylene chelate compounds were performed by chelate titration, NMR, IR, and vapor-phase chromatography(VPC). The degree of association was measured in benzene by the cryoscopic method. The results obtained are shown in Tables 2—6 and in Figs. 1—5.

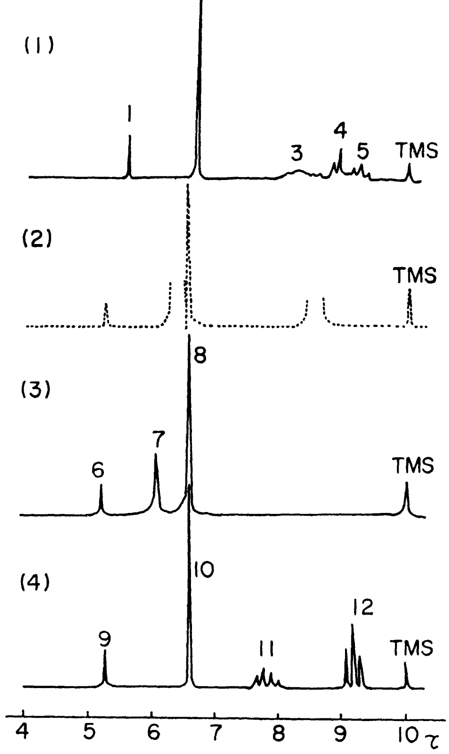


Fig. 2. NMR spectra of XZnDMM (in benzene).
(1) n-BuZnDMM (2) ClZnDMM (in THF)
(3) MeOZnDMM (4) $Et_2NZnDMM$

These results show that one alkyl group of every metal alkyl derivative, *e. g.*, RZnX, was quantitatively reacted with an active methylene compound, while alkane was eliminated, as follows:

$$RZnX + CH_2(CO_2Me)_2 \longrightarrow \underset{(XZnDMM)}{XZnCH(CO_2Me)_2} + RH$$

Procedure for Reactions with α,β-Unsaturated Carbonyl Compounds. Into a magnetic-stirred solution of a metal alkyl-active methylene chelate compound in a 30-ml, one-necked flask fitted with a three-way cock, an α,β-unsaturated carbonyl compound was added through the three-way cock from a syringe. After a given time interval, the reaction was stopped by adding acetic acid and the reaction products were determined by VPC. All the procedures described above were carried out under a dried nitrogen atmosphere. The NMR spectra were obtained by the use of a Japan Electron Optics Lab. Co., model C-60, high-resolution spectrometer using a 10 mol% benzene solution of a metal alkyl-active methylene chelate compound. The τ-values were determined by the use of tetramethylsilane as the internal standard. The IR spectra were obtained by the use of a Hitachi IR spectrometer, model EPI-G3, between KBr plates.

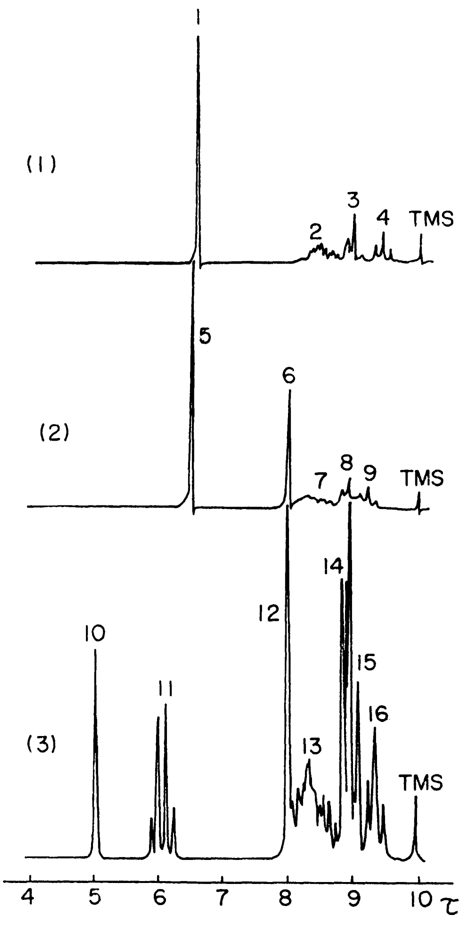


Fig. 3. NMR spectra of n-BuZnC(X)(Y)CO$_2$Me (in benzene).
(1) n-BuZnDMCM (2) n-BuZnDMMM (3) n-BuZnEAA

Results and Discussion

1. Structure of Meta Alkyl - Active Methylene Chelate Compounds. As is shown in Figs. 2—5 and in Tables 2, 3, and 6, each of the products from the metal alkyl - active methylene compound systems is a stoichiometric compound. The IR spectra of the carbonyl region is shown in Fig. 6.

The frequency of >C=O stretching is shifted to a region lower by 100—150 cm^{-1}, a fact which seems to indicate a chelating structure produced through the oxygen atom of the carbonyl group. Most of the chemical shifts of the methine proton in the NMR data are observed in the vicinity of 5.3 τ, which shows that the methine carbon is not linked directly with the metal atom. In order to elucidate the structure of the aluminum alkyl - active methylene chelate compound more clearly, the coupling constant, $J^{13}{}_{\text{C-H}}$ at the methine proton was measured by using a neat sample. The results are shown in Table 7.

Table 7. Coupling constant $J_{^{13}\text{C-H}}$ at C–H

Compound	$J_{^{13}\text{C-H}}$(cps)
Et$_2$AlDMM	170
EtClAlDMM	168
Et$_2$AlEAA	168
DMM	130

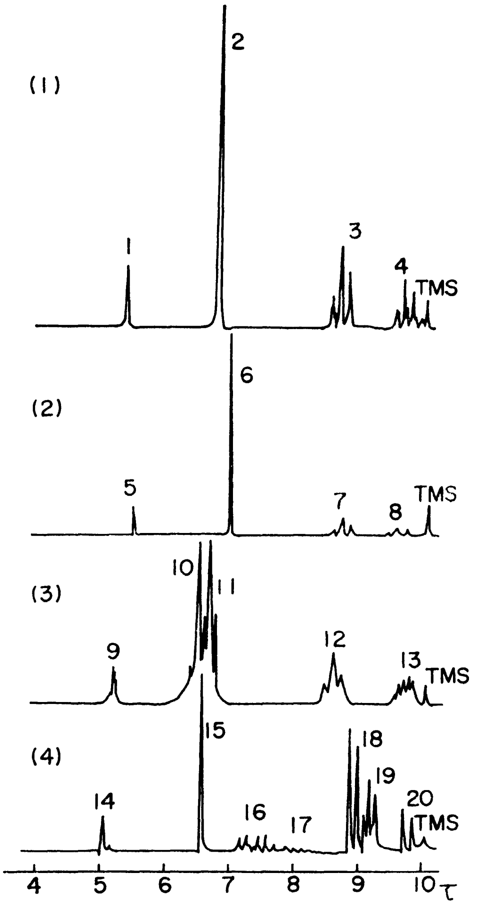
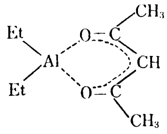


Fig. 4. NMR spectra of EtXAlDMM (in benzene).
(1) Et$_2$AlDMM (2) EtClAlDMM
(3) EtMeOAlDMM (Sample only dried up was used.)
(4) i-BuEt$_2$NAlDMM

The value of $J^{13}{}_{\text{C-H}}$ is regarded as a measure of the s-character of the carbon atom.[13] As is shown in the table, the value is about 170 cps for the aluminum chelate, a fact which indicates that the central carbon of the active methylene compound in the aluminum chelate compound is in the sp^2 valence state. Kroll and Naegele[14] reported that diethyl(acetylacetonato)-aluminum has the following chelating structure:



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[13] a) N. Muller and D. E. Pritchard, *J. Chem. Phys.*, **31**, 768, 1471 (1959). b) J. N. Shoolery, *ibid.*, **31**, 1427 (1959). c) C. Juan and H. S. Gutowsky, *ibid.*, **37**, 2198 (1962).

[14] W. R. Kroll and W. Naegele, *J. Organometal. Chem.*, **19**, 439 (1969).

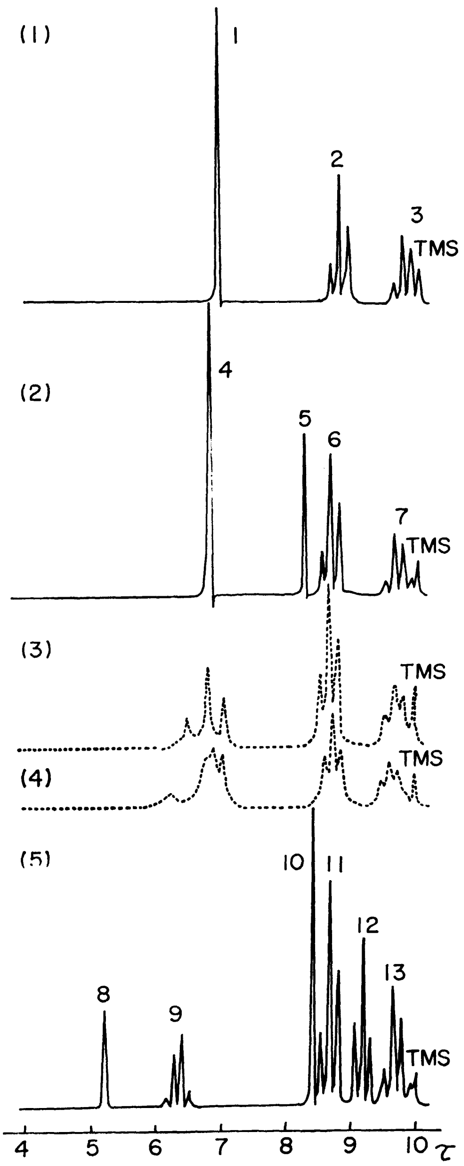


Fig. 5. NMR spectra of $Et_2AlC(X)(Y)CO_2Me$ (in benzene).
(1) $Et_2AlDMCM$ (2) $Et_2AlDMMM$
(3) Et_2AlMCA (Sample only dried up was used.)
(4) $EtClAlMCA$ (Sample only dried up was used.)
(5) Et_2AlEAA

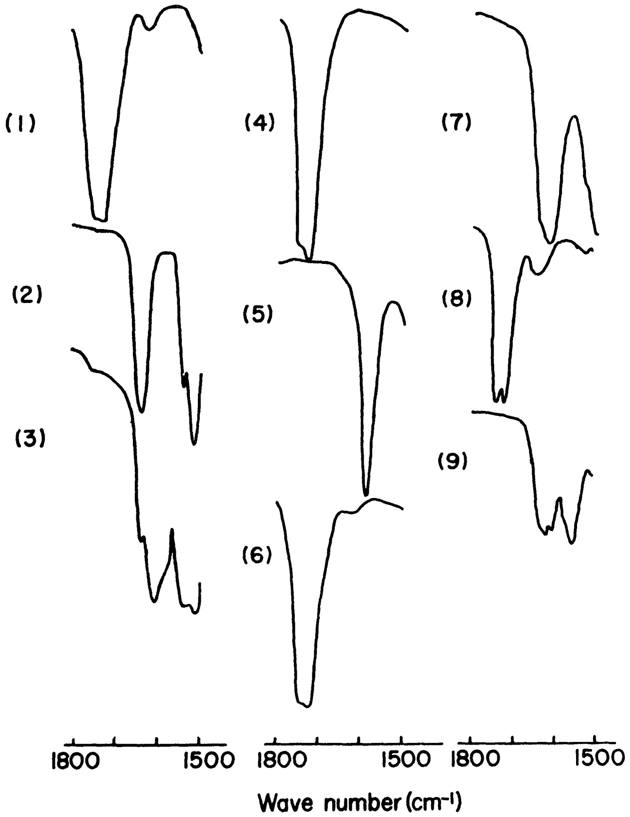


Fig. 6. IR spectra of aluminum alkyl chelate compounds in carbonyl region.
(1) Dimethyl malonate (2) Et_2AlDMM (3) $EtClAlDMM$
(4) Dimethyl chloromalonate (5) $Et_2AlDMCM$
(6) Dimethyl methylmalonate (7) $Et_2AlDMMM$
(8) Ethyl acetoacetate (9) Et_2AlEAA

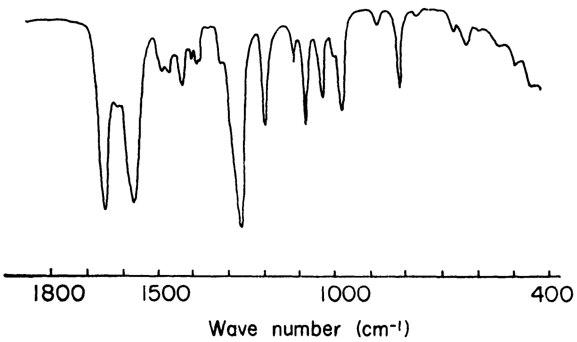


Fig. 7. IR spectrum of *n*-BuZnEAA.

Judging from Figs. 4—6 and Table 7, the products from aluminum alkyl-active methylene compound systems can reasonably be concluded to have a similar structure of the chelate ring.

Measurements of $J^{13}{}_{C-H}$, however, were not possible for the zinc alkyl-active methylene compound system, because all of the zinc compounds prepared, *e. g.*, XZnDMM, were solid. We may, though, suppose the structure of the zinc compound to be similar to the aluminum chelate from the NMR data (Figs. 2 and 3) as well as the IR data (Fig. 7).

2. *Reaction Mode of Zinc (or Aluminum) Alkyl-Active Methylene Chelate Compounds with α,β-Unsaturated Carbonyl Compounds.* In the reaction of *n*-BuZnDMM with methyl acrylate (MA), dimethyl malonate was found to decrease in the course of the reaction, ultimately almost disappearing, a fact which shows that no hydrogen abstraction by DMM occurred, and an addition product, $(MeOOC)_2CHCH_2CH_2CO_2Me$, of DMM to MA was detected by VPC. Since the formation of methanol in the reaction mixture was not detected, the possibility of the carbonyl addition reaction can be excluded. The addition product, fractionated by VPC, was identified by a comparison of its IR spectrum with that of an authentic sample.

These results show the only elementary reaction in this case to be a Michael-type 1,4 addition reaction. Reactions with α,β-unsaturated ketones and nitriles were also studied. The reactivity of the aluminum alkyl-active methylene chelate compound is rather lower than that of the zinc chelate, no addition reactions to α,β-unsaturated esters or nitriles being observed at 30°C

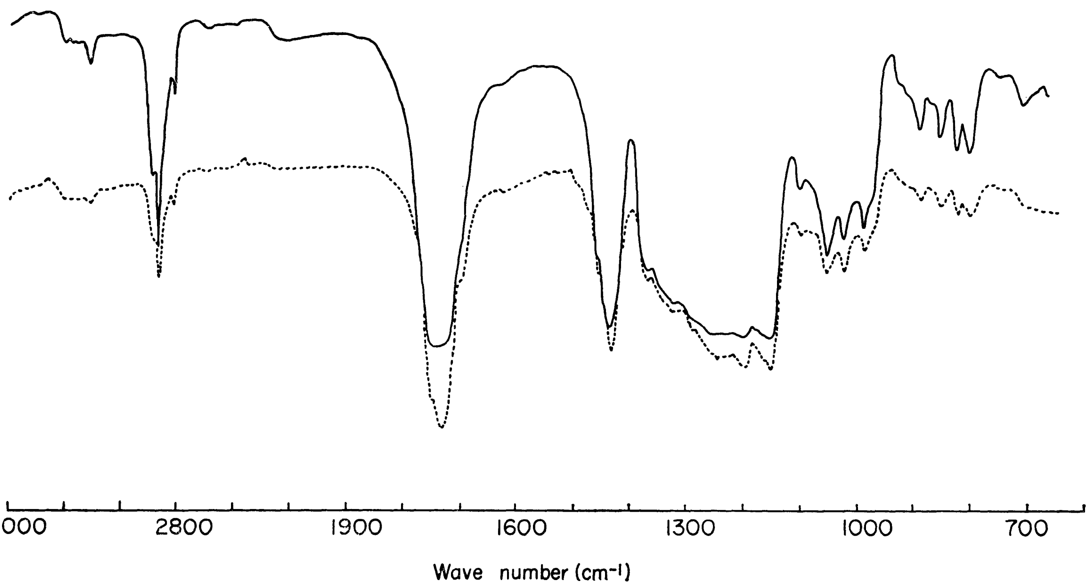


Fig. 8. IR spectra of the reaction products of BuZnDMM with MA and authentic sample (---).

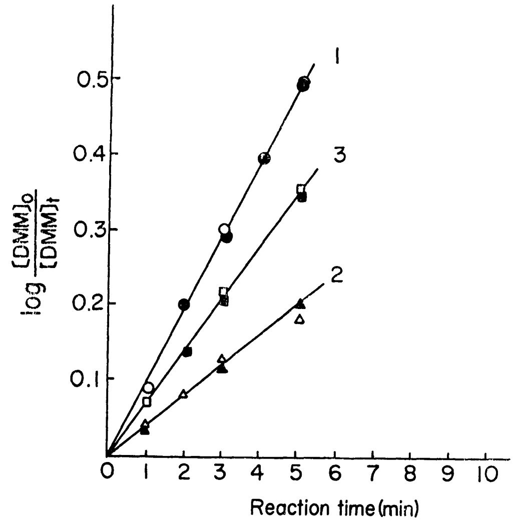


Fig. 9. Reaction of *n*-BuZnDMM with α,β-unsaturated carbonyl compounds.

(1) MIPK (2) MA (3) AN
○ [Zn]=0.20 mol/*l* △ [Zn]=0.23 mol/*l*
□ [Zn]=0.20 mol/*l* ● [Zn]=0.10 mol/*l*
▲ [Zn]=0.12 mol/*l* ■ [Zn]=0.10 mol/*l*

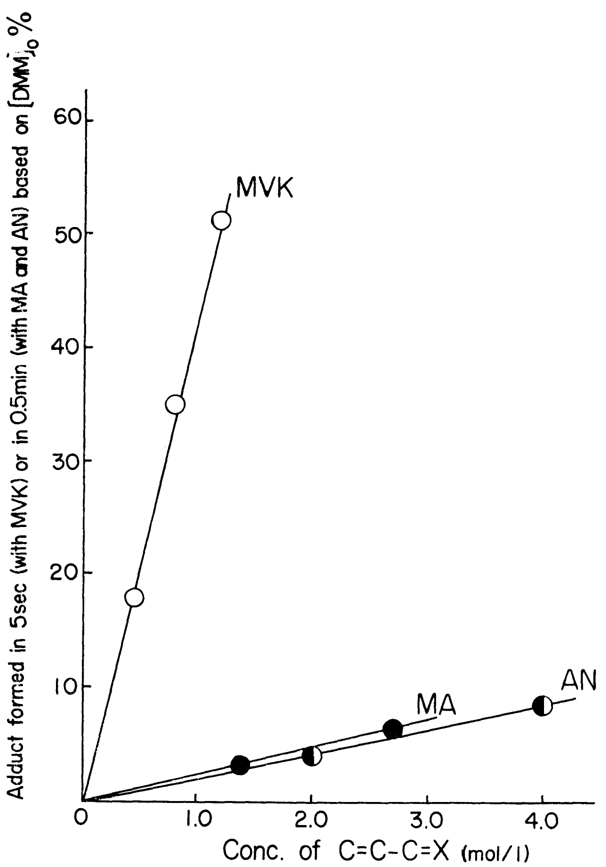


Fig. 10. Dependence of rate on the concentration of α,β-unsaturated carbonyl compound in the reaction with *n*-BuZnDMM (0.1 mol/*l*).

in benzene. The reactivity of EtClAlDMM, however, was found to be high enough to add to the α,β-unsaturated ester or nitrile under the same conditions. The mode of the addition reaction was confirmed to be also a Michael-type reaction in the case of the aluminum chelate just as with the zinc-chelate compound.

3. *Reaction-rate Analysis.* The rate of the addition reaction was determined by measuring the quantities of dimethyl malonate recovered after the interruption of the reaction. To ascertain the effect of substituents on the metal atom, the reaction of XZnDMM (X=*n*-Bu, Cl, MeO, *n*-BuS, Et_2N) with MA was kinetically studied in detail. Substituent effects on the central carbon of DMM were also studied. Besides dimethyl malonate, ethyl acetoacetate, and methyl cyanoacetate were examined for the sake of comparison. In all cases, the Michael-type addition of an active methylene compound to an α,β-unsaturated carbonyl compound was confirmed to take place. The results are tabulated in Tables 8, 9, 10, and 11.

The data in Tables 8—11 were found to fit the first-order rate law with respect to the metal alkyl-active methylene chelate compound. This was confirmed also by the further experiments shown in Fig. 9,

TABLE 8. REACTION OF ZXnDMM WITH α,β-UNSATURATED CARBONYL COMPOUND[a]

Carbonyl compd.	X	Reaction time (min)	X[b] Recovered (%)	Dimethyl malonate (%)	Carbonyl compd.	X	Reaction time (min)	X[b] Recovered (%)	Dimethyl malonate (%)
MVK	*n*-Bu	0	100	100	MVK	MeO	0	100	100
		0.083	100	5.0			0.5	—	52.2
		5	100	0			1	—	27.2
MIPK	*n*-Bu	0	100	100			2	—	7.4
		1	100	66.4	MIPK	MeO	0	100	100
		3	99	29.5			0.5	—	85.5
		5	101	13.6			1	—	79.6
		10	98	10.5			2	—	63.7
		20	100	6.7			3	—	50.8
MNPK	*n*-Bu	0	100	100			5	100	32.2
		2	100	28.9	MNPK	MeO	0	100	100
		5	98	3.7			1	—	94.3
		10	102	1.0			2	—	89.0
MA	*n*-Bu	0	100	100			3	—	84.0
		1	100	91.0			5	—	74.8
		2	98	81.9			10	100	56.2
		3	99.4	74.0	MA	MeO	0	100	100
		5	100	67.3			60	—	64.3
		10	—	44.6			120	—	45.0
		1200	100	3.5			180	—	29.9
MMA	*n*-Bu	0	100	100			300	102	17.4
		60	99	98	AN	MeO	0	100	100
		120	102	96			60	—	—
		1440	100	58.8			120	—	29.7
MCr	*n*-Bu	0	100	100			1200	100	3.7
		60	—	96.5	MVK	Cl	0	—	100
		120	—	93.5			1/2	—	42.2
		240	99	87.7			1/6	—	17.5
AN	*n*-Bu	0	100	100			5	—	0
		1	—	83.7	MA	Cl	0	—	100
		3	—	59.6			0.5	—	93.2
		5	—	43.1			1	—	87.1
		10	100	17.7			2	—	75.9
MAN	*n*-Bu	0	100	100			5	—	51.9
		60	—	98.3	MA	*n*-BuS	0	100	100
		120	—	94.6			180	—	88.7
		300	—	87.0			420	—	75.6
		600	100	76.0			720	—	61.4
CrN	*n*-Bu	0	100	100			1260	100	44.4
		30	—	98.0	MA	Et_2N	0	100	100
		60	—	93.5					
		120	—	87.5			420	—	80.4
		300	—	71.8			1260	100	68.4
		600	100	50.0					

a) All reactions were carried out in benzene at 30°C. [MVK] 0.4 mol/*l*, [MIPK] 1.5 mol/*l*, [MNPK] 1.5 mol/*l*, [MA] 1.4 mol/*l*, [MMA] 2.44 mol/*l*, [MCr] 2.44 mol/*l*, [Nitrile] 2.0 mol/*l* for BuZnDMM; [MVK] 0.56 mol/*l*, [MIPK] or [MNPK] 2.0 mol/*l*, [MA] 2.4 mol/*l*, [AN] 1.6 mol/*l* for MeOZnDMM; [MA] 2.0 mol/*l*, 1.0 mol/*l* and 2.0 mol/*l* for ClZnDMM, *n*-BuSZnDMM, and $Et_2NZnDMM$ respectively. [MVK] 0.48 mol/*l* for ClZnDMM. The concentration of zinc compounds was 0.1 mol/*l*.

b) Recovered X: *n*-BuH, MeOH, *n*-BuSH, and Et_2NH, respectively. Chlorine was not measured.

Table 9. Reaction of n-BuZnC(XY)CO_2Me with methyl acrylate[a)]

X	Y	Reaction time (min)	Recovered C(XY)CO_2Me (%)
Cl	CO_2Me	0	100
		1	88.0
		2	78.0
		3	68.7
		5	55.0
		10	33.0
CH_3	CO_2Me	0	100
		1	60.8
		2	37.2
		3	24.1
		5	14.3
		10	9.9
H	CH_3CO[b)]	0	100
		300	66.6

a) MA 2.0 mol/*l*: Zinc compound 0.1 mol/*l*
b) Ethyl acetoacetate was used.

Table 10. Reaction of EtXAlDMM with α,β-unsaturated carbonyl compound[a)]

Compound	X	Reaction time (min)	Recovered DMM (%)
MVK	Et	0	100
		2	95.2
		5	88.4
		10	77.5
		30	52.7
MVK	Cl	0	100
		0.333	5
MA	Cl	0	100
		10	87.5
		20	77.0
		30	67.3
		60	45.4
		120	20.7
MVK	MeO	0	100
		2	98.2
		5	96.8
		10	93.7
		30	82.5
MVK	Et_2N[b)]	0	100
		60	93.0
		120	87.0
		180	80.5
		600	71.2
		1230	23.8

a) MVK 2.56 mol/*l*, 0.5 mol/*l*, 2.0 mol/*l*, and 4.0 mol/*l* for X=Et, Cl, MeO, and Et_2N, respectively.
MA 1.5 mol/*l*
Aluminum compound 0.1 mol/*l*
b) *i*-$BuEt_2NAlDMM$ was used.

Table 11. Reaction of $Et_2AlC(XY)CO_2Me$ with α,β-unsaturated carbonyl compound[a)]

Carbonyl compound	X	Y	Reaction time (min)	Recovered C(XY)CO_2Me (%)
MVK	Cl	CO_2Me	0	100
			30	68.6
			60	46.5
			150	14.8
MVK	CH_3	CO_2Me	0	100
			120	78.7
			1440	10.1
MVK	H	CN	0	100
			0.5	13.6
MA	H	CN	0	100
			10	61.2
			20	37.6
			30	23.0
			60	12.0
MVK	H	CH_3CO[b)]	0	100
			1440	100

a) Carbonyl compound 1.0 mol/*l*
Aluminum compound 0.1 mol/*l*
b) Ethyl acetoacetate was used.

in which the concentration of the metal component is a half of that in Table 7.

The straight line in Fig. 9 shows that the addition reaction is a first-order one with respect to the metal compound. The dependence of the reaction rate on the concentration of the α,β-unsaturated carbonyl compound was also examined, as is shown in Fig. 10.

From the above data, the rate expression for the addition reaction can be given as Eq. (1):

$$\frac{d[\mathrm{DMM}]}{dt} = k[\mathrm{M}][\text{carbonyl compound}] \qquad (1)$$

Table 12. Rate constants[a)] of addition reaction of Et(X)Al-Y with methyl vinyl ketone and methyl acrylate

X	Y	MVK	MA
Et	DMM	9.7×10^{-3}	b)
Cl		3.0	8.8×10^{-3}
MeO		3.2×10^{-3}	b)
Et_2N		4.0×10^{-4}	b)
Et	DMMM	2.0×10^{-3}	b)
	DMCM	1.3×10^{-2}	b)
	MCA	16	4.9×10^{-2}

a) *l*/mol·min
b) No reaction occurred.

Table 13. Rate constants[a)] of addition reaction of X-Zn-Y with α,β-unsaturated carbonyl compound

X	Y	MVK	MIPK	MNPK	MA
n-Bu	DMM	44	0.28	0.44	6.9×10^{-2}
Cl		21.5	—	—	6.9×10^{-2}
MeO		2.6	0.12	0.029	2.9×10^{-3}
Et_2N		—	—	—	2.6×10^{-4}
n-BuS		—	—	—	6.7×10^{-4}
n-Bu	DMMM	—	—	—	4.7×10^{-1}
	DMCM	—	—	—	6.2×10^{-2}
	EAA	0.64	—	—	6.8×10^{-4}

a) *l*/mol·min

where [M] is the concentration of the metal compound. Equation (1) was found to be true for all the reactions examined between metal alkyl-active methylene chelate compounds and α,β-unsaturated carbonyl compounds. The rate constants of the second-order reaction are listed in Tables 12 and 13.

4. *Reactivity of Metal Alkyl-Active Methylene Chelate Compounds.* It can be seen from the preceding sections that RZnDMM exhibits much higher reactivity than $\mathrm{ZnR_2}$ in the addition reaction to α,β-unsaturated esters or nitriles. As we reported previously, $\mathrm{ZnR_2}$ or $\mathrm{AlR_3}$ can add to α,β-unsaturated ketones,[5] but not to the unsaturated esters (*e. g.*, methyl acrylate, methyl methacrylate, and methyl crotonate) or nitriles (*e. g.*, acrylonitrile, methacrylonitrile, and crotononitrile). Contrary to RZnDMM, the reactivity of $\mathrm{R_2AlDMM}$ was not enough to result in the addition reaction with the unsaturated esters or nitriles, though the latter chelate compound adds easily to more reactive double bonds of α,β-unsaturated ketones.

Since significant effects were noticed in the reactivity of XZnDMM or EtXAlDMM (X: R, Cl, RO, RS, $\mathrm{R_2N}$) in the addition reactions to α,β-unsaturated carbonyl compounds, systematical studies of the substituent effect were undertaken. From Tables 12 and 13, the main features of the reactions of metal alkyl-active methylene chelate compounds can be listed as follows:

i) The reactivity of XZnDMM or EtXAlDMM increases in the order, X: $\mathrm{Et_2N} < n\text{-BuS} < \mathrm{MeO} < n\text{-Bu}$(or Et)$\leqq$Cl, which is in accordance with the order of the methine proton chemical shift from a lower to a higher field.

ii) The more stable chelate ring seems to have a more diminished reactivity.

iii) The substituent effect on the central carbon atom of $n\text{-BuZn[XC(CO_2Me)_2]}$ is the reverse of that of $\mathrm{Et_2Al[XC(CO_2Me)_2]}$. The reactivity of $n\text{-BuZn[XC(CO_2Me)_2]}$ increases in the order; X: $\mathrm{Cl} < \mathrm{H} < \mathrm{CH_3}$, while the reactivity of $\mathrm{Et_2Al[XC(CO_2Me)_2]}$ decreases in this order.

An electron-withdrawing substituent, X, in EtXAlDMM causes the chemical shift of the methine proton to a higher field. This could be interpreted in terms of the decrease in the ring current, because of the electron-withdrawing nature of X, in the pseudo-aromatic system of the aluminum chelate compound. A linear relationship is observed between Hammett's substituent constants, $\sigma_{p,x}$ and the chemical shift of the methine proton in EtXAlDMM, as is shown in Figs. 11 and 12. It is assumed from the above data that the reactivity of the EtXAlDMM system is governed by the stability of the chelate ring. For instance, an electron-withdrawing substituent, Cl, attached to methine or aluminum, decreases the electron density (or ring current) of the chelate ring, meaning the loss of the aromaticity of the chelate ring. Therefore, the more diminished ring current (or the lower aromaticity) is closely related to the higher reactivity of EtXAlDMM.

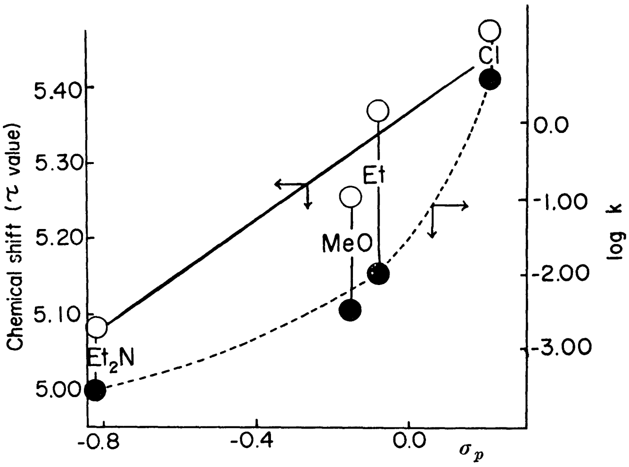


Fig. 11. Correlation among Hammett's σ_p, the chemical shift of methine proton in EtXAlDMM and reactivity.

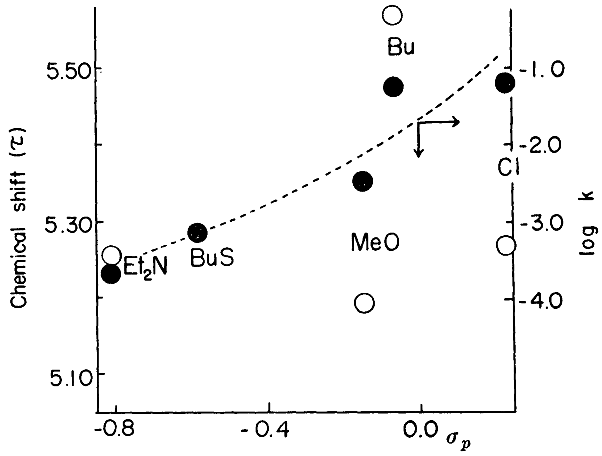


Fig. 12. Correlation among Hammett's σ_p, the chemical shift of methine proton in XZnDMM and reactivity.

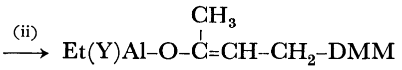
In the case of XZnDMM, no linear relationship was observed; between $\sigma_{p,x}$ and the chemical shift of methine proton in XZnDMM this might be ascribed at least partly to the association of the zinc compound or to the intrinsic nature of the zinc atom. The correlation between the reactivity, log k, and the σ_p of XZnDMM was, however, found to be similar to that in EtXAlDMM.

On the other hand, an electron-donating substituent (*e. g.*, $\mathrm{CH_3}$), attached to the active methylene group, was found to increase the reactivity of $n\text{-BuZn[XC(CO_2Me)_2]}$, a situation which is in contrast with the substituent effect in $\mathrm{Et_2Al[XC(CO_2Me)_2]}$. An electron-withdrawing substituent such as halogen in $n\text{-BuZn[XC(CO_2Me)_2]}$ also exerts an effect opposite to that in $\mathrm{Et_2Al[XC(CO_2Me)_2]}$.

It seems not to be easy to draw a consistent interpretation of the reactivities of the chelate complexes of aluminum and of zinc. We are inclined to consider, however, that the opposite substituent effects can be understood if we assume two steps [(i) and (ii)] in determining the rate of the addition reaction of the chelate complexes to the unsaturated carbonyl compounds.

For instance,

$$\mathrm{Et(Y)Al[DMM]} \xrightarrow{(i)} \mathrm{Et(Y)Al\cdots\cdots[DMM]}\quad \mathrm{O{=}C(CH_3){-}CH{=}CH_2}$$



$$\xrightarrow{\text{(ii)}} \mathrm{Et(Y)Al{-}O{-}\overset{\overset{\Large CH_3}{|}}{C}{=}CH{-}CH_2{-}DMM}$$

The chelate ring is probably loosened (Step (i)) before the β-carbon atom of the unsaturated carbonyl compound is attacked by [DMM] at Step (ii). We have discussed the reactivity of $\mathrm{Et(Y)Al[C(X)(CO_2Me)_2]}$ in terms of the stability of the chelate ring, which means the rate-determining step is probably Step (i).

In the light of the stability constants of metal acetylacetonates, according to Block *et al.*,[15-17] the chelate ring of the zinc alkyl complex system can be assumed to be much more unstable than the aluminum alkyl complex.

Table 14. Stability constants of metal acetylacetonates

Metal	Stability constant (log k)	Ion strength
Zn	9.11 (k_1)	75% dioxane[15]
	4.98 (k_1)	0[16]
	8.09 (k_2)	75% dioxane[15]
	3.83 (k_2)	0
Al	8.6 (k_1)	0[16]
	7.9 (k_2)	0[17]
	5.8 (k_3)	0[17]

Therefore, it is not unreasonable to deduce that the rate-determining step is Step (ii) with the zinc alkyl complex, the reactivity of which is governed, rather, by the reactivity of the active methylene component itself. For example, the chlorine substituent on the central carbon stabilized the [DMCM] anion, resulting in a decrease in the reactivity of the malonate anion. The methyl substituent has a reverse effect. It should be pointed out at this stage that the substituent effect in dimethyl malonato sodium in the Michael reaction[18] is in the same direction as with the zinc alkyl complex, a fact which is consistent with the above discussion, because the ability of chelate-ring formation should be extremely small in dimethyl malonato sodium in comparison with the case of the aluminum chelate.

5. *Vinyl Polymerization with Metal Alkyl - Active Methylene Chelate Compounds.* The possibility of polymerization was examined with several α,β-unsaturated carbonyl compounds by the use of the metal alkyl - active methylene chelate as the initiator, but high polymers were not formed in benzene at 30°C. When dimethyl sulfoxide or hexamethylphosphoric triamide was used as the solvent, MA was polymerized, as is shown in Table 15. When malononitrile was used instead of dimethyl malonate, the metal alkyl complex was also able to initiate the polymerization of MA. The anionic character of the polymerization was confirmed by the copolymerization method with styrene.

Table 15. Polymerization of α,β-unsaturated esters by the metal alkyl - active methylene chelate compound as catalyst

Monomer	Catalyst[a]	Solvent	Temp. (°C)	Time (day)	Yield (%)
MA	n-BuZnDMM	DMSO	20	4	5
MA	n-BuZnDMM	HMPA	20	4	10
MMA	n-BuZnDMM	HMPA	20	4	11
MCr	n-BuZnDMM	DMSO	20	4	0
MA	$\mathrm{Et_2AlDMM}$	DMSO	20	4	0
MA	i-$\mathrm{Bu_2Al \cdot MN}$	Bz	20	1	20

a) 5 mol% to monomer.

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