

The regioselectivity of Diels–Alder reaction of myrcene with carbonyl-containing dienophiles catalysed by Lewis acids

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Abstract

The effects of various Lewis acids and reaction temperature on the regioselectivity of the Diels–Alder reaction of myrcene (7-methyl-3-methene-1,6-octadiene) with acrolein or methyl acrylate have been studied. The high regioselective ‘*para*’ adducts were obtained when acrolein and methyl acrylate were used as dienophiles in the presence of ZnCl_2 and AlCl_3 catalyst, respectively. UV, ^1H NMR and IR spectroscopic methods, were first used to investigate the interactions between acrolein and ZnCl_2 or methyl acrylate and AlCl_3 . The absorbance of the dienophile decreases and the maximum peak of the dienophile shifts to longer wave region in the UV spectra. All the protons’ chemical shifts of the dienophile moves to downfield in the ^1H NMR spectra. The C=O stretching vibration of the dienophile shifts to a lower wave number region in the IR spectra. It is attributed to the coordination of acrolein with ZnCl_2 and of methyl acrylate with AlCl_3 . The dienophile activated by Lewis acid catalyst is advantageous for improving the ‘*para/meta*’ regioselectivity and enhancing the reaction rate. © 1999 Elsevier Science B.V. All rights reserved.

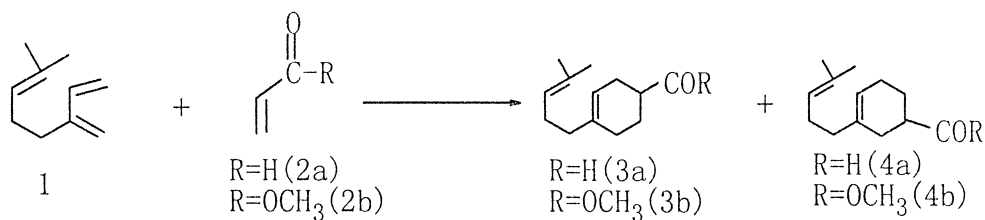
Keywords: Regioselectivity; Diels–Alder reaction; Myrcene; Lewis acid catalyst; Coordination catalysis

1. Introduction

Diels–Alder reaction, leading to cyclic products with controlled regioselectivity and stereochemistry, is a powerful tool in organic synthesis [1–4]. Myrcene (7-methyl-3-methene-1,6-octadiene) prepared by cracking β -pinene which was obtained from turpentine oil, can react with different dienophiles giving rise to a variety of

fragrant compounds or their intermediates [5–9]. The cycloadduct products often include ‘*para*’ and ‘*meta*’ adducts which are outlined in Scheme 1. Especially, the ‘*para*’ adduct is more important than the ‘*meta*’ adduct in the synthesis of new perfumes, medical drugs, and biological active substances [7–9]. Usually, the Diels–Alder reaction not only requires the most stringent thermal conditions and necessary solvent, but also gives very poor yield and ‘*para/meta*’ regioselectivity. How to synthesize ‘*para*’ adduct high regioselectively became very interesting. Veselovsky et al. [6] found that the reaction rate were greatly enhanced and the

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Scheme 1. The Diels–Alder reaction of myrcene (1) with acrolein (2a) or with methyl acrylate (2b).

regioselectivity improved remarkably when the reactants were adsorbed on SiO_2 support. Recently, some inorganic solids such as zeolites, clays, alumina, silica gel and magnesium silicate were used as catalysts in the Diels–Alder reactions of cyclopentadiene [10–14]. However, there were few reports about the Diels–Alder reaction of myrcene.

The Diels–Alder reaction can be catalysed by Lewis acids which makes it proceed easily under mild conditions with good selectivity [15–17]. The mode of action of the Lewis acid appears to involve coordination of the carbonyl group of the dienophile with the metal ions of the Lewis acid sites, thus, causing the carbonyl group to become more electron withdrawing. The interaction has the effect of lowering the energy level of the LUMO (Lowest Unoccupied Molecular Orbital) of the dienophiles, enabling it more efficient to overlap with HOMO (Highest Occupied Molecular Orbital) of the diene. Therefore, the reaction proceeds with great ease. The opinion regarding the catalytic mechanism by Lewis acid is consensus, but how to characterize the coordination catalysis from experiment has rarely been reported.

In this paper, we present the reaction results of myrcene with acrolein and with methyl acrylate catalysed by various Lewis acids in the absence of solvent. Both the reaction rate and the ‘*para/meta*’ regioselectivity were greatly enhanced. The high regioselective ‘*para*’ adducts were obtained by choosing the appropriate Lewis acid catalysts and reaction temperature. The interactions between acrolein with ZnCl_2 and methyl acrylate with AlCl_3 were

first investigated by Ultraviolet spectrum (UV), proton nuclear magnetic resonance spectrum (^1H NMR) and IR spectrum.

2. Experimental

2.1. Preparation of myrcene

Myrcene was prepared by cracking β -pinene ($\geq 98\%$) in a continuous flow reactor at 723 K under evacuation [18]. The cracking products were analysed by a Shanghai-1102 chromatograph fitted with FID detector. The column of the quartz capillary was 25 m long (0.25 mm i.d.) with SE-30 as fixed phase. Nitrogen was used as a carrier gas. The temperature in the injector and the detector were 200°C and 180°C, respectively. The oven temperature was 120°C. The compositions of the cracking products were myrcene (80%), β -pinene (4.0%), menthadiene (4.9%), and limonene (11.0%). The retention times were: 3.54 min for myrcene, 3.65 min for β -pinene, 3.88 min for menthadiene, and 4.10 min for limonene.

2.2. Preparation of catalysts

All the catalysts (with exception of AlCl_3 and FeCl_3 being AR grade chemical reagent) were prepared by using dichlorosulfoxide (SOCl_2) to dehydrate crystal water in their chlorinates, the left SOCl_2 was then removed by distillation under vacuum. These anhydrous chlorides were kept in a vacuum desiccator over night prior to use.

2.3. General reaction procedures

Acrolein and methyl acrylate were dried and purified according to the standard procedures. The dried flask were charged with the catalyst (3% mol, based on myrcene) and acrolein (6.16 g, 0.11 mol) or methyl acrylate (9.46 g, 0.11 mol) under nitrogen with vigorously stirring in a magnetic stirrer. After the mixture was heated at the specified temperature, myrcene (18.0 g, 0.10 mol) was added via a syringe. The reaction was monitored by gas chromatography (FID, SE-30 column, 25 m × 0.25 mm, nitrogen as a carrier gas, injector temperature 200°C, the detector temperature 180°C, oven temperature program 120°C (4 min) → 24°C/min → 190°C (9 min), using *trans*-naphthene as an internal standard substance. The retention times were: 6.78 min for *trans*-naphthene, 12.33 min for ‘*para*’ adduct 3a, 12.01 min for ‘*meta*’ adduct 4a, 15.93 min for ‘*para*’ adduct 3b, 15.10 min for ‘*meta*’ adduct 4b.

2.4. Characterization of interaction of dienophile with Lewis acids

2.4.1. Determination of ultraviolet (UV)

A standard solution (100 ml) was prepared with 0.644 g acrolein and using *n*-heptane as the solvent. Then, anhydrous ZnCl₂ (0.2 g) was added into the half (50 ml) of the above standard solution. The solution containing ZnCl₂ was dispersed by ultrasonic oscillation at room temperature for 0.5 h. The clear liquor (1 ml) was taken from the solution and diluted to 1000 times with *n*-heptane. The standard solution of acrolein (1 ml) was also diluted to 1000 times with *n*-heptane. Then, the UV spectra of the diluted solutions were recorded on Perkin-Elmer λ-17 Ultraviolet-visible spectrometer. Another standard solution (100 ml) was prepared with 2.140 g methyl acrylate and using *n*-heptane as the solvent. AlCl₃ (0.63 g) was then added into half (50 ml) of the above standard solution. The latter procedure was the same as the above.

2.4.2. Determination of ¹HNMR and IR spectrum

Acrolein and anhydrous ZnCl₂ with the same concentration as used in the Diels–Alder reaction were added into a flask and the mixture was then stirred in a magnetic stirrer for 0.5 h. The clear liquor was taken from the solution. The ¹HNMR spectra of the acrolein with ZnCl₂ as well as the free acrolein were measured at room temperature using a Bruker AC-80 nuclear magnetic resonance spectrometer. CDCl₃ was used as the solvent. The IR spectra of the acrolein with ZnCl₂ and the free acrolein were recorded on Perkin-Elmer 783 Infrared spectrometer. Similarly, The ¹HNMR and IR spectra of the methyl acrylate with AlCl₃ and the free methyl acrylate were measured, respectively.

3. Results and discussion

3.1. Thermal reaction

The results of the reaction between myrcene (1) with acrolein (2a) and myrcene with methyl acrylate (2b) at different temperatures without any catalyst are given in Table 1. In the thermal reaction, it can be predicated by considering the frontier orbitals contributions as well as the reported data for other 2-substituted 1,3-diene [14,15], the yield of ‘*para*’ adduct is more than ‘*meta*’ adduct. It is worth noting that the ‘*para/meta*’ regioselectivity is independent on the reaction temperature. The selectivity of cycloadducts is decreased with increasing the reaction temperature. The reason could be that myrcene containing long branch chain is easily polymerized at high temperature. Thus, it cannot be achieved to synthesize ‘*para*’ adduct high regioselectively by increasing temperature.

At the same reaction temperature, acrolein gives higher yield of cycloadducts and ‘*para/meta*’ regioselectivity than methyl acrylate when they are used as dienophiles. The

Table 1

The results of thermal reaction between myrcene (1) and acrolein (2a) or methyl acrylate (2b) at different temperature^a

Temperature (°C)	Conversion of myrcene (%)		Selectivity of cycloadduct (%)		Regioselectivity (<i>p/m</i>)	
	A ^b	B ^c	3a + 4a	3b + 4b	3a/4a	3b/4b
30	6.2	trace	99.2	–	2.6	–
45	15.6	3.2	97.0	97.5	2.6	2.0
60	45.6	14.6	91.2	93.1	2.6	2.0
140	66.4	48.5	76.3	80.1	2.6	2.0

^amyrcene: acrolein = 1:1.1 (mole ratio), reaction time is 6 h.^bin the Diels–Alder reaction between myrcene and acrolein.^cin the Diels–Alder reaction between myrcene and methyl acrylate.*p/m*—*para/meta*

results indicate that acrolein is more active than methyl acrylate in the thermal reaction.

3.2. Effect of different Lewis acid catalysts on the '*para/meta*' regioselectivity

Table 2 shows that various Lewis acid catalysts can make the conversion of myrcene and the '*para/meta*' regioselectivity improve in different values, but the selectivity of cycloadducts decreases comparing with the thermal reaction. It is well known that the unsaturated aldehyde can also be easily dimerized in the presence of Lewis acid catalyst. The amount of dimerization is proportional to the Lewis acid strength. The order of Lewis acid strength of various catalysts is as follows: AlCl₃ > FeCl₃ > ZnCl₂ > CuCl₂ > CuCl.

In the Diels–Alder reaction between myrcene and acrolein, the Lewis acid strength of the catalysts has different influence on the reaction

rate, the selectivity of cycloadducts, and the '*para/meta*' regioselectivity. Although the high regioselectivity of the '*para*' myrac aldehyde (3a) can be obtained over the strong Lewis acid catalysts, such as AlCl₃ and FeCl₃, but the selectivity of cycloadducts is too low and the conversion of myrcene is decreased adversely. The reason may be that the strong Lewis acid easily leads to acrolein dimerization and myrcene oligomerization. When CuCl₂ is used as a catalyst, the selectivity of cycloadducts also becomes very low even if the acid strength is weaker than ZnCl₂.

The anhydrous ZnCl₂ shows the best catalytic activity as well as higher selectivity of cycloadducts and '*para/meta*' regioselectivity than other chlorinates. It could be due to the property of its mid-strong Lewis acid.

CuCl has the lowest catalytic activity and the regioselectivity among all the catalysts. This is due to its acid strength too weak.

Table 2

The results of myrcene (1) reacted with acrolein (2a) or methyl acrylate (2b) catalyzed by various Lewis acids^a

Catalyst	Conversion of myrcene (%)		Selectivity of cycloadduct (%)		Regioselectivity (<i>p/m</i>)	
	A ^b	B ^c	3a + 4a	3b + 4b	3a/4a	3b/4b
None	45.6	14.6	91.2	93.1	2.6	2.0
AlCl ₃	50.7	96.6	45.4	70.4	10.6	4.8
FeCl ₃	53.6	86.7	56.9	75.0	8.3	4.7
ZnCl ₂	85.4	56.8	82.9	80.3	8.3	4.2
CuCl ₂	58.1	45.5	56.6	58.1	3.3	2.6
CuCl	53.8	16.6	85.8	85.5	3.1	2.2

^{a,b,c}Same as in Table 1, reaction temperature is 60°C.*p/m*—*para/meta*

Table 3
Effect of temperature on the catalytic reaction^a

Temperature (°C)	Conversion of myrcene (%)		Selectivity of cycloadduct (%)		Regioselectivity (<i>p/m</i>)	
	A ^b	B ^c	3a + 4a	3b + 4b	3a/4a	3b/4b
20	33.1	61.7	95.6	92.1	16.2	11.6
30	82.7	84.4	92.7	85.0	15.0	12.4
45	84.4	95.0	88.6	76.5	13.4	7.4
60	85.4	96.6	82.9	70.4	8.3	4.8

^aSame as in Table 1, the reaction of myrcene (1) with acrolein (2a) and methyl acrylate (2b) is catalyzed by ZnCl₂ and AlCl₃, respectively.

^{b,c}Same as in Table 1.

p/m—*para/meta*

Methyl acrylate is a less active dienophile than acrolein in the Diels–Alder reaction. So, the methyl acrylate is more difficult to be dimerized than acrolein in the presence of the strong Lewis acid catalyst. When AlCl₃ or FeCl₃ was used as a catalyst, the conversion of myrcene and the selectivity of cycloadducts enhanced more than that of acrolein used as a dienophile, but the '*para/meta*' regioselectivity did not increase significantly. According to the results in Table 2, anhydrous AlCl₃ showed the best catalytic properties in the Diels–Alder reaction of myrcene and methyl acrylate.

The results of the catalytic reaction show that the Lewis acid strength of selected catalysts should match the activity of dienophiles. Acrolein is more active and more easily dimerized than methyl acrylate on the strong acidic centers and thus it needs the mid-strong Lewis acid catalyst, such as ZnCl₂, and methyl acrylate needs the strong Lewis acid catalyst, such as AlCl₃, for the purpose of synthesizing '*para*' adduct high regioselectively.

3.3. Effect of reaction temperature on the '*para/meta*' regioselectivity

The reaction temperature, which cannot change the '*para/meta*' regioselectivity in the thermal reaction (Table 1), has a remarkable effect on the catalysed reaction by Lewis acid (presented in Table 3). The '*para/meta*' regioselectivity and the selectivity of cycloadducts

decrease with increasing the reaction temperature.

3.4. The interaction of dienophile with Lewis acid characterized by UV, ¹HNMR, and IR spectrum methods

The interaction between myrcene, acrolein, and methyl acrylate with ZnCl₂ and AlCl₃, respectively, are studied by UV, ¹HNMR, and IR spectra. No characteristic change of spectroscopy was found between myrcene and ZnCl₂ or AlCl₃. Thus it is considered that the dienophile is activated by the Lewis acid catalyst.

3.4.1. UV spectrum

It is well known that the catalytic action in the Diels–Alder reaction by Lewis acid is due

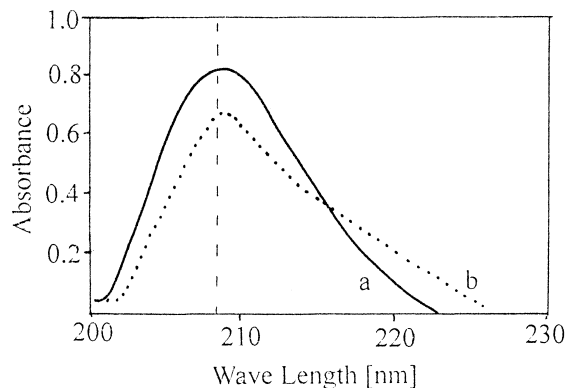


Fig. 1. UV spectra of acrolein (a) and acrolein with addition of ZnCl₂ (b).

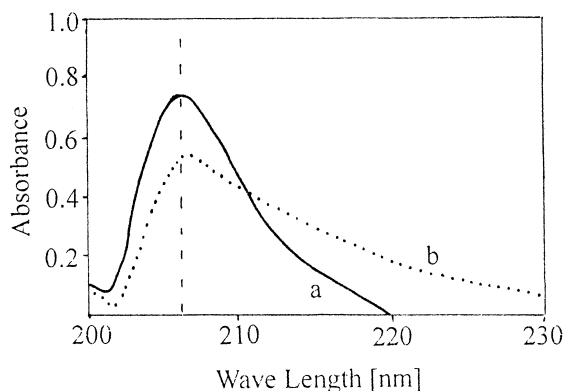


Fig. 2. UV spectra of methyl acrylate (a) and methyl acrylate with addition of AlCl_3 (b)

to the formation of coordination between the Lewis acid and the dienophile. As it can be seen, when acrolein and methyl acrylate interacted with ZnCl_2 and AlCl_3 , respectively, the absorbance of the dienophiles decreases and the absorbed maximum peak of carbonyl shifts to the longer wave region (presented in Figs. 1 and 2 and Table 4). They are described by the coordination between the carbonyl of the dienophile and Lewis acid site. The interaction results in a part of electron cloud above the $\text{C}=\text{C}$ bond having shifted to the electron withdrawing group in the dienophile. The following ^1H NMR and IR spectra have provided direct evidences for this behavior.

3.4.2. ^1H NMR spectrum

The chemical shifts of all the protons' signals of the dienophiles in the absence and in the presence of ZnCl_2 and AlCl_3 are given in Tables 5 and 6. As expected, the coordination occurs via the carbonyl group and Lewis acid

Table 4
Comparison of UV spectra results

Dienophile	C (mg/l)	λ_{max} (nm)	Absorbance
Acrolein	6.44	207.4	0.837
Acrolein + ZnCl_2	6.44	208.2	0.620
Methyl acrylate	21.40	206.2	0.706
Methyl acrylate + AlCl_3	21.40	206.7	0.517

Table 5
 ^1H chemical shift data for acrolein and acrolein with addition of ZnCl_2

H number	Acrolein (ppm)	Acrolein with addition of ZnCl_2 (ppm)	$\Delta\delta$ (ppm)
$=\text{CH}_2$	6.245	6.469	+0.224
$=\text{CH}$	6.581	6.808	+0.227
$-\text{CHO}$	9.620	9.848	+0.228

site. So, all the protons' chemical shifts of acrolein and methyl acrylate are moved to downfield by the addition of ZnCl_2 and AlCl_3 , respectively. For example, comparing with the free acrolein, the protons' chemical shift in the $=\text{CH}_2$, $=\text{CH}$, and $-\text{CHO}$ groups increase $\Delta\delta = 0.224$, 0.227 , and 0.228 ppm, respectively, when ZnCl_2 was added into acrolein. Comparing with the free methyl acrylate, all the protons' chemical shifts in the $=\text{CH}_2$, $=\text{CH}$, and $-\text{OCH}_3$ groups increase $\Delta\delta = 0.136$, 0.076 , and 0.079 ppm, respectively, with addition of AlCl_3 into methyl acrylate. The protons' signals shift to downfield are attributed to the electron cloud above $\text{C}=\text{C}$ bond deviating to the electron withdrawing group.

As can be seen from the Tables 5 and 6, there is a large difference in the magnitude of the chemical shift changes ($\Delta\delta$) between the two dienophiles when they interact with ZnCl_2 and AlCl_3 , respectively. The $\Delta\delta$ value of acrolein with ZnCl_2 is more than that of methyl acrylate with AlCl_3 . We can conclude that the degree of coordination of acrolein with ZnCl_2 is stronger than that of methyl acrylate with AlCl_3 . It is

Table 6
 ^1H chemical shift data for methyl acrylate and methyl acrylate with addition of AlCl_3

H number	Acrolein (ppm)	Acrolein with addition of ZnCl_2 (ppm)	$\Delta\delta$ (ppm)
$=\text{CH}_2$	5.727	5.863	+0.136
$=\text{CH}$	6.555	6.631	+0.076
$-\text{OCH}_3$	3.748	3.827	+0.079

consistent with the increased ‘*para/meta*’ regioselectivity of the Diels–Alder reaction catalysed by the two Lewis acids, respectively.

3.4.3. IR spectrum

The complex formation between carbonyl and Lewis acid sites requires perturbation of the C=O bond, and the strength of the donor–acceptor bond must be reflected in the extent of polarization of the C=O bond stretching force constant or by the change in the C=O bond stretching frequency [19]. The IR spectra of the dienophiles and their interaction with Lewis acid were also investigated.

The major change (presented in Fig. 3), compared with the spectra of the free acrolein, is the carbonyl stretching frequency decreased from 1690 cm^{-1} in the free acrolein to 1680 cm^{-1} in the acrolein with the addition of ZnCl_2 . The frequency of C=O has shifted about 10 cm^{-1} to the low wave number region and a weak

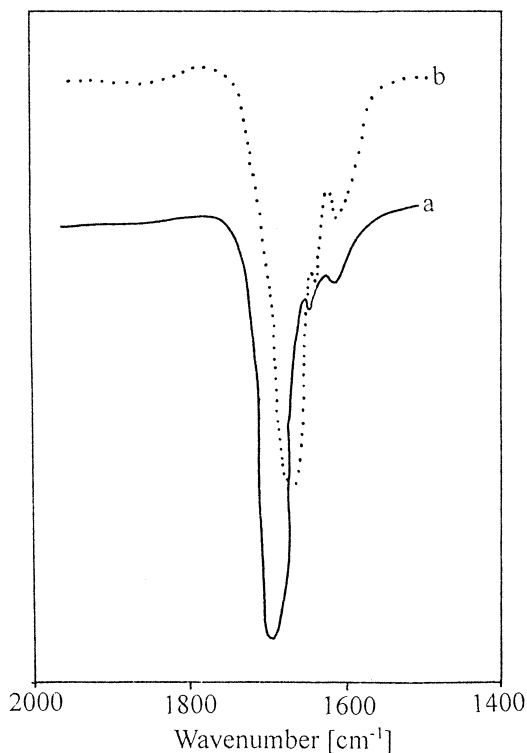


Fig. 3. IR spectra of acrolein (a) and acrolein with addition of ZnCl_2 (b).

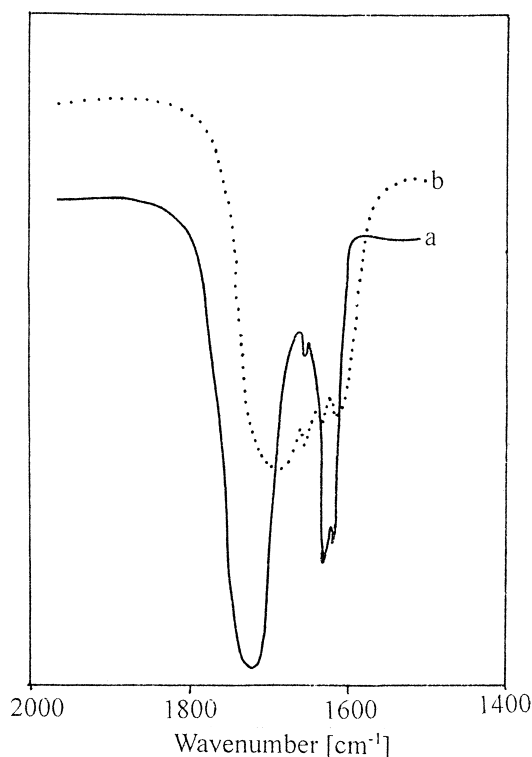
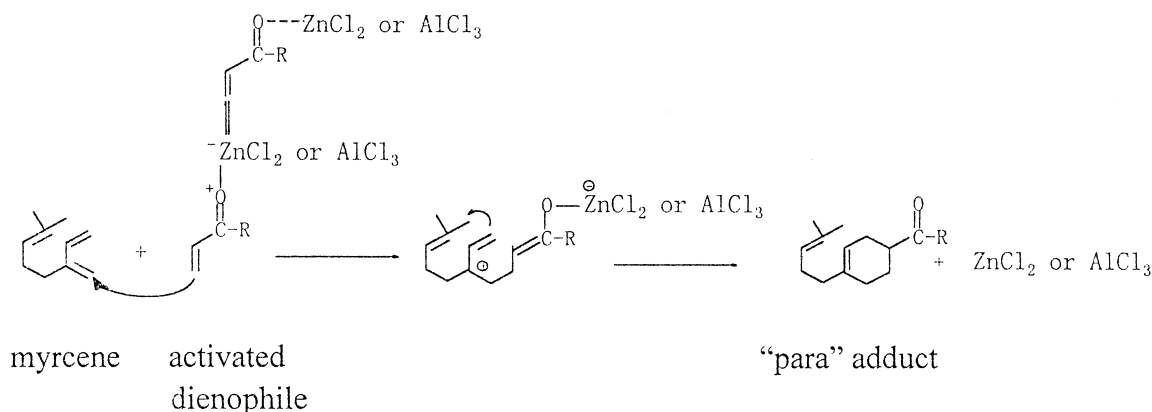


Fig. 4. IR spectra of methyl acrylate (a) and methyl acrylate with addition of AlCl_3 (b).

Zn-Cl vibration band appeared at about 380 cm^{-1} by the addition of ZnCl_2 to the acrolein. Cativiela et al. assigned the frequency shift of C=O to low wave number region to be the coordination of metal ion with the carbonyl of the dienophile [20].

The IR spectra of the free methyl acrylate and the coordinated methyl acrylate with AlCl_3 are presented in Fig. 4. The principal changes, compared with the spectra of the free methyl acrylate, are the carbonyl stretching frequency shifted from 1760 cm^{-1} in the former to 1750 cm^{-1} and a weak Al–Cl vibration band appeared at about 490 cm^{-1} in the AlCl_3 coordinated methyl acrylate. The band of C=O not only shifted about 10 cm^{-1} to the low wave number region but also appeared a broad carbonyl band by the addition of AlCl_3 into the methyl acrylate. The width of this band is assigned to be several kinds of carbonyl groups coordinated by AlCl_3 .



Scheme 2. The mechanism of the Diels–Alder reaction catalyzed by Lewis acid.

All these experiment results indicate that the mechanism of the Diels–Alder reaction catalysed by Lewis acids is that the carbonyl of dienophile is coordinated with Lewis acid sites (Scheme 2). The activated dienophile makes its electrophile of β -C atom increase, and get more favorable to attack the electron-rich carbon of conjugated diene of myrcene. Consequently, the attack way is advantageous for producing ‘para’ adduct high regioselectively, and also enhance the reaction rate.

4. Conclusion

The Diels–Alder reactions of myrcene with acrolein and with methyl acrylate can be accelerated in the presence of Lewis acid catalysts. The regioselectivity is dependent on the Lewis acid strength and the reaction temperature. ZnCl_2 and AlCl_3 are revealed to be efficient catalysts in the high regioselective synthesis of ‘para’ adduct when acrolein and methyl acrylate is used as a dienophile, respectively. The coordination between acrolein and ZnCl_2 or methyl acrylate and AlCl_3 results in the absorbance to decrease and the maximum peak of the dienophiles to shift to the longer wave region in the UV spectra. All the protons’ chemical shifts of the dienophiles to downfield in the ^1H NMR spectra and the $\text{C}=\text{O}$ stretching vibra-

tion shifting to a lower wave number region in the IR spectra are observed. A reasonable catalysis mechanism is proposed.

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