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The Metal-Ion-Catalyzed Alcoholysis of β-Dicarbonyl Compounds[1)]

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The alcoholysis of β-dicarbonyl compounds of the type $CH_3COCHRCOR'$ is catalyzed by a variety of metal ions. In the presence of a large excess of β-diketone compared with metal ions, the rate is given by the expression: rate$=k_{obsd}[M^{2+}][ROH]$. The values of k_{obsd} decrease with M^{2+} in the order $Zn^{2+}>Co^{2+}>Ni^{2+}>Cu^{2+}$. The reaction rate is remarkably affected by the substituents (R,R′), the kinds of alcohol and solvent used, the addition of a chelating agent, and also by the counter anion of the metal ion. The alcoholysis proceeds more slowly in CH_3OD than in CH_3OH by a factor of 1.4. These are interpreted in terms of a mechanism in which the β-dicarbonyl compound coordinated to a metal ion is attacked by the alcohol which is also coordinated to the metal ion to cleave the C^2–C^3 or C^3–C^4 bond of the dicarbonyl compound. A convenient method for the preparation of β,γ-unsaturated ketones and esters is provided by the alcoholysis of alkenyl substituted β-dicarbonyl compounds in the presence of zinc acetate.

Acid- and base-catalyzed cleavages of β-diketones and ketoesters are well known.[2)] Alkaline alcoholysis of acetylacetone has been previously studied by Kutz and Adkins,[2d)] and Pearson and Sandy.[2h)] Recently, we have found that certain metal salts and chelates catalyze the alcoholysis of 3-(1-alkenyl)-2,4-pentanediones to give β,γ-unsaturated ketones.[3)]

It has been shown that the β-diketo compounds react with a metal ion to form a certain type of chelate and consequently are activated toward the electrophilic attack of various reagents.[4–9)] On the other hand, it has been reported that metal complexes containing both methoxy and β-dicarbonylate ions as ligands, $[M(acac)(CH_3O)(CH_3OH)_x]$,[10–12)] effectively catalyze the ester exchange reactions of ethyl picolinate, ethyl 2-pyridylacetate, and ethyl esters of α-amino acids.[13)]

In this paper, the metal-ion-catalyzed alcoholysis of 3-substituted β-dicarbonyl compounds will be discussed in more detail; we will propose a possible mechanism involving an intermediate in which both β-dicarbonyl compound and alcohol are coordinated to a metal ion.

Results and Discussion

Kinetic Studies. The dependences of the reaction rate on the concentration of zinc acetate, 3-(1-butenyl)-2,4-pentanedione, and methanol have been investigated. The results are shown in Table 1 and Fig. 1. It is seen that the metal-ion-catalyzed alcoholysis of 3-substituted β-diketones follows the rate equation: rate$=k_{obsd}$ [Metal ion] [Alcohol]. The rate of alcoholysis is independent of [β-diketone] under the present condition of [β-diketone]≫[metal ion]. This may be due to the fact that the metal ion exists only as a metal chelate of β-diketone and the reaction species is not the metal ion itself but the metal chelate. The band of 3-(1-butenyl)-2,4-pentanedione at 288 nm was found to shift to 303 nm by the addition of $Zn(OAc)_2$, as shown in Fig. 2. The large red shift should be ascribed to the zinc enolate formation.

Table 1. Alcoholysis of 3-(1-butenyl)-2,4-pentanedione by zinc acetate in methanol at 70 °C (reflux)

Run No.	$[Zn(OAc)_2]\times10^3$ (M)	[β-Diketone]×10 (M)	Rate×10^3 ($M\,s^{-1}$)
1	20.8	13.1	4.41
2	20.1	13.1	4.76
3	13.9	13.1	3.48
4	7.33	13.1	1.79
5	4.54	13.1	1.16
6	0	13.1	0
7	7.33	6.50	1.55
8	7.33	9.75	1.62
9	7.33	19.5	1.70

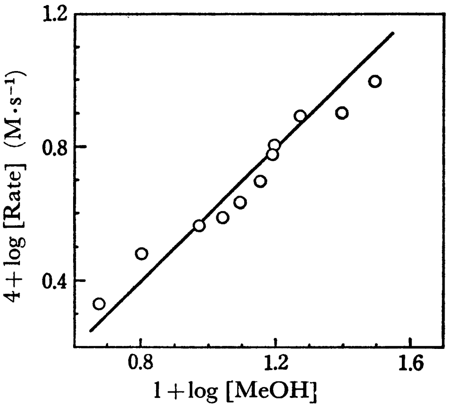


Fig. 1. Plot of log (Rate) *vs.* log $[CH_3OH]$ in dioxane at 70 °C $[Zn(OAc)_2]=7.0\times10^{-3}$ M, [β-Diketone]$=$ 1.31 M.

Effect of 3-Substituent. The effect of the substituent at the 3-position of acetylacetone is shown in Table 2. The rate of alcoholysis of 3-substituted 2,4-pentanediones was found to be markedly affected by the property of the substituent. 3-(1-Butenyl)-2,4-pentanedione showed the highest reactivity and 3-benzyl- or 3-butyl-2,4-pentanedione showed a moderate reactivity. Acetylacetone, however, was inactive toward the alcoholysis. The rate of reaction increases with decrease in activation energy E_a. 3,3-Dimethyl-, 3-benzylidene-, and 3-furfurylidene-2,4-pentanedione which have no labile hydrogen to form the metal enolate showed less or no reactivity in the metal-ion-catalyzed alcoholysis, in contrast to the very high reactivity in alkaline alcoholysis of the 3,3-dialkyl

TABLE 2. EFFECTS OF SUBSTITUENTS ON THE METHANOLYSIS OF 3-SUBSTITUTED 2,4-PENTANEDIONE BY ZINC ACETATE IN DIOXANE

3-Substituent	k_{obsd} (70 °C) × 10^5 (M^{-1} s^{-1})	E_a (kcal mol^{-1})
1-Butenyl	83.8	12.8
Benzyl	12.6	19.4
Butyl	5.25	24.0
Dimethyl	0.32	—
Benzylidene	0	—
Furfurylidene	0	—
None (Acetylacetone)	0	—

TABLE 3. SOLVENT EFFECTS ON THE ALCOHOLYSIS OF 3-(1-BUTENYL)-2,4-PENTANEDIONE

[β-Diketone] = 1.30 M, $[Zn(OAc)_2] = 6.86 \times 10^{-3}$ M
$[CH_3OH] = 1.40$ M

Solvent	k_{obsd} (70 °C) × 10^4 (M^{-1} s^{-1})	E_a (kcal mol^{-1})
Benzene	14.81	16.8
Ethyl acetate	10.73	—
Dioxane	8.38	12.8
Dioxane(+Trien)$^{a)}$	3.57	—
Acetonitrile	6.39	11.0

a) 1.58×10^{-2} M of triethylenetetramine was added.

substituted β-diketone.[2d)]

Solvent Effects. The methanolysis of 3-(1-butenyl)-2,4-pentanedione by zinc acetate was carried out using benzene, ethyl acetate, dioxane, and acetonitrile as diluents. The solvent effects on the reaction are summarized in Table 3. It is clear that the rate is much greater in a nonpolar solvent than in a polar solvent, in spite of the unfavorable activation energy for the former. The reaction cannot be facilitated in a nonpolar solvent. In fact, from the data of Table 1, k_{obsd} in methanol is calculated to be 9.5×10^{-3} M^{-1} s^{-1}, which is larger than in benzene. The solvent effect in Table 3 may be explained as follows: The polar solvent should compete with the alcohol for the occupation of the coordination site of the metal chelate so as to depress the formation of the intermediate (c) as described below.

Effect of Chelating Agent. Addition of a small amount of triethylenetetramine (Trien), which is known as a more effective chelating agent than β-diketone, induces a marked decrease in the reaction rate, as shown in Table 3. This effect may be accounted for by a reduction of the net concentration of the metal ion acting as catalyst.

Effect of Alcohol. As shown in Table 4, the rates of alcoholysis varied with the kind of alcohol used. The order of the reactivity was anti-parallel to that of the basicity as follows: methanol>ethanol>propan-2-ol>*t*-butyl alcohol. The observed reactivity order of the alcohols is attributable to the steric effect rather than the activation energy. This effect and the data of Table 3 seem to suggest that the reaction proceeds *via* the coordination of alcohol to the metal of the β-diketone complex.

TABLE 4. EFFECTS OF ALCOHOL ON THE ALCOHOLYSIS OF 3-(1-BUTENYL)-2,4-PENTANEDIONE IN DIOXANE

[β-Diketone] = 1.30 M, $[Zn(OAc)_2] = 7.0 \times 10^{-3}$ M

Alcohol	k_{obsd} (70 °C) × 10^4 (M^{-1} s^{-1})	E_a (kcal mol^{-1})
Methanol	8.38	12.8
Ethanol	4.37	10.7
Propan-2-ol	0.86	—
t-Butyl alcohol	0.00	—

TABLE 5. EFFECTS OF METAL SALTS ON THE ALCOHOLYSIS OF 3-(1-BUTENYL)-2,4-PENTANEDIONE IN METHANOL

[β-Diketone] = 3.25×10^{-1} M, at 70 °C (reflux)

Metal salt	$k_{obsd} \times 10^4$ (s^{-1})
Cu(OAc)	1.02
$Ni(OAc)_2$	1.93
$Co(OAc)_2$	7.44
$Zn(OAc)_2$	48.7
$Zn(acac)_2$	33.4
$ZnSO_4$	1.83
$ZnCl_2$	1.19

Deuterium Isotope Effect. The alcoholysis of 3-(1-butenyl)-2,4-pentanedione in a large amount of monodeuteriomethanol (CH_3OD) by zinc acetate gave 3,3-dideuterio-4-hepten-2-one, which was identified by means of mass spectra (parent peak, *m/e* 114) and NMR spectra (a practical disappearance of the signal of 4-hepten-2-one at 6.98 τ(2H, d, $-C\underline{H}_2COCH_3$)). The alcoholysis proceeds more slowly in CH_3OD than in CH_3OH by a factor of $k_H/k_D = 1.4$. The isotope effect may be caused by a rapid and reversible reaction, which involves breakage of the O–H (or O–D) bond and is followed by the slow rate-determining step.[15)] The catalysis of divalent metallic ions for the exchange of alcohol hydroxyl protons has been reported.[16)]

Effects of Metal Salts. The activities of metal salts used as the catalyst of the alcoholysis are shown in Table 5. The order of the activity of metal acetates ($M(OAc)_2$) was as follows: Zn(II)>Co(II)>Ni(II)>Cu(II). The observed activity order of $M(OAc)_2$ was anti-parallel with the stability constants[14)] of metal acetylacetonates ($M(acac)_2$). The catalytic activity of a metal ion is altered by its counter anion. The rate constant of $Zn(OAc)_2$ is 40-fold larger than that of $ZnCl_2$. The lower activity of $ZnCl_2$ may be attributed to a reluctance to form metal enolate(A). Kawaguchi *et al.*[17)] reported the presence of a zinc(II) complex, $ZnCl_2$(acacH), which has a tetrahedral structure containing a ketonic molecule of acetylacetone (B). As already shown in Fig. 2, the small change in the absorption spectra of 3-(1-butenyl)-2,4-pentanedione by the addition of $ZnCl_2$ also gives evidence for the reluctance of $ZnCl_2$ to form metal enolate (A). The higher activity of $Zn(OAc)_2$ compared with that of $ZnCl_2$ or $ZnSO_4$ seems to be because the HOAc liberated by chelation is a much weaker acid than HCl or H_2SO_4 and consequently $Zn(OAc)_2$ is more likely to form the metal enolate(A).

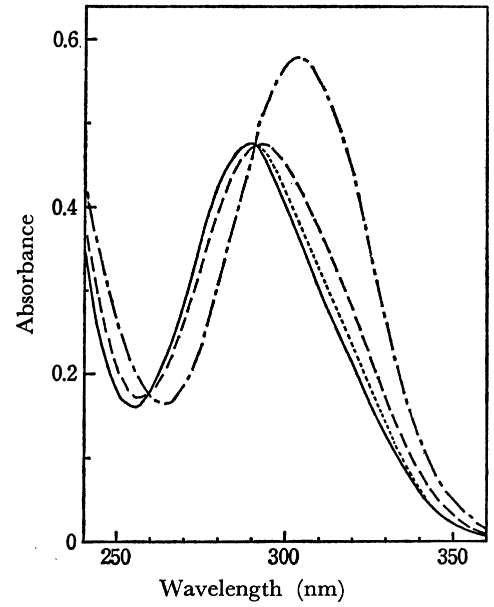


Fig. 2. Absorption spectra of 3-(1-butenyl)-2,4-pentanedione (1.03×10^{-4} M) in the absence and presence of zinc salt in methanol.

——: Absence of zinc salt,
– – –: $[Zn(OAc)_2]=5.11\times10^{-4}$ M,
- - - - -: $[ZnSO_4]=5.18\times10^{-4}$ M,
······: $[ZnCl_2]=6.31\times10^{-4}$ M.

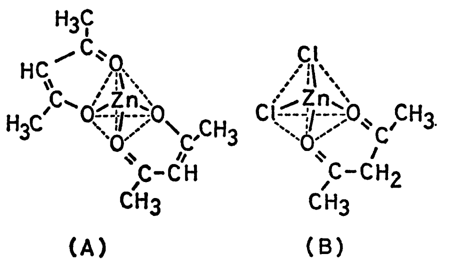


Fig. 3.

The observed effects of metal salts suggest that the formation of metal enolate is essential for a high catalytic activity. However, an extremely stable O–M bond is unfavorable, because the present catalysis presumably proceeds *via* the dissociation of the O–M bond followed by the protonation to carbonyl oxygen to form the intermediate(d) as described below.

Alcoholysis of Unsymmetrical β-Diketones. Unsymmetrical β-diketones, RCO-CHR′-COR″, can be cleaved in either of two ways.[2a,2c,2e] Metal-ion-catalyzed alcoholysis of several 3-(1-butenyl)-4-substituted-2,4-butanediones was carried out in order to find the direction of the cleavage. The results are shown in Table 6, where k_1 is the rate constant of the alcoholysis of the C–COCH$_3$ bond (deacetylation) and k_2 is that of the C–COR bond (deacylation).

An electron-donating substituent increases the rate ratio k_1/k_2. Except for 3-(1-butenyl)-4-phenyl-2,4-butanedione, the direction of cleavage is found to be determined by the strength of the carboxylic acid of the two possible esters: the stronger acid is formed in a larger proportion as in the alkaline hydrolysis reported by Bradley and Robinson.[2a] The effect of phenyl substitution resulting in the k_1/k_2 value of 2.56 may be explained from the viewpoint of steric hindrance.

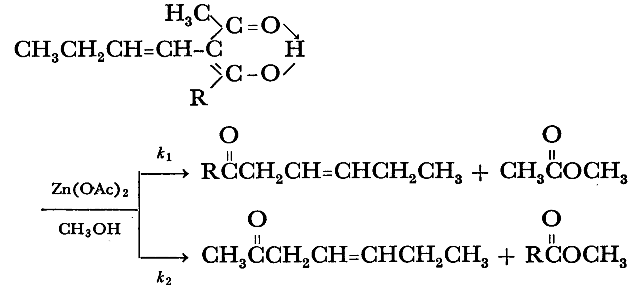
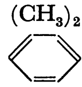
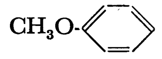


TABLE 6. EFFECTS OF 4-SUBSTITUENT IN THE METHANOLYSIS OF 3-(1-BUTENYL)-4-SUBSTITUTED-2,4-BUTANEDIONE BY $Zn(OAc)_2$

4-Substituent	k_1 (70 °C)$\times10^5$ ($M^{-1}s^{-1}$)	k_2 (70 °C)$\times10^5$ ($M^{-1}s^{-}$)	k_1/k_2
CH$_3$-	41.9	41.9	1.0
(CH$_3$)$_2$CH-	27.1	4.09	6.63
	36.3	14.2	2.56
	6.14	0.414	14.8

Mechanism. On the basis of the experimental results described above, a possible mechanism for the metal-ion-catalyzed alcoholysis of β-diketone may be proposed as follows:

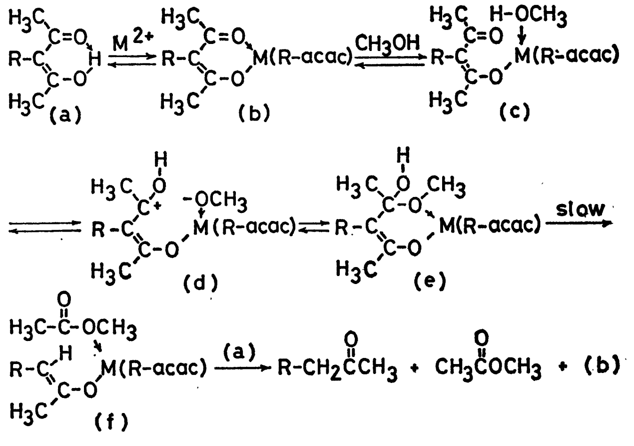
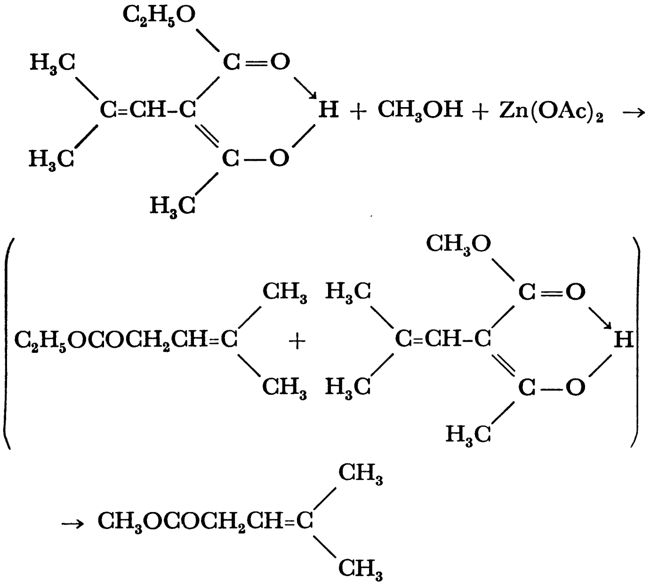


Fig. 4.

The mechanism is consistent with the observed kinetic results and the reaction products. The independence of the rate of alcoholysis from β-diketone concentration, the small or absent reactivity of 3,3-disubstituted-2,4-pentanedione, and the lower activity of zinc chloride suggest that the metal enolate(b) is the reactive species in the present alcoholysis. The presence of a pre-equilibrium (b)+CH$_3$OH$\rightleftharpoons$(e) is supported by the observed kinetic isotope effect and the effects of the kinds of solvent and alcohol on the rate of the alcoholysis. The effects of 3-substituents and solvents on the activation energy E_a may be explained in terms of the stabilization of the intermediate in the transition state of the rate-determining step (e)$\rightarrow$(f). The effect of 4-substituents on the rate ratio k_1/k_2 in unsymmetrical β-diketones shows that the cleavage occurs at the more electron-deficient C–C bond. Monoketone and acetate are liberated from the coordinated site by the ligand exchange with another β-diketone(a) to re-form the metal chelate of β-diketone (b) and the cycle recurs many times.

Alcoholysis of 1-Alkenyl Substituted β-Ketoesters. It was found that in the presence of metal acetate 1-alkenyl substituted β-ketoesters underwent alcoholysis involving an ester exchange to give esters of β,γ-unsaturated carboxylic acid. For example:



The metal-ion-catalyzed ester exchange of β,γ-unsaturated carboxylates formed by the deacetylation was found to proceed much more slowly than that of the parent β-ketoesters. Thus, in the initial stage of the methanolysis, ethyl esters of 1-alkenylacetic acid were formed predominantly as the alcoholysis product. The initial rate of the deacetylation of ethyl (2-methyl-1-propenyl)acetoacetate by the various metal acetates is shown in Table 7.

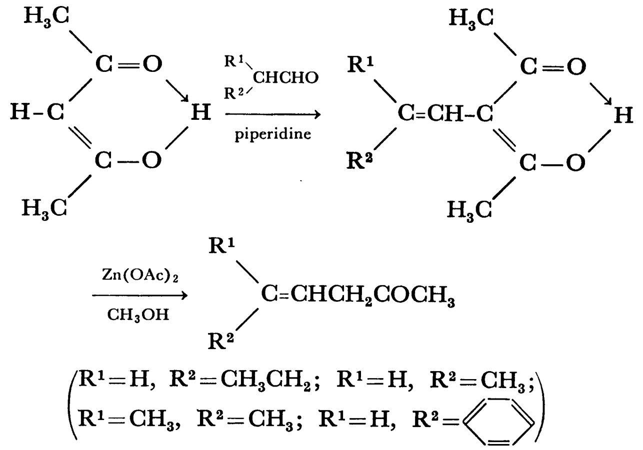
The order of the activities of metal acetates used as the catalyst is as follows: Mn(II)>Cd(II)>Zn(II)>Co(II)>Ni(II)>Cu(II). The observed activity order of $M(OAc)_2$ was again anti-parallel to the stability constants of $M(acac)_2$.

Synthesis of β,γ-Unsaturated Ketones and Esters. It has been known that β,γ-unsaturated ketones are prepared by the steam distillation of an aqueous acidic solution of 3-alkene-2,5-diols,[18] by the acid catalyzed isomerization of α,β-unsaturated ketones,[19] and by several other methods.[20–23] The present reaction seems to be interesting as a general synthetic method of β,γ-unsaturated ketones of the type $RR'C=CHCH_2COCH_3$ starting from aldehyde and acetylacetone, because of the ease of isolation of the β,γ-unsaturated ketone from its reaction mixture by fractional distillation with high purity and a fair yield. Zinc acetate is an efficient catalyst for the alcoholysis of 3-(1-alkenyl)-2,4-pentanediones without catalyzing side reactions such as rearrangements of double bond and alcohol additions.

Table 7. Effects of metal ion on the deacetylation of ethyl (2-methyl-1-propenyl)acetoacetate in methanol

$[\beta\text{-Ketoester}]=2.73\times10^{-1}$ M, $[M(OAc)_2]=7.00\times10^{-3}$ M

Metal acetate	k_{obsd} (70 °C) $\times10^5$ (s^{-1})
$Mn(OAc)_2$	19.1
$Cd(OAc)_2$	9.42
$Zn(OAc)_2$	7.20
$Co(OAc)_2$	2.80
$Ni(OAc)_2$	0.535
$Cu(OAc)_2$	<0.1



It is known that β,γ-unsaturated carboxylic acids are prepared by the condensation of malonic acid with aldehyde followed by decarboxylation[24] and that the esterification of β,γ-unsaturated carboxylic acids is carried out by the reaction of its Ag salt with alkyl iodide.[25] The present reaction seems to provide a more convenient route to the ester of β,γ-unsaturated carboxylic acid in spite of its lower yield.

Experimental

Materials. 3-Substituted-2,4-pentanedione was prepared by the method described in the previous paper.[26] 3,3-Dimethyl-2,4-pentanedione was prepared by the method of Pearson:[2g] bp 68—68.5 °C/18 mmHg, n_D^{23} 1.4283 (lit,[2g] bp 170—173 °C, n_D^{25} 1.4330). Benzoylacetone,[27] isobutyrylacetone,[28] and *p*-methoxybenzoylacetone[29] were allowed to react with butyraldehyde in the presence of piperidine to give Knoevenagel condensates: 3-(1-butenyl)-4-phenyl-2,4-butanedione, bp 107—110 °C/1 mmHg, n_D^{18} 1.5487, yield 52.5%; 3-(1-butenyl)-4-isopropyl-2,4-butanedione, bp 106—117 °C/16 mmHg, n_D^{17} 1.4724, yield 54%: Copper chelate, Found: C, 61.59; H, 7.99%. Calcd for $C_{22}H_{34}O_4Cu$: C, 62.02; H, 8.04%. 3-(1-Butenyl)-4-*p*-methoxyphenyl-2,4-butanedione, bp 133—141 °C/1 mmHg.

The Knoevenagel condensates of ethyl acetoacetate with aldehydes were prepared by a similar method. Ethyl (1-butenyl)acetoacetate, bp 117—120 °C, yield 41%. Ethyl (2-methyl-1-propenyl)acetoacetate, bp 115—117 °C/20 mmHg, yield 33%. Ethyl (1-propenyl)acetoacetate, bp 110—115 °C/20 mmHg, yield 21%.

Metal acetates and other metal salts were G. R. -grade reagents. Alcohols and solvents were purified by the ordinary methods and were distilled before use. Monodeuteriomethanol was supplied by E. Merck Co. and used without further purification.

Kinetic Measurements. An alcoholic solution of β-dicarbonyl compound was allowed to undergo alcoholysis in the presence of a metal salt at the desired temperature. Aliquots of the reaction mixture were withdrawn at regular intervals and analyzed by means of gas-liquid chromatography on a column packed with Apiezone grease L (30%) on chromosorb. A Shimadzu GC-4APT gas chromatograph equipped with an integrator, model ITG-2A, was used as the analyzer. Toluene was usually employed as an internal standard, but in some experiments, cumene, ethyl benzoate, propyl benzoate, or diethyl phthalate was also used. The increase of products was measured as a function of time for various β-dicarbonyl compounds.

Spectral Measurements. The IR spectra were measured as a liquid film by means of a Hitachi Model EPI-G2 infrared spectrometer. The UV spectra were measured using a Shimadzu recording spectrophotometer model UV-200. The NMR spectra were determined by means of a Hitachi Model R-20 spectrometer. Tetramethylsilane was used as the internal standard, and carbon tetrachloride was used as the solvent. The mass spectra were recorded on a Hitachi Model RMU-6E mass spectrometer under the following conditions: chamber voltage 80 V, total emission current 80 μA, vacuum 2×10^{-6} mmHg, sample temp. 160 °C.

Synthesis of β,γ-Unsaturated Ketones. 80 g (0.52 mol) of 3-(1-butenyl)-2,4-pentanedione[26)] and 0.8 g (0.0036 mol) of zinc acetate in 150 ml of methanol were heated under reflux at 70 °C for 16 h. The reaction mixture was subjected to fractional distillation. The volatile fraction is a mixture of methanol, methyl acetate, and a small amount of acetic acid. From the second fraction (bp 60—62 °C/25 mmHg), 4-hepten-2-one[30)] was obtained in a yield of 64% (37 g); its purity was found to be above 99% from glc-analysis by double fractional distillation.

The following 4-alken-2-ones were obtained by the Zn(OAc)$_2$-catalyzed methanolysis of the Knoevenagel condensates of acetylacetone with propionaldehyde, isobutyraldehyde, and phenylacetaldehyde in a similar manner to that described above (yield 60—80%): 4-Hexen-2-one, bp 61—62 °C/52 mmHg (lit,[18)] 45 °C/29 mmHg). n_D^{21} 1.4265. IR spectrum (liquid film): $\nu_{C=O}$ 1710 cm^{-1}. λ_{max}^{MeOH}(C=O) 275 nm. Mass spectrum: *m/e* 98, 83, 55, 43. Semicarbazone (mp 142—143 °C), Found: C, 54.53; H, 8.31; N, 27.32%. Calcd for $C_7H_{13}ON_3$: C, 54.17; H, 8.44; N, 27.07%. 5-Methyl-4-hexen-2-one: bp 61—62 °C/25 mmHg, n_D^{23} 1.4384. IR spectrum(liquid film): $\nu_{C=O}$ 1705 cm^{-1}. λ_{max}^{MeOH} (C=O) 278 nm. Semicarbazone (mp 155—156 °C), Found: C, 56.17; H, 8.65; N, 25.28%. Calcd for $C_8H_{15}ON_3$: C, 56.17, H, 8.65; N, 25.28%. Calcd for $C_8H_{15}ON_3$: C, 56.78; H, 8.93; N, 24.83%. 5-Phenyl-4-penten-2-one: bp 85—87 °C/1 mmHg. n_D^{27} 1.5472. IR spectrum(liquid film); $\nu_{C=O}$ 1708 cm^{-1}. Semicarbazone (mp 151—152 °C), Found: C, 66.97; H, 6.97; N, 19.66%. Calcd for $C_{12}H_{15}ON_3$: C, 66.35; H, 6.91; N, 19.35%.

Synthesis of Esters of β,γ-Unsaturated Carboxylic Acids. The following 1-alkenylacetates were obtained by the Zn(OAc)$_2$-catalyzed ethanolysis or methanolysis of the Knoevenagel condensates of ethyl acetoacetate with butyraldehyde, isobutyraldehyde, and propionaldehyde in a similar manner to that described above: Ethyl 1-butenylacetate, bp 71—72 °C/20 mmHg, yield 14%. n_D^{24} 1.4228. IR spectrum ($\nu_{C=O}$), 1735 cm^{-1}. NMR spectrum (δ, ppm): 1.0 (3H,t), 1.2 (3H, t), 2.0 (2H, m), 2.9 (2H, t), 4.1 (2H, m), 5.5 (2H, m). Benzyl amide (mp 251—252 °C), Found: C, 77.15; H, 8.14; N, 7.03%. Calcd for $C_{13}H_{17}ON$: C, 76.85; H, 8.37; N, 6.90%. Methyl 1-butenylacetate, bp 61—62 °C/20 mmHg, yield 46%. Ethyl (2-methyl-1-propenyl)acetate, bp 67.5—68 °C/18 mmHg, yield 24%. n_D^{24} 1.4286. IR spectrum ($\nu_{C=O}$): 1730 cm^{-1}. NMR spectrum (δ, ppm): 1.2 (3H, t), 1.7 (6H, t), 2.9 (2H, t), 4.1 (2H, m), 5.2 (1H, m). Methyl (2-methyl-1-propenyl)acetate: bp 62—63 °C/18 mmHg, yield 40%. Ethyl propenylacetate: bp 64—66 °C/20 mmHg, yield 6%. n_D^{24} 1.4209. IR spectrum ($\nu_{C=O}$): 1735 cm^{-1}. NMR spectrum (δ, ppm): 1.2 (3H, t), 1.7 (3H, t), 2.9 (2H, t), 4.1 (2H, m), 5.5 (2H, m). Mass spectrum: *m/e* 128, 85, 55, 45.

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