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FORMATION OF β,γ-UNSATURATED KETONES BY THE DEACETYLATION OF 3-(1-ALKENYL)-2,4-PENTANEDIONES CATALYZED BY METAL SALTS[1]

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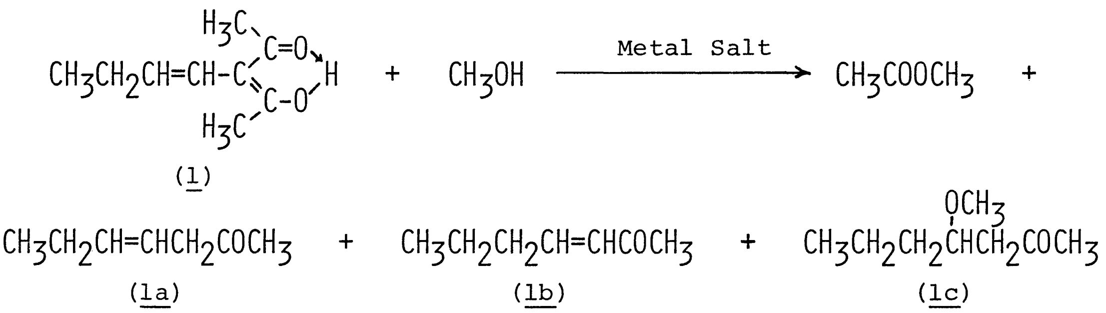
A general method of obtaining β,γ-unsaturated ketone was provided by the deacetylation of 3-(1-alkenyl)-2,4-pentanedione in the presence of metal acetate ($M(OAc)_n$) or acetylacetonate ($M(acac)_n$). $Zn(OAc)_2$, $Pb(OAc)_2$, $Cd(OAc)_2$, $Fe(acac)_3$, and $Zn(acac)_2$ were found to be effective catalysts. 4-Hepten-2-one, 4-hexen-2-one, 5-methyl-4-hexen-2-one, and 5-phenyl-4-penten-2-one were given in high yields.

In a recent paper,[2] we have reported briefly that 3-(1-butenyl)-2,4-pentanedione (1)[3] is deacetylated in methanol with its copper(II) chelate to give 4-hepten-2-one (1a) in a low yield. Metal salts such as $M(OAc)_n$, MCl_n, MSO_4, or $M(acac)_n$ were expected to react with 1 to form certain types of chelate in which the diketo group was co-ordinated to the metal and consequently activated toward nucleophillic attack of methanol. Hence, in the present paper, a further study of the deacetylation of β-diketones catalyzed by various metal salts in place of copper(II) chelate of 1 in alcohols is described to extend our investigation of forming β,γ-unsaturated ketones.

A methanol solution of 1 was heated under reflux at 70°C in the presence of metal salts. The reaction mixture was subjected to distillation and was analyzed by means of gas-liquid chromatography (30% Apiezone grease L column at 140°C). The ketones 1a, 1b, and 1c were obtained together with methyl acetate as shown in Table I. The relative composition and the total yield of 1a, 1b, and 1c were found to be markedly affected by both the kind of metal and that of ligand of the metal salts. The ketone 1a was obtained selectively in a high yield (57.0 - 68.6%) when $Zn(OAc)_2$, $Pb(OAc)_2$, $Cd(OAc)_2$, $Fe(acac)_3$, and $Zn(acac)_2$ were used as the catalyst.



$$CH_3CH_2CH{=}CH{-}C(COCH_3)_2H + CH_3OH \xrightarrow{\text{Metal Salt}} CH_3COOCH_3 + CH_3CH_2CH{=}CHCH_2COCH_3 + CH_3CH_2CH_2CH{=}CHCOCH_3 + CH_3CH_2CH_2CH(OCH_3)CH_2COCH_3$$

Metal salts such as $Mn(OAc)_2$, $Co(OAc)_2$, $Ca(OAc)_2$, $ZnSO_4$, $CaCl_2$, $Cu(OAc)_2$, $Ca(acac)_2$, $ZnCl_2$, and $Cu(acac)_2$ gave also 1a selectively but in lower yields (50.9 - 9.6%).

On the other hand, alternative products (1b and 1c) were obtained mainly together with methyl acetate when $AlCl_3$, $FeCl_3$, $HgCl_2$, $CuCl_2$, and $HgSO_4$ were used as the catalyst. It was found that 1a was convertible into 1b and 1c in refluxing methanol in the presence of $AlCl_3$ or $FeCl_3$. This fact suggests that 1b and 1c might be produced by a subsequent side reaction, although the mechanism of the reaction is yet unclear. Further experiments are required to rationalize the effect of the structure of the metal salt on the catalytic activity in the deacetylation.

Table I. The Deacetylation of 1 with Metal Salts

$[1]=1.55\times10^{-2}$mole/l, [Metal Salt]$=3.08\times10^{-4}$mol/l, 70°C, 48hr in metanol

Metal Salt	Yield (%)			
	1a	1b	1c	Total
$Cd(OAc)_2$	61.7	4.9	1.0	67.6
$Pb(OAc)_2$	60.3	3.8	2.5	66.6
$Zn(OAc)_2$	57.0	7.6	0.6	65.2
$Fe(acac)_3$	68.6	-	-	68.6
$Zn(acac)_2$	68.6	-	-	68.6
$AlCl_3$	6.6	24.9	20.3	51.8
$FeCl_3$	3.2	24.3	22.2	49.7
$HgCl_2$	1.9	17.7	29.6	49.2
$HgSO_4$	2.0	32.5	3.7	38.2

The deacetylation of 1 was carried out in various alcohols. The results obtained are shown in Table II. The rate of the deacetylation was decreased in the order, methanol > ethanol > isopropyl alcohol > tert-butyl alcohol, using either $Cd(OAc)_2$ or Cu(II) chelate of 1 as the catalyst, which gave 1a predominantly as the deacetylation product. The deacetylation of 1 in monodeuteriomethanol gave 3,3-dideuterio-4-hepten-2-one (1a'), which was identified by means of mass spectra (parent peak, m/e 114) and NMR spectra (a practical disappearance of the signal of 1a at 6.98τ(2H,d, $-C\underline{H}_2COCH_3$)).

$$\underline{1} + CH_3OD \xrightarrow{Zn(OAc)_2} \underset{(\underline{1a}')}{CH_3CH_2CH{=}CHCD_2COCH_3} + CH_3COOCH_3$$

When other solvents such as dioxane, tetrahydrofuran, benzene, toluene, or ethyl acetate were used in place of an alcohol, the deacetylation of 1 could not be observed.

The deacetylation of various 3-substituted-2,4-pentanediones was carried out in methanol in the presence of $Zn(OAc)_2$ or $Cu(OAc)_2$. The results obtained are shown in Table III. 3-Alkenyl- and 3-alkyl-2,4-pentanedione gave the corresponding substituted acetones. Attempts to deacetylate from acetylacetone(9), 3-benzylidene-2,4-pentanedione(7), and 3-furfurylidene-2,4-pentanedione(8) were unsuccessful and starting mate-

Table II. The Deacetylation of 1 in Various Alcohols

[1]=1.55×10^{-2} mol/l, [Metal Salt]=3.08×10^{-4} mol/l, 70°C, 48hr

Alcohols	Yield of 1a (%)	
	$Cd(OAc)_2$	Cu(II) Chelate of 1
Methanol	67.6	26.1
Ethanol	51.0	19.0
Isopropyl alcohol	13.0	11.1
tert-Butyl alcohol	0	5.0

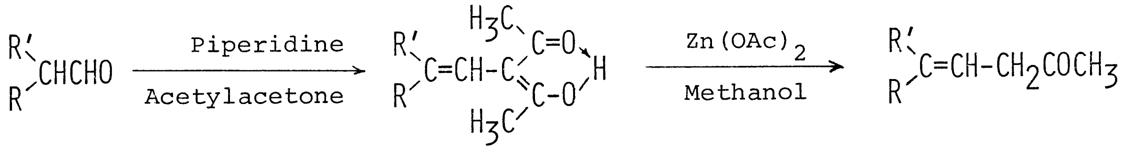
Table III. The Deacetylation of Various β-Diketones in Methanol

[β-Diketone]=1.55×10^{-2} mole/l, [$M(OAc)_2$]=3.08×10^{-4} mole/l, 70°C, 48hr

3-Substituted-2,4-pentanedione		Product	Yield (%)	
No	3-Substituent		$Zn(OAc)_2$	$Cu(OAc)_2$
1	1-Butenyl	4-Hepten-2-one (1a)[2)]	65.2	16.9
2	1-Propenyl	4-Hexen-2-one (2a)[5)]	82.4	14.3
3	2-Methyl-1-propenyl	5-Methyl-4-hexen-2-one (3a)[6)]	76.6	--
4	Styryl	5-Phenyl-4-penten-2-one (4a)[7)]	65.6	--
5	n-Butyl	2-Heptanone (5a)	67.3	trace
6	Benzyl	4-Phenyl-2-butanone (6a)	82.5	trace
7	Benzylidene	---	0	0
8	Furfurylidene	---	0	0
9	None (Acetylacetone)	---	0	0

rials were recovered unchanged.

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-diol,[5)] by the acid catalyzed isomerization of α,β-unsaturated ketone,[8)] and by several other methods.[9-13)] Each of these methods suffers at least one serious disadvantage, i.e. difficulty of isolation of the β,γ-unsaturated ketone from its reaction mixture by fractional distillation. The present reaction, therefore, seems to be interesting as a synthetic method of β,γ-unsaturated ketones of the type $RR'C{=}CHCH_2COCH_3$ starting from aldehyde and acetylacetone. A detailed mechanistic study is now in progress.



1 and 1a : R = H ; R' = CH_3CH_2 , 2 and 2a : R = H ; R' = CH_3

3 and 3a : R = R'= CH_3 , 4 and 4a : R = H ; R' = 

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7) bp 85-87°C/1mmHg, n_D^{27} 1.5472, $\nu_{C=O}$(neat) 1708 cm^{-1}, λ_{max}^{MeOH} 275^{sh},284, 293 nm, MS(Parent Peak) m/e 160.
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