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Aldol Condensations with Metal(II) Complex Catalysts

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Aldol condensations of aldehydes with ketones catalyzed by the first-row transition metal(II) complexes have been widely studied. Complexes of Co(II), Ni(II), Cu(II), and Zn(II) acetates with 2,2′-bipyridine were effective catalysts to afford cross-aldol condensation products, α,β,-unsaturated ketones, in high yields without any self-condensation products. The reaction of 2-butanone, unsymmetrical aliphatic ketone, with benzaldehyde took place regioselectively to give base-catalyzed-type products.

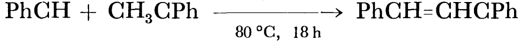
Aldol condensation reactions catalyzed by transition metal(II) ions have been reported by several workers.[1] For example, Akabori reported that the aldol condensation of bis(glycinato)copper(II) with aldehydes gave copper(II) complexes of serine and so on under basic conditions.[1] In these reactions, however, no reaction products could be liberated without removing the Cu(II) ion from the complexes.

Recently, we have found that the copper(II)–2,2′-bipyridine(bpy) complex catalyzes the aldol condensation of aldehydes with ketones under neutral conditions to afford liberated α,β-unsaturated ketones without any by-product.[2] The product yield in this reaction increases remarkably in comparison with that catalyzed by the copper(II) ion itself. On the other hand, bpy itself has no catalytic activity at all.

It is of great importance that the reaction is largely affected by the kinds of ligands and counter ions of the complexes. We have examined the effects of the first-row transition metal(II) ions, various kinds of ligands, and some counter ions on the reactions. Furthermore, in order to ascertain the scope and limitation of the aldol condensations promoted by the metal(II) complexes, the reactions of various kinds of aldehydes and ketones were carried out. The results will be described in this paper.

Results and Discussion

Effects of Ligands on the Catalysis. In this study, the condensations of benzaldehyde and acetophenone in the presence of Cu(II) complexes were carried out. In order to examine the effects of ligands on the catalyst in the reaction, twelve kinds of ligands(L) were employed.

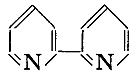
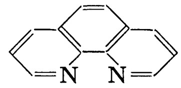
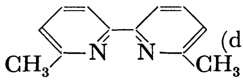
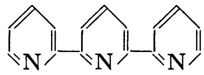


$$\mathrm{Ph\overset{O}{\overset{\|}{C}}H + CH_3\overset{O}{\overset{\|}{C}}Ph \xrightarrow[80\,^\circ C,\ 18\,h]{Cu(II)L,\ DMF} PhCH{=}CH\overset{O}{\overset{\|}{C}}Ph}$$

A solution of benzaldehyde, acetophenone, copper(II) acetate, and a ligand in DMF was heated at 80 °C for 18 h. The complex formation in the solution was observed by means of the color change from the green of copper(II) acetate to other colors when the ligands were added. The amount of the complex catalyst was 16 mol% of the benzaldehyde used. The reaction product was chalcone, and the yield was determined by GLC analysis. The results are shown in Table 1.

The reaction catalyzed only by copper(II) acetate gave chalcone in a 53% yield. Then, upon the addition of Group I ligands, the yields decreased remarkably (Table 1). These carboxylic acids seem to be unfavorable ligands for the reaction. When Group II ligands (aliphatic amines) were employed, the yields of chalcone (53—54%) were similar to the case with copper(II) acetate itself. These results indicate that these aliphatic-amine ligands have no "ligand effect" on this reaction. When Group III ligands (tertiary aromatic amines) were employed, chalcone was formed in increased or decreased yields (22—82%). Such ligands as 2,2′-bipyridine(bpy), 1,10-phenanthroline (phen), and pyridine(py) were found to be fairly effective, since the yields increased predominantly (70—82%). On the other hand, such ligands as 6,6′-dimethyl-2,2′-bipyridine(dm-bpy) and 2,2′:6′,2″-terpyridine(terpy) seemed to inhibit the reactions (22—30%); this could be ascribed as steric hindrance by the bulky ligand molecules. These amines themselves did not catalyze the reaction.

Table 1. The yields of chalcone in the aldol condensation of benzaldehyde and acetophenone with Cu(II) complexes

Group No.	Ligand	Color of complex	Yield of chalcone/%[a)]
	None	green	53
I	$(COOH)_2$	blue	0[b)]
	$HSCH_2COOH$	black	0[b)]
	NH_2CH_2COOH	red	17
II	$NH_2CH_2CH_2NH_2$	blue	53
	$(NH_2CH_2CH_2)_2NH$	blue	53
	$(CH_2NHCH_2CH_2NH_2)_2$	blue	54
	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	dark green	53
III	 (py)	blue	70
	 (bpy)	blue	82
	 (phen)	blue	82
	 (dm-bpy)	yellow green	30
	 (terpy)	blue	22

a) Based on the amount of benzaldehyde. b) Heterogeneous solution.

Effects of Metal Ions on the Catalysis. Next, we

Table 2. The yields of chalcone in the reactions of benzaldehyde and acetophenone in the presence of various metal$(OAc)_2$-bpy complexes

$(bpy)_n$ / M(II)	Product yield/%[a]					
	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
$n=0$	11	15	31	4	53	43
$n=1$	26	51	93	100	82	100
$n=2$	45	17	84	100	93	68
$n=3$	22	47	67	66	88	82

a) Based on the amount of benzaldehyde and determined by GLC. b) The reaction conditions were the same as those of Table 1.

Table 3. Effects of counter ions of metal(II)-bpy complexes on the yields of the aldol condensation of benzaldehyde with acetone

Counter ion	Yield of benzylideneacetone/%[a]					
	Mn(II)	Fe(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
AcO^-	52	60	78	65	47	67
NO_3^-	0	—	33	0	52	31
Cl^-	0	—	47	0	0	25

a) The yields of the reaction products were determined by NMR. In the cases with NO_3^- and Cl^-, 4-hydroxy-4-phenyl-2-butanone was formed predominantly, along with benzylideneacetone.

studied the catalytic effect of the first-row transition metal (II) acetates with the bpy ligand on the formation of chalcone, since it was found that bpy or phen was the most effective ligand for the reaction. The effects of the molar ratio of bpy on these metal(II) ions were also examined. The results are summarized in Table 2.

When a ligand was not added to the reaction mixture ($n=0$), the copper(II) acetate gave the highest yield. When the molar ratio of bpy to metal(II) acetate was 1:1 ($n=1$), the yields increased very much with all the metal(II) ions. Especially, the reactions with Co(II), Ni(II), and Zn(II) complexes gave quantitative yields. When the molar ratio of bpy to the metal was 2:1 ($n=2$), the yields decreased with Fe(II), Co(II), and Zn(II) and increased with Mn(II) and Cu(II). In the case of $n=3$, the yields decreased in comparison with that of $n=1$. In the case of $n=1$, the order of the product yields is in good agreement with the Irving-Williams series, which is known as the stabilization series of general complexes.[3] It is concluded that the more favorable combinations in the complex catalysts are bpy and Co(II), Ni(II), Cu(II), or the Zn(II) ion and that the molar ratio of M(II) to bpy of 1:1 ($n=1$) is the best.

Effects of Counter Ions on the Catalysis. In our previous report,[2] the yields of the condensation product were reported to be affected by the kinds of counter ions in the Cu(II)X_2-bpy catalysts. In order to clarify the effects of the counter ions of metal(II) complexes, nitrate, chloride, and acetate ions were chosen in M(II)-bpy complexes (1:1). In this study, the aldol condensation of benzaldehyde with acetone was examined in the presence of the complex catalysts at a reflux temperature for 18 h in DMF. The product yields were determined by NMR; the results are summarized in Table 3.

When the counter ion of the metal(II) complex was the acetate ion, benzylideneacetone was formed in a good yield. On the other hand, reactions catalyzed by the bpy-complex of metal(II) nitrate and chloride gave condensation products in a low yield. Therefore, the acetate ion was the best among these three counter ions, and the counter ion played a very important role in the aldol condensation with these metal(II) complex catalysts.

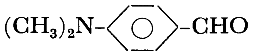
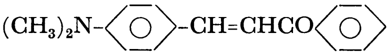
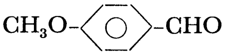
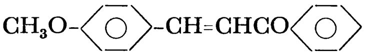
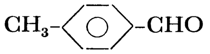
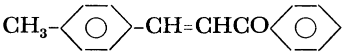
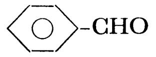
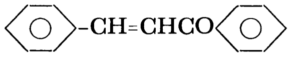
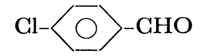
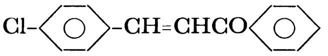
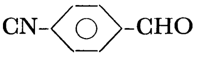
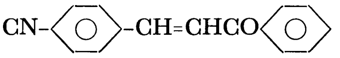
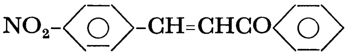
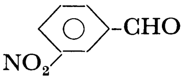
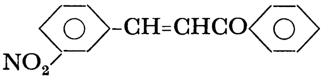
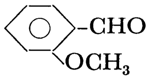
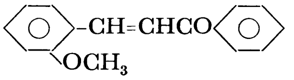
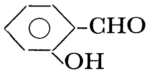
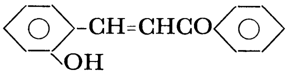
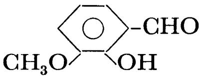
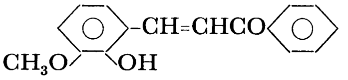
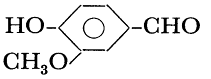
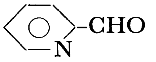
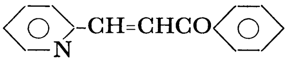
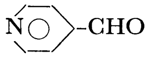
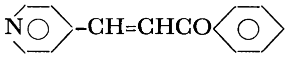
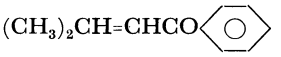
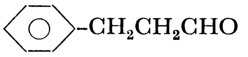
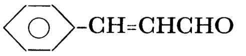
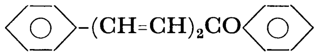
Solvent Effects. In this reaction system, the selection of solvent is important for dissolving the complex catalysts. The condensation of benzaldehyde with acetophenone in the presence of the Zn(II)-bpy complex was carried out in five kinds of polar solvents at 80 °C for 18 h, after which the reaction products were determined by GLC. The results showed that chalcone was formed in good yields in aprotic solvents, such as DMF (100%), DMSO (88%), and CH_3CN (78%). On the other hand, the yields of chalcone were low in protic solvents, such as MeOH (45%) and H_2O (18%). Thus, DMF was the best solvent for the complex-catalyzed reactions.

Condensations of Various Aldehydes with Acetophenone. Next, in order to develop this reaction system, we investigated further the aldol condensations of various kinds of aldehydes and ketones in the presence of the Co(II) acetate-bpy complex catalyst, one of the more favorable M(II) acetate-bpy complex catalysts (M(II): Ni, Co, Cu, Zn). First, the reactions of eighteen kinds of aldehydes with acetophenone were carried out.

To a solution of cobalt(II) acetate in DMF, an equimolar amount of bpy was added. The color of the solution was thus changed to reddish purple, indicating the complex formation. A mixture of aldehyde and acetophenone was then added to the complex solution, and the mixture was stirred at 80 °C for 18 h. The amount of the complex catalyst was 16 mol% of the aldehyde used. Each reaction product was isolated by preparative TLC and was identified as a α,β-unsaturated ketone by the NMR, IR, and the mp. The results are summarized in Table 4.

In the reactions of the *p*-substituted benzaldehydes, **1**—**8**, the substituted chalcones, **28**—**35**, were obtained in good yields, regardless of the kind of substituent group. Further, to examine the effects of substituted groups of aldehydes on the reactivity, the reactions of mono- and di-substituted benzaldehydes, such as *o*-anisaldehyde, **9**, salicylaldehyde, **10**, 2-hydroxy-3-methoxybenzaldehyde, **11**, and 4-hydroxy-3-methoxybenzaldehyde, **12**, were carried out. The reactions of **9** and **10** gave 2-methoxychalcone, **36**, and 2-hydroxychalcone, **37**, both in 72% yields. The reaction of **12** did not occur, the starting materials being recovered, while **11** gave 2-hydroxy-3-methoxychalcone, **38**, in a 47% yield. The difference in the reactivities of **11** and **12** seemed to account for the coordination

Table 4. Reactions of various aldehydes with acetophenone in the presence of the Co(II)-bpy complex catalyst

Aldehyde	Product	Yield/%	Mp/°C (lit,[4])
 **1**	 **28**	77	117.5—119 (114)
 **2**	 **29**	96	72—74 (72—74)
 **3**	 **30**	88	99—100 (96)
 **4**	 **31**	81	57—58 (57—58)
 **5**	 **32**	72	114—117 (114)
 **6**	 **33**	56	159—160[a]
 **7**	 **34**	86	158—160 (158—160)
 **8**	 **35**	67	143—145 (145—146)
 **9**	 **36**	72	61—61.5 (59—60)
 **10**	 **37**	72	152—153 (152—153)
 **11**	 **38**	43	112—113.5[a]
 **12**	—	none	
 **13**	 **39**	31	62—63 (60—61)
 **14**	 **40**	66	79—80 (70—71)
$(CH_3)_2CHCHO$ **15**	 **41**	23	oil[b]
CCl_3CHO **16**	—	none	—
 **17**	—	none	—
 **18**	 **42**	80	104—105 (102—103)

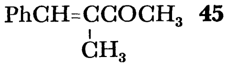
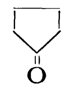
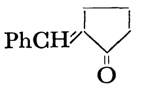
The condensation reactions of aldehydes (1.875 mmol) with acetophenone (5 ml) were carried out in the presence of $Co(OAc)_2$+bpy(1:1)(0.300 mmol) at 80 °C for 18 h in DMF (5 ml).

a) Identified by elemental analysis. b) The reaction was carried out at the reflux temperature, and the product was identified by MS, NMR, and IR.

to Co(II). A chelation of the hydroxyl and formyl groups to Co(II) is possible in the reaction of **11**, since the hydroxyl group is in an ortho position to the formyl group. In **12**, the chelation of the *p*-hydroxyl and *m*-methoxyl groups to Co(II) seemed to be more predominant than that of the formyl group. The reaction of 2-pyridine-, **13**, or 4-pyridinecarbaldehyde, **14**, proceeded smoothly at room temperature for 3 d to give 1-phenyl-3-(2-pyridyl)-2-propen-1-one, **39** or 1-phenyl-3-(4-pyridyl)-2-propen-1-one, **40**, in a 31 or 66% yield respectively. The aldehyde, **14**, gave the reaction product to an extent similar to that in the reactions of *p*-substituted benzaldehyde, **1**—**8**, and no by-product was obtained. On the other hand, **13** gave three kinds of by-products besides the major product, **39**, by TLC. The reactions of the aliphatic-saturated aldehyde showed features different from those of aromatic aldehydes. The reactions of isobutanal, **15**, afforded 1-phenyl-4-methyl-2-penten-1-one, **41**, in a low yield (23%), and 3-phenylpropanal **17**, and chloral, **16**, did not react at all under similar reaction conditions. On the other hand, the reaction of α,β-unsaturated aldehyde, *trans*-cinnamaldehyde, **18**, gave 1,5-diphenyl-2,4-pentadien-1-one, **42**, in a good yield (80%). It may be concluded that the aldol condensations catalyzed by the Co(II)–bpy complex are smoothly promoted in the case of unsaturated aldehydes (aromatic, aliphatic).

Condensations of Various Ketones with Benzaldehyde. Since aromatic aldehydes are favorable substrates in a complex-catalyzed reaction system, the aldol condensations of ten kinds of ketones with benzaldehyde

TABLE 5. REACTIONS OF VARIOUS KETONES WITH BENZALDEHYDE IN THE PRESENCE OF THE Co(II)-bpy COMPLEX CATALYST

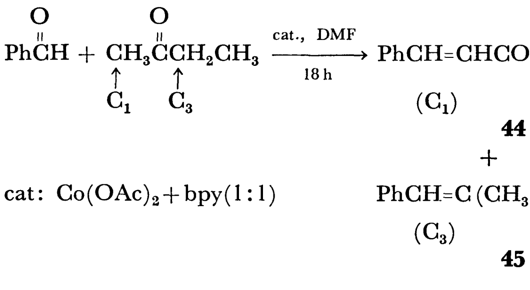
Ketone and ester		Temp / °C	DMF / ml	Product	Yield/%	Mp/°C (lit,[4])
$PhCOCH_3$	**4**	80	5	$PhCH{=}CHCOPh$ **31**	81	57—58 (57—58)
CH_3COCH_3	**19**	reflux	6	$PhCH{=}CHCOCH_3$ **43**	63	41 (41.5)
$CH_3COCH_2CH_3$	**20**	reflux	5	$PhCH{=}CHCOCH_2CH_3$ **44** +  $PhCH{=}C(CH_3)COCH_3$ **45**	95 $[C_1{:}C_3=96{:}4]$	39—40 (38.5—39.5) (C_1)
$CH_3COCH_2CH_2CH_3$	**21**	100	5	$PhCH{=}CHCOCH_2CH_2CH_3$ **46**	91	98—99 (99—100)[a]
$CH_3CH_2COCH_2CH_3$	**22**	100	5	—	none	—
	**23**	80	2	 **47**	38	66—67 (67—68)
$CH_3COCH_2COCH_3$	**24**	80	10	$PhCH{=}C(COCH_3)_2$ **48**	19	oil[b]
$CNCH_2COOCH_2CH_3$	**25**	r.t.	5	$PhCH{=}C(CN)COOCH_2CH_3$ **49**	79	52—53 (66—67)
$BrCH_2COOCH_2CH_3$	**26**	r.t.	5	—	nono	—
$CH_3COOCH_2CH_3$	**27**	reflux	5	—	none	—

The condensation reactions of ketones (5 ml) with benzaldehyde (1.875 mmol) were carried out in the presence of $Co(OAc)_2+bpy(1{:}1)(0.300\ mmol)$ for 18 h in DMF.

a) Melting point of the phenylhydrazone derivative. b) Identified by NMR and IR.

were carried out. The reaction methods and conditions were almost the same as in Table 4. The results are shown in Table 5.

The reactions of benzaldehyde with methyl ketones, such as acetophenone, **4**, and acetone, **19**, gave chalcone, **31**, and benzylideneacetone, **43**, in 81 and 63% yields respectively. Thus, aliphatic and aromatic ketones showed similar reactivities toward benzaldehyde. The self-condensation reaction of acetone or acetophenone was also examined, but no condensation product was obtained and the starting material was recovered. The reaction of 2-butanone, **20**, an unsymmetrical aliphatic ketone, with benzaldehyde took place regioselectively.



$$\overset{\overset{O}{\|}}{PhCH} + CH_3\overset{\overset{O}{\|}}{C}CH_2CH_3 \xrightarrow[18\,h]{cat.,\ DMF} \underset{(C_1)}{PhCH{=}CHCOCH_2CH_3}\ \mathbf{44} + \underset{(C_3)}{PhCH{=}C(CH_3)COCH_3}\ \mathbf{45}$$

$$\text{(}CH_3 \text{ marked } \uparrow C_1,\ CH_2 \text{ marked } \uparrow C_3\text{)}$$

cat: $Co(OAc)_2+bpy(1{:}1)$

A mixture of 1-phenyl-1-penten-3-one(C_1), **44**, and 3-methyl-4-phenyl-3-buten-2-one(C_3), **45**, was isolated in a 95% yield, and the ratio of $C_1{:}C_3$ was determined to be 96:4 by NMR. It was known that the base-catalyzed reaction of 2-butanone gave, preferentially, the condensation product at C_1 of ketone, while the acid-catalyzed reaction occurred preferentially at C_3.[4] The reaction of 2-pentanone, **21**, was also regiospecific, affording a C_1-condensation product, 1-phenyl-1-hexen-3-one, **46**, in a 91% yield. The reaction of the diethyl ketone, **22**, gave no condensation product, probably because it has no α-methyl group. This finding may explain why acyclic unsymmetrical methyl ketones gave regioselective products in these complex-catalyzed reactions. The reaction of cyclopentanone, **23**, as a cyclic α-unsubstituted methylene ketone gave the 2-benzylidenecyclopentanone, **47**, in a 38% yield. It seemed that the difference in the reactivities between cyclic and acyclic α-methylene ketones was ascribable to those pK_a values in the ketones. The reaction of acetylacetone, **24**, as a diketone gave 3-benzylidene-2,4-pentanedione, **48**, in a 19% yield. The reaction of ethyl cyanoacetate, **25**, was carried out at room temperature for 18 h. When a solution of **25** and benzaldehyde in DMF was added to a solution of the Co(II)-bpy complex in DMF, the reddish purple color of the complex was immediately changed to black. Similarly, the color of the reaction mixture of ethyl bromoacetate, **26**, changed to green. The reaction of **25** gave ethyl α-cyanocinnamate, **49**, in a 79% yield, while **26** gave no reaction product, and the starting materials were recovered. Similarly, the reaction of ethyl acetate, **27**, did not give any condensation product at all.

It is generally concluded that M(II)-bpy complexes catalyze cross-aldol condensations of aldehydes with ketones under neutral conditions in DMF to give α,β-unsaturated ketones in good yields. Further, the reactions give base-catalyzed-type products regioselectively. This catalyst system has also been applied to the polymer complex catalyst with good results.[5]

Conclusion. Several reactions catalyzed by the M(II)-bpy complex have been reported.[6] The methylation of ethylenediamine catalyzed by Pt(II)-amine complexes was examined; the *N*-methyl-substituted ethylenediamine was obtained only when the Pt(II)-bpy complex was used.[6a] In this reaction, the driving force of the catalytic activity by the bpy ligand was explained by attributing it to the back π-bonding in the Pt(II)-bpy complex. That is, a higher positive charge is induced on the metal(II) ion by the coordination of the bpy ligand. Our results shown in Tables 1 and 2 also seem to be elucidated by this "ligand effect" of bpy. The oxygen atoms in the carbonyl groups of aldehyde and ketone may be more activated by coordination to the M(II)–bpy complex than by that to the M(II) ion itself.

It has been known that aldol condensations in a biological system are catalyzed by aldolase enzymes, Class I and Class II.[7] Class II aldolase is known as a metalloenzyme containing the Zn(II) ion at the catalytic site. However, in the reaction of Class II aldolase, the catalysis of Zn(II) ion has not been elucidated enough, since it has never been established that Zn(II) complexes catalyze the aldol condensations. Therefore, our reaction system with the Zn(II)–bpy gives a new clue for understanding the catalysis of Class II aldolase from the point of view of organic catalytic reactions. An investigation of the reaction mechanism is now in progress in connection with Class II aldolase.

Experimental

Materials. All the aldehyde, **1**—**18**, ketones, and esters were commercially available. The **13**—**18** aldehydes were purified by distillation before use. The ligand compounds, such as oxalic acid, mercaptoacetic acid, glycine, ethylenediamine, diethylenetriamine, triethylenetetramine, pyridine, 2,2′-bipyridine, 2,2′:6′,2″-terpyridine, 1,10-phenanthroline, *N*,*N*,*N*′,*N*″-tetramethylethylenediamine, and 6,6′-dimethyl-2,2′-bipyridine, were provided by the Tokyo Kasei Co. Anhydrous metal(II) acetate(Kojundo Chemical Reseach) was used. In the reactions shown in Table 3, hydrous metal(II) salts (Wako Pure Chemicals) were used.

Instruments. The NMR and IR spectra were taken with a Hitachi Perkin-Elmer R-20A spectrophotometer (60 MHz) and a Hitachi 215 Grating Infrared spectrophotometer respectively. The mass spectra were determined on a Shimadzu-LKB 9000 gas chromatograph-mass spectrometer at 70 eV. The GLC was carried out with a Hitachi K-53 gas chromatograph with a flame ionization detector, using a 1.0 m stainless tube column packed with 10% Carbowax 20M on Diachrom A. The product yields were determined by the two methods of GLC and NMR analyses. Benzophenone and 1,1,2,2-tetrachroloethane were used as the internal standards in the GLC and NMR analyses respectively.

General Procedure of Metal-complex-catalyzed Aldol Condensation Reactions. Reaction of Benzaldehyde with Acetophenone: The Zn(II)–bpy complex was prepared by the addition of 2,2′-bipyridine (0.20 mmol) to a solution of anhydrous zinc(II) acetate (0.2 mmol) in DMF (1 ml), and then benzaldehyde (1.25 mmol) and acetophenone (5 ml) were added to a yellow solution of the complex. The reaction mixture was stirred for 18 h at 80 °C; then the solvent and the excess of acetophenone were removed under reduced pressure to give an oil which was subsequently purified by preparative TLC, using a 1:4 ether–hexane mixture as the eluent. The yellow crystals thus obtained were identified as chalcone by the mp of 55—56 °C (lit,[8a] 55—57 °C), the NMR, and the IR in comparison with an authentic sample. The isolated yield of chalcone was 86%, and the GLC-analyzed yield was 100%.

Reaction of Benzaldehyde with Acetone: The Zn(II)–bpy complex was prepared by the addition of 2,2′-bipyridine (4.0 mmol) to a solution of zinc(II) chloride ($ZnCl_2 \cdot H_2O$, 4.0 mmol) in DMF (10 ml), and then benzaldehyde (2.5 mmol) and acetone (10 ml) were added to a yellow solution of the complex. The reaction mixture was stirred for 18 h at the reflux temperature. Then, the solvent and the excess of acetone were removed under reduced pressure at room temperature to give an oil which was subsequently extracted with an ethyl acetate-and-water system. The organic layer was dried over anhydrous sodium sulfate and then evaporated under reduced pressure at room temperature to give an oil whose NMR showed a mixture of two kinds of products. The curde oil was recrystallized from petroleum ether to give colorless crystals which were identified as benzylideneacetone by the mp of 38—39 °C (lit,[8b] 40—42 °C), the NMR, and the IR in comparison with an authentic sample. The other product was identified as 4-hydroxy-4-phenyl-2-butanone on the basis of sepctroscopic evidence; Mass: *m/e* (%), 164 (M^+, 3), 146 (3), 131(26), 105(100); NMR (CCl_4); δ 2.10 (s, 3H, CH_3), 3.50 (s, OH, H-D-exchange), 5.00 (t, 1H, CH). The total yield of these two products (25%) was determined by its crude NMR, adding 1,1,2,2-tetrachloroethane as the internal standard; the product ratio of benzylideneacetone to 4-hydroxy-4-phenyl-2-butanone was 29:71.

Condensation Products. 4-(Dimethylamino)chalcone, **28**; Mp 117.5—119 °C (lit,[4] 114 °C); IR:1645 cm^{-1}; NMR ($CDCl_3$): δ 2.95 (6H, s, $N(CH_3)_2$).

4-Methoxychalcone, **29**; Mp 72—74 °C (lit,[4] 72—74 °C); IR 1660 cm^{-1} NMR (CCl_4): δ 3.75 (3H, s, CH_3).

4-Methylcahlcone, **30**; Mp 99—100 °C (lit,[4] 96 °C); IR 1650 cm^{-1}; NMR (CCl_4): δ 2.32 (3H, s, CH_3).

Chalcone, **31**; Mp 57—58 °C (lit,[4] 57—58 °C); IR 1650 cm^{-1}; NMR (CCl_4): δ 7.00—8.00 (aromatic proton).

4-Chlorochalcone, **32**; Mp 114—117 °C (lit,[4] 114 °C); IR 1660 cm^{-1}; NMR (CCl_4): δ 7.00—8.00 (aromatic proton).

4-Cyanochalcone, **33**; Mp 162.5—163 °C; IR 2200, 1660 cm^{-1}; NMR ($CDCl_3$): δ 7.50—8.13 (aromatic proton). Mass: *m/e*, 233 (M^+), 156 ($M^+-C_6H_5$), 128 ($M^+-C_6H_5CO$).

4-Nitrochalcone, **34**; Mp 158—160 °C (lit,[4] 158—160 °C); IR 1660 cm^{-1}; NMR ($CDCl_3$) δ 7.50—8.50 (aromatic proton).

3-Nitrochalcone, **35**; Mp 143—145 °C (lit,[4] 145—146 °C); IR 1660 cm^{-1}; NMR ($CDCl_3$), δ 7.20—8.20 (aromatic proton).

2-Methoxychalcone, **36**; Mp 61—61.5 °C (lit,[4] 59—60 °C); IR 1660 cm^{-1}; NMR (CCl_4) δ 3.78 (3H, s, OCH_3).

2-Hydroxychalcone, **37**; Mp 152—153 °C (lit,[4] 152—153 °C); IR 1640 cm^{-1}; NMR (DMSO-d_6) δ 7.00—8.00 (aromatic proton), 9.80 (br., OH, H-D exchange).

2-Hydroxy-3-methoxychalcone, **38**; Mp 112—113.5 °C; IR 1650 cm^{-1}; NMR (acetone-d_6) δ 3.87 (3H, s, OCH_3); Found: C, 75.21; H, 5.63%. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55%.

1-Phenyl-3-(2-pyridyl)-2-propen-1-one, **39**; Mp 62—63 °C (lit,[4] 60—61 °C); IR 1660 cm^{-1}; NMR (CCl_4) δ 7.00—8.50 (aromatic proton).

1-Phenyl-3-(4-pyridyl)-2-propen-1-one, **40**; Mp 79—80 °C (lit,[4] 70—71 °C); IR 1660 cm^{-1}; NMR (CCl_4) δ 7.30—9.00 (aromatic proton).

1-Phenyl-4-methyl-2-penten-1-one,, **41**; IR 1670, 1650 cm^{-1}; NMR ($CDCl_3$) δ 1.15 (6H, d, CH_3), 1.70 (1H, m, CH), 6.90—8.00 (aromatic proton); Mass: *m/e*, 174 (M^+), 159 (M^+-CH_3), 144 (M^+-2CH_3), 131 ($M^+-CH(CH_3)_2$).

Cinnamylideneacetophenone, **42**; Mp 104—105 °C (lit,[4] 102—103 °C); IR 1655 cm^{-1}; NMR (CCl_4) δ 7.00—8.10 (aromatic proton).

Benzylideneacetone, **43**; Mp 41 °C (lit,[4] 41.5 °C); NMR

($CDCl_3$) δ 2.30 (3H, s, CH_3), 6.62 (1H, d, =CH).

1-Benzylidene-2-butanone, **44**; Mp 39—40 °C (lit,[4] 38.5—39.5 °C); NMR ($CDCl_3$) δ 1.17 (3H, t, CH_3), 2.67 (2H, q, CH_2), 6.70 (1H, d, =CH).

1-Phenyl-1-hexen-3-one, **46**; Mp 98—99 °C (lit,[4] 99—100 °C, phenylhydrazone); IR 1690, 1660 cm^{-1}; NMR ($CDCl_3$) δ 0.92 (3H, t, CH_3), 1.60 (2H, m, CH_2), 2.66 (2H, t, CH_2).

2-Benzylidenecyclopentanone, **47**; Mp 66—67 °C (lit,[4] 67—68 °C); IR 1710 cm^{-1}; NMR ($CDCl_3$) δ 2.10 (4H, m, $-CH_2CH_2-$), 2.94 (2H, dt, $COCH_2$), 7.40—7.45 (aromatic proton).

3-Benzylidene-2,4-pentanedione, **48**; IR 1710 cm^{-1}; NMR (CCl_4) δ 2.22 (3H, s, CH_3), 2.38 (3H, s, CH_3).

Ethyl α-cyanocinnamate, **49**; Mp 52—53 °C (lit,[4] 66—67 °C); IR 2230, 1710 cm^{-1}; NMR ($CDCl_3$) δ 1.40 (3H, t, CH_3), 4.35 (2H, q, CH_2); Found: C, 71.55; N, 6.82; H, 5.49%. Calcd for $C_{12}H_{11}NO$: C, 71.63: N, 6.96; H, 5.51%.

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