Asian Journal of Chemistry Vol. 14, Nos. 3–4 (2002), 1335–1340

Metal Chelates of 5-Aryl-1-Phenyl-4-Pentene-1,3-diones

MATHEW PAUL, P. VENUGOPALAN and K. KRISHNANKUTTY*
Department of Chemistry, University of Calicut, Calicut-673 635, India

A series of 5-aryl-1-phenyl-4-pentene-1,3-diones and their Co(II), Ni(II), Cu(II), Zn(II), Pd(II) chelates of ML_2 and Fe(III) chelates of ML_3 composition have been synthesized and characterized. The electronic, IR, ^1H and ^{13}C NMR and mass spectral data of the compounds are discussed.

Key Words: 5-Aryl-1-phenyl-4-pentene-1,3-diones, Metal chelates, IR-spectra, NMR spectra, Mass spectra.

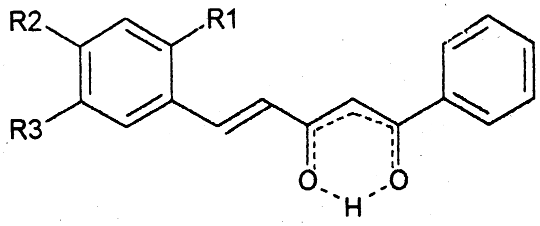
INTRODUCTION

Structurally, the active chemical components present in the traditional Indian medicinal plants such as *Curcuma longa* (turmeric) and related species are 1,3-diketones in which the carbonyl functions are directly linked to olefinic (—CH=CH—) group[1]. In continuation of our studies[2] on such biologically important α,β-unsaturated dicarbonyl compounds we here report the synthesis and characterization of a series of 5-aryl-1-phenyl-4-pentene-1,3-diones **(1a–j)** and their Fe(III), Co(II), Ni(II), Cu(II), Zn(II) and Pd(II) chelates.

EXPERIMENTAL

Preparation of 5-aryl-1-phenyl-4-pentene-1,3-diones: The compounds (Structure–I) were prepared by the condensation of benzaldehyde/substituted benzaldehyde with benzoylacetone as reported earlier.[2]

Benzoylacetone (0.005 mol) mixed with boric oxide (0.005 mol) and dry ethyl acetate (5 mL) was stirred for *ca.* h. The stirring was further continued for 1 h with the slow addition of a solution of aromatic aldehyde (0.005 mol) in dry ethyl acetate (5 mL), followed by tri-(*sec*-butyl) borate (0.01 mol) and *N*-butylamine (0.05 mL). After stirring for an additional period of *ca.* 3 h, the solution was set aside overnight. Hot (*ca.* 60°C) hydrochloric acid (0.4 M, 7.5 mL) was then added to the reaction mixture and again stirred for *ca.* 1 h, before extraction with ethyl acetate. The washed extracts were combined, concentrated and the residual paste obtained was stirred with hydrochloric acid (2 M, 10 mL). The separated solid product was collected, washed with water, ethanol and dried in *vacuo*. The compounds were recrystallized from hot benzene to get chromatographically (TLC) pure material.



(I)

	R_1	R_2	R_3
a	H	H	H
b	H	OCH_3	H
c	H	OH	H
d	H	OH	OCH_3
e	H	OCH_3	OCH_3
f	CH_3	H	H
g	H	$OCH_2—CH_3$	H
h	H	$-N\begin{smallmatrix}CH_3\\CH_3\end{smallmatrix}$	H
i	H	NO_2	H
j	H		3,4 $CH_2\begin{smallmatrix}O\\O\end{smallmatrix}$

Preparation of Metal Complexes: Cu(II), Ni(II), Zn(II), Co(II), Fe (III) and Pd(II) chelates of the diketones were prepared by the following general method. To a refluxing ethanolic solution of the compound (0.002 mol, 20 mL), an aqueous solution of metal(II) acetate (0.001 mol, 5 mL) was added and the reaction mixture was refluxed for *ca.* 2 h, and the volume was reduced to half. The precipitated complex on cooling to room temperature was filtered, washed with water and dried in vacuum. Ferric chloride and palladium(II) chloride were used for the preparation of the Fe^{3+} and Pd^{2+}chelates.

Carbon and hydrogen percentages reported are by microanalysis and the metal percentage by using a Perkin-Elmer 2380/AAS. Magnetic susceptibilities were determined at room temperature on a Gouy type magnetic balance. Electronic spectra were recorded is methanol solution (10^{-4}M) on a UV-1601 Schimadzu recording spectrophotometer. IR spectra (KBr pellets) on a Schimadzu 8101A FTIR spectrophotometer, ^{1}H NMR on a Jeol 400 NMR spectrometer, mass spectra on a Jeol/SX-102 (FAB) mass spectrometer and ^{13}C NMR using a Brucker WM 400 NMR spectrometer.

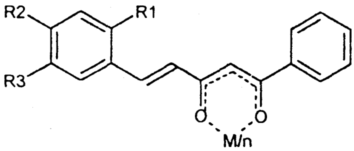
RESULTS AND DISCUSSION

The synthesized dicarbonyl compounds are crystalline in nature with sharp melting points and the carbon and hydrogen percentages (Table-1) are in agreement with their formulation.

TABLE-1
ANALYTICAL AND PHYSICAL DATA OF 5-ARYL-1-PHENYL-4-PENTENE-1,3-DIONES

Compounds		Yield (%)	m.p. (°C)	Elemental analysis %, Calculated/(Found)		λ_{max} (nm)
				C	H	
1a	$C_{17}H_{14}O_2$	55	158	81.63 (80.53)	5.60 (5.20)	365 260
1b	$C_{18}H_{16}O_3$	60	202	71.14 (70.34)	5.71 (5.38)	380 261
1c	$C_{17}H_{14}O_3$	63	183	76.69 (76.10)	5.26 (5.08)	385 263
1d	$C_{18}H_{17}O_4$	70	198	72.97 (72.08)	5.41 (5.25)	404 265
1e	$C_{19}H_{14}O_4$	68	218	73.55 (72.85)	5.81 (5.58)	420 266
1f	$C_{18}H_{16}O_2$	50	120	81.80 (81.50)	6.06 (6.03)	406 230
1g	$C_{19}H_{16}O_3$	60	106	77.55 (77.28)	5.44 (5.42)	410 328
1h	$C_{19}H_{19}NO_2$	70	108	77.80 (76.60)	4.80 (4.80)	451 333
1i	$C_{17}H_{13}O_4N$	60	90	69.15 (68.91)	4.40 (4.39)	474 —
1j	$C_{18}H_{14}O_4$	50	142	73.77 (73.46)	4.76 (4.71)	383 310

All the metal complexes are stable, crystalline and their carbon, hydrogen and metal percentages agree with ML_2 stoichiometry except Fe(III) complexes which are of ML_3. All the complexes behave as non-electrolytes (specific conductance $< 15\ \Omega^{-1}\ cm^{-1}$ DMF) and do not contain the anion of the metal salt used for their preparation. The Fe(III), Cu(II) and Co(II) complexes are paramagnetic. The electronic, IR, NMR and mass spectral data of the complexes are compatible with the structure that would result when the chelated enol proton of the ligand is replaced by metal ion as in structure **2.**



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$M = Cu^{2+}, Ni^{2+}, Zn^{2+}, Pd^{2+}, Co^{2+}$ for n = 2 and $M = Fe^{3+}$ n = 3 for

The UV spectra of the diketones showed two broad bands at *ca.* 420 nm and *ca.* 265 nm respectively due to the carbonyl and olefinic functions. In metal complexes the bands showed a bathochromic shift (5–8 nm) indicating the involvement of the dicarbonyl function in complexation.

The infrared spectra of all the dicarbonyls are characterized by the presence of two strong bands at *ca.* 1635 and *ca.* 1615 cm^{-1}and several medium intensity bands in the region 1600–1500 cm^{-1}. It is to be pointed out that no free benzoyl carbonyl (*ca.* 1660 cm^{-1}) or cinnamoyl carbonyl bands (*ca.* 1645 cm^{-1}) are observed in the spectra. The observed bands in this region suggest that the compounds exist in strong intramolecular hydrogen bonding as in structure **1.** The occurrence of an intense broad band in the region 3500–2500 cm^{-1} also support the hydrogen bonding[3]. A medium intensity band appear at *ca.* 970 cm^{-1} in the spectra of the compounds can be assigned to the *trans* —CH=CH— absorption. The important IR absorptions and their probable assignments are given in Table-2.

TABLE-2

Characteristic IR data (cm^{-1}) of 5-aryl-1-phenyl-4-pentene-1, 3-diones compounds										Probable Assignments
1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**	
1635	1638	1639	1636	1638	1639	1635	1630	1640	1635	ν(C=O) benzoyl
1615	1613	1618	1619	1618	1610	1601	1595	1596	1608	ν(C=O) cinnamoyl
Characteristic IR data (cm^{-1}) of copper(II) chelates of 5-aryl-1-phenyl-4-pentene-1,3-diones										
1607	1605	1606	1603	1601	1610	1610	1610	1610	1615	ν(C=O) chelated benzoyl
1582	1585	1583	1582	1580	1585	1598	1598	1594	1590	ν(C=O) chelated cinnamoyl
450	445	438	448	452	453	472	468	476	441	ν(Cu—O) chelate ring
418	418	412	418	418	418 408	418	418		403	

In the spectra of metal complexes bands in the region 1700–1620 cm^{-1} almost disappeared but instead two new bands appeared at *ca.* 1600 cm^{-1} and 1580 cm^{-1} of appreciable intensity assignable to the metal chelated carbonyl groups[2,4]. Several medium intensity bands arising from aromatic and alkenyl ν(C=C) vibrations also appeared in the region. This is further supported by the appearance of medium intensity bands at *ca.* 448 and *ca.* 418 cm^{-1} presumably due to ν(M—O) vibrations[4]. The replacement of enolic proton by metal ion is also evident from the absence of the broad free ligand band in the region 3200–2700 cm^{-1} in the spectra of the complexes. The non involvement of the phenolic OH group in complex formation is evident from the appearance of a relatively broad band in the region 3600–3200 cm^{-1} in the spectra of chelates of **1c** and **1d.** Important IR spectral bands of the only Cu(II) chelates are given in Table-2 as typical of all the complexes.

The ^{1}H NMR spectra of all the dicarbonyls displayed a one proton signal above 16 ppm due to the strong intramolecularly hydrogen bonded enol form. Other signals appearing are in the range δ 6.02–6.87 ppm (methine protons), 7.88–8.27 (alkenyl protons) and 7.26–8.13 (aryl protons). The phenolic proton signals of **1c** and **1d** are at *ca.* 9.6 ppm. The *trans* orientation of the alkenyl groups of the compounds is evident from their observed J values (*ca.* 16 Hz).

In the ^{1}H NMR spectra of Pd(II) chelates of **1a** to **1e** and Ni(II) chelates of **1f** to **1j** the low field signal due to the chelated enol proton of the ligands is absent indicating the replacement of the enol proton by the metal ion. The phenolic OH protons of **1c** and **1d** remained almost unaltered in the spectra of their chelates which strongly suggests that chelate formation has occurred exclusively through the dicarbonyl moiety. The integrated intensities of the aryl and alkenyl protons agree well with the formulation as in structure **2**. The characteristic chemical shifts of various protons are summarized in Table-3.

TABLE-3

CHARACTERISTIC ^{1}H NMR SPECTRAL OF 5-ARYL-1-PHENYL-4-PENTENE-1,3-DIONES

Chemical shift (δ ppm)

Compounds										Probable Assignments
1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**	**1h**	**1i**	**1j**	
16.85	16.86	16.75	16.87	16.86	16.17	16.15	16.47	15.89	16.15	enolic
(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	
7.99	7.95	7.94	8.00	8.00	8.00	7.96	7.96	8.27	7.96	alkenyl
(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	
7.97	7.88	7.88	7.97	7.96	7.97	7.94	7.94	8.25	7.95	
(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	
7.50–	7.49–	7.46–	7.47–	7.46–	7.21–	7.45–	7.44–	7.26–	7.44–	aryl
7.79	7.80	7.66	7.57	7.94	7.62	7.68	7.68	8.13	7.94	
(10H	(9H)	(9H)	(8H)	(8H)	(9H)	(9H)	(9H)	(9H)	(8H)	
6.85	6.86	6.87	6.86	6.85	6.60	6.31	6.28	6.41	6.02	methine
(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	(1H)	

The ^{13}C NMR spectra of **1a** and **1d** show two well separated carbonyl carbon signals at *ca.* 198 and 189 ppm due to benzoyl and cinnamoyl groups respectively. The methine carbon signal is at *ca.* 70 ppm and in the region 129–146 ppm contain signals due to the phenyl and olefinic carbons. The methoxy carbon signal of **1d** is at 56.354 ppm. The ^{13}C NMR spectra of the Pd(II) chelates of **1a** and **1d** show that benzoyl carbonyl carbon signal of the free ligand shifted appreciably to low field while the cinnamoyl carbonyl carbon signal shifted slightly to upfield which suggests the presence of strong delocalization in the metal chelates compared to the free ligands.

Mass spectra of all the dicarbonyls show intense molecular ion peaks $P^+/P + 1^+$. peaks due to $(P—Ph)^+$, $(P—PhCO)^+$, $(PhCO)^+$, Ph^+ and elimination of R_1, R_2, R_3 from P^+ are characteristic of all the spectra. The FAB mass spectra of the Cu(II) chelates show prominent peaks due to $[CuL_2]^+$ which justifies the formulation of the chelates. The base peak in all the cases is due to the ligand,

and peaks due to $[CuL]^+$, L^+ and fragments of L^+ are sometimes more intense than the molecular ion peak. Another striking feature of the spectra of all complexes is the presence of a large number of fragments containing copper.

The observed diamagnetism and broad medium intensity bond at 17,775 cm^{-1} in the visible spectra of the nickel(II) chelates suggests their square-planar geometry. In conformity with this observation, the visible spectra of the chelates from their pyridine solution (IO^{-3} M) showed three bonds at *ca.* 8000 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{2g}$), *ca.* 13500 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{1g}(F)$) and *ca.* 24000 cm^{-1} ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$) corresponding to a configurational change from square planar to octahedral due to the association of pyridine. The calculated ligand parameters such as LFSE (22.82–23.27 kcal/mol), D_q (798.6-814.2 cm^{-1}), B (875.8–913.3), β (0.829–0.865), β% (13.51–17.06) D_q also support their octahedral geometry. The copper(II) chelates have a very broad band centred at *ca.* 14750 cm^{-1} and the measured value indicating their square-planar geometry.

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(*Received:* 26 February 2002; *Accepted:* 6 May 2002) AJC–2692