Synthesis and Spectroscopic Studies of some Phenolic β-diketones

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(Received 11th July, 1989, revised 16th September, 1990)

Introduction

1-(o-Hydroxyphenyl)-3-substituted-1,3-prop -adiones commonly referred as phenolic β-diketones have gained a lot of interest due to their importance as good ligands [1] for chelation with metals, as intermediate in the synthesis of flavones [2] and as starting material for preparation of CNS active 1,5-benzodiazepines [3]. The synthesis of such compounds have been achieved by intramolecular acylation reactions, the well-known Baker-Venkataraman [4,5] rearrangment. The detailed spectroscopic data of these compounds is however not available in the literature.

In an attempt to seek for new ligands to be used for chelation with transition metals we are able to synthesize 1-(o-hydroxyphenyl)-3-phenyl-1,3-propadione (**1**). Its p-substituted derivatives (**2-4**) and 1-(o-hydroxyphenyl)-4,4-dimethyl-1, 3-pentadione (**5**) (Fig. 1) in much higher yields than the literature values [5]. The synthesis and spectroscopic data of these compounds is reported here. The work on transition metal complexes and tin complexes is in progress.

Results and Discussion

The spectroscopic data of these compounds depend upon three tautomeric forms [6] they are capable of existing in (Fig. 2).

The UV-spectra in EtOH generally show two maxima one at 260-270 nm, and another relatively more intense at 300-400 nm. These absorptions may be assigned to carbonyl substituted phenyl ring and α-β-unsaturated carbonyl group of enol tautomers respectively, incidating the presence of enolic structure [II & III] for these compounds. IR spectra in KBr show very weak and broad absorption of hydrogen bonded OH. There is no absorption in the free carbonyl region indicating the absence of keto form in solid state. Multiple absorption in the region 1650- 1400 cm^{-1} shows the presence of hydrogen bonded conjugated carbonyl, and conjugated C = C st. vibrations.

^{1}H-NMR data (Table-1) also prove the presence of enolic forms in solution. Singlets of different compounds at δ 4.12-4.63, indicative of CH_2 protons, integrating to 0.1-0.26 H show the

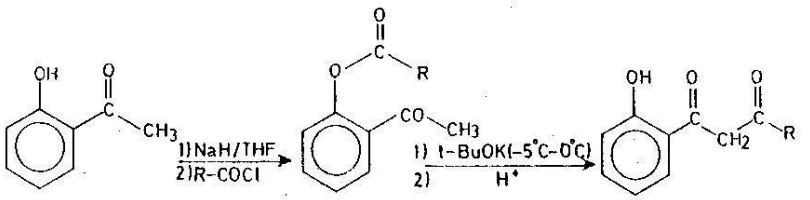
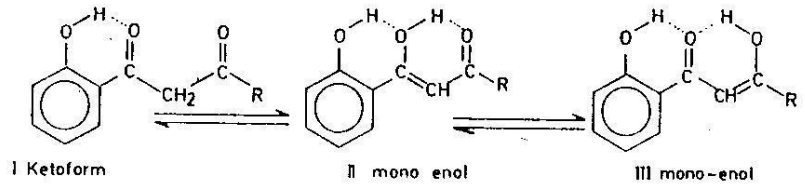


FIG. 1.

1. R = C_6H_5
2. = p-F C_6H_4
3. = p-Cl-C_6H_4
4. = p-CH_3O-C_6H_4
5. = $(CH_3)_3C$



I Ketoform II mono enol III mono-enol

FIG. 2.

Table-1: NMR spectral data in $CDCl_3$ δ-values (ppm)

Compd.	R	-CH_2-	-CH-	OH- (Phenolic)	OH- Enolic	Ar-H	Any other
1.	C_6H_5	4.63 (s, 0.17H)	6.85 (s, 0.72H)	12.0 (s,1H)	15.5 (s,0.95H)	6.88-7.89 (m, 9H)	
2.	p-F-C_6H_4	4.59 (s, 0.25H)	6.9 (s, 0.88H)	12.0 (s, 1H)	15.6 (s, 0.8H)	6.887.-.76 (m, 8H)	
3.	p-Cl-C_6H_4-	4.61 (s, 0.1H)	6.8 (s, 0.92H)	12.2 (s, 1H)	15.5 (s, 0.93H)	6.88-7.86 (m, 8H)	
4.	p-OCH_3-C_6H_4-	4.54 (s, 0.1H)	6.7 (s,0.95H)	12.1 (s,1H)	15.8 (s,0.8H)	6.9-8.0 (m, 8H)	3.8 (s, 3H, CCH_3)
5.	$(CH_3)_3C$-	4.12 (s, 0.26H)	6.24 (s,0.83H)	12.0 (s,1H)	15.4 (s,0.7H)	6.8-8.01 (m, 3.9H) (s, 9H, $C(CH_3)_3$)	1.26 & 1.23

presence of very small amount of keto form [1]. However, singlets at δ 6.2-6.9 integrating to 0.8-0.9 show that mono-enol forms II and III are the actual tautomers present. The phenolic OH appear at δ 12.0 ppm in almost all the cases and hydrogen bonded enolic OH at δ 15.4-15.8. Aromatic protons appears as multiplets between 6.8-8.0 ppm.

The fragmentation pattern in mass spectra of these compounds is depicted in Fig. 3 and the different fragments are tabulated in Table 2. The mass peak is very weak in almost all the compounds. RCO^+ (fragment V) forms the parent peak. The rest of the fragmentation pattern is in accordance with the structure of these compounds.

Table-2: Detailed mass spectral data m/z (rel.intensities)

Fragment Cmpd	I	II	III	IV	V	VI	VII	VIII	IX
1.	240(18)	163(6)	77(33)	135(10)	105(100)	121(21)	147(8)	93 (6)	223 (8)
2.	258(17)	163(8)	95(21)	135(10)	123(100)	121(22)	165(7)	93(8)	141(5)
3.	274(21)	163(8)	111(17)	135(8)	139(100)	121(33)	181(7)	93(7)	257(8)
	276(8)	--	113(5)	---	141(30)	---	183(2)	---	259(2)
4.	270(14)	163(7)	107(7)	--	135(100)	121(12)	----	93 (5)	253 (6)
5.	220 (18)	163 (8)	57(20)	135 (15)	85(100)	121(40)	127(7)	93(20)	203(20)

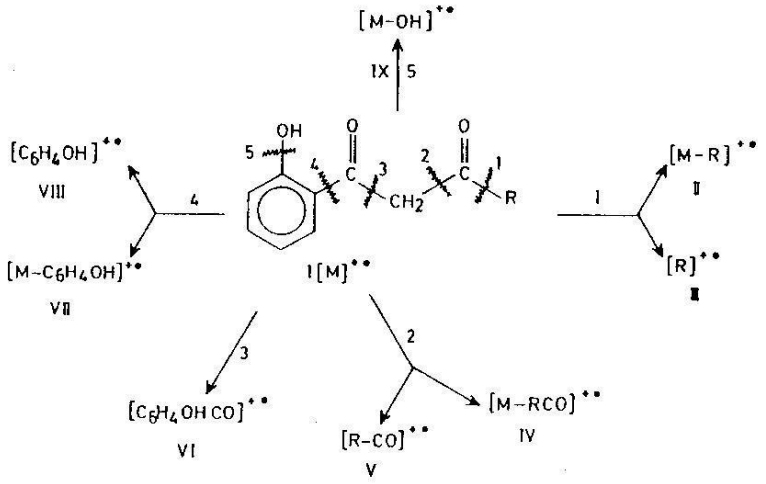


FIG. 3. General Fragmentation Pattern in Mass Spectra .

Table-3: Physical data of compound 1-5

Compd	R.	mp °C	Yield %	UV λ_{max} EtOH nm(ε) ν_{max},cm^{-1}	IR (KBr)	Elemental analysis (%) C-	H-	Other
1	C_6H_5	121-22° (lit 120)[5]	80 (lit.61)	263 (7840), 364 (19150) 1565, 1490, 1440, 1300, 900, 790	3050, 3040, 1610	C. 75.00 O. 75.3	5.00 5.30	- - F
2	p-FC_6H_4	118-119°	93	264 (8120) 365 (19450) 1575, 1520, 1470 1320, 1220, 820	3000, 2850, 1640, O. 70.00	C. 69.77 4.48	4.26 7.26	7.36
3	p-ClC_6H_4	113-114°	80	265 (8250) 364 (19550) 1580, 1510, 1450 1320, 820, 760	3100, 1640, 1600 O. 65.47	C. 65.57 4.20	Cl 4.00 12.80	12.93
4	p-CH_3O-C_6H_4	115-116°	89	267(9780) 375 (26920) 1625, 1600, 1525 1510, 1480, 1460 1320, 1200	3100, 3000, 2875 O. 71.00	C. 71.11 5.18	5.18 -	-
5	$(CH_3)_3C$-	65°	80 (7820), 338 (9280)	262(6460), 314 1450, 1400, 1300 1220, 760	3000, 2950, 2900 1600, 1580, 1500	C. 70.91 O. 71.1	7.27 7.35	- -

All compounds were recrystallized from alcohol.

The compounds were prepared by usual method [5], the rearrangement was carried out at -5 -0°C, using t-BuOK as base. The physical data of the compounds is summarized in Table-3.

Acknowledgement

We are thankful to Pakistan Science Foundation, Islamabad for funding the project and H.E.J. Research Institute of Chemistry, University of Karachi for recording NMR spectra, mass spectra and elemental analysis.

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