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Synthesis of Propan-1,3-diones and Chromens

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The present work deals with the synthesis 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (**3a-3a**), 2-bromo/iodo-1-[2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (**4a-4f**), 2-styryl-7,8-benzophenyl chromones (**5a-5c**), 3-bromo/iodo-2-styryl chromones (**6a-6f**). Structure of these compounds were established on the basis of element analysis spectral analysis (IR, ^{13}C NMR).

Key Words: Propan-1,3-diones, Chromones.

INTRODUCTION

β-Diketones are considered to be the most important dicarbonyl compounds because of their usefulness as versatile intermediate for synthesis of heterocycles with different biological activities[1,2]. Diketones are 1,3-dicarboxyl compounds containing a reactive methylene group between two carbonyl groups. 1,3-Diones are precursor of heterocyclic compounds like pyrazoles[3,4], isoxazoles, flavanones, flavones, chromones[5], *etc*. The present work deals with the synthesis 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (**3a-3a**), 2-bromo/iodo-1-[2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (**4a-4f**), 2-styryl-7,8-benzophenyl chromones [**5a-5c**], 3-bromo/iodo-2-styryl chromones (**6a-6f**). Structure of these compounds were established on the basis of element analysis spectral analysis (IR, ^{13}C NMR).

EXPERIMENTAL

All melting points were taken in silicon oil bath with instrument in an open capillary and are uncorrected. Purity of compounds was checked by TLC on silica gel-G. IR spectra were recorded on a Perkin-Elmer-577 spectrophotometer, PMR spectra on a Brucker AC 300 NMR spectrometer (300 MHz) and ^{13}C spectrum on Brucker AC 400 NMR spectrometer.

Preparation of 2-acetyl-1-naphthol (1): 2-Acetyl-1-naphthol was synthesized by modified Nenchi method, in which hot glacial acetic acid and fused $ZnCl_2$ were mixed and refluxed till $ZnCl_2$ dissolved in acetic acid then to it powdered 1-naphthol was added. This mixture was refluxed for 8 h. Then the reaction mixture was cooled and poured in acidulated water. The solid was filtered and crystallized from rectified spirit to get 2-acetyl-1-naphthol, m.p. 98 °C, yield 75 %.

Preparation of 3,4-benzophenyl-2-cinnamoyloxy-acetophenones (2a-2c): 2-Acetyl-1-naphthol (0.04 mol, 7.12 g) and cinnamic acid (0.05 mol, 7.40 g) were dissolved in pyridine (30 mL). $POCl_3$ (3 mL) was added dropwise with constant stirring. During addition of $POCl_3$ temperature was maintained below 40 °C. The reaction mixture was slowly thickened. After 6 h it was treated with ice cold HCl (50 %). The granular product obtained was washed with cold water and then with $NaHCO_3$ (10 %). The product was finally washed with water and crystallized from ethanol yield 80 %.

Preparation of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (3a-3c): 3,4-Benzophenyl-2-cinnamoyloxy acetophenone (0.01 mol) was suspended in DMF (10 mL) and pulverized KOH (0.03 mol, 3 g) was added with stirring. The reaction mixture was slowly warmed up to 50 °C. After 2 h, it was decomposed with ice cold HCl (50 %). The crude mass was washed with $NaHCO_3$ (10 %) solution to remove mineral acid. The product was crystallized from acetic acid and ethanol mixture (1:1), yield 70-75 %.

Preparation of 2-bromo/iodo-1-[2-hydroxy-3,4-benzophenyl]-3-styryl-propan-1,3-diones (4a-4f): 1-(2-Hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (0.01 mol) was suspended in acetic acid (20 mL) and sodium acetate solution (10 %, 10 mL). Solution of bromine or iodine monochloride in acetic acid (6.5 mL, 25 % w/v) was added dropwise with constant stirring. After 1 h the reaction mixture was diluted with water to get dark yellow product. The crude product was washed with water and crystallized from ethanol, yield 45-50 %.

Preparation of 2-styryl-7,8-benzophenyl chromones (5a-5c): 1-(2-Hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (0.01 mol) was refluxed in acetic acid (30 mL) containing H_2SO_4 (5 mL, 2 %), for about 1 h. The reaction mixture was cooled and poured into water, white wooly product was separated. It was filtered and washed with water and crystallized from ethanol (70 %) to get shiny white wooly compound, yield 70-80 %.

Preparation of 3-bromo/iodo-2-styryl-(7,8-benzophenyl) chromones (6a-6f): To the suspension of 1-(2-hydroxy-3,4-benzophenyl)-3-styryl-propan-1,3-diones (0.01 mol) in acetic acid (30 mL) bromine in acetic acid/ICl in acetic acid (6.4 mL, 25 % w/v) was added dropwise with constant stirring. After 1 h, reaction mixture was poured in water. Solid obtained was filtered, washed with water. It was recrystallized from ethanol to obtain compounds (**6a-6f**), yield 60-70 %.

The physical and analytical data of compounds **2a-2c**, **3a-3c**, **4a-4f**, **5a-5c**, **6a-6f** are given in Table-1.

Spectral data

Compound 2a: IR: 3066 m CH=CH *str.*, 2823 m - CH_3 st, 1721 s >C=O *str.*, 1679 s C-CH_3 *str.*, 1629-1597 *sym.* –COCH=CH– *str.*, 1494 m, -C=C-Ar *str.*, 1625 m -C=C-Ar *str.*, 1358 s -C-O-C- *str.*, 1203 m -C-O-C- *asym. str.*, 1129 s -C-O-C- *str.*, 989 m *trans* -CH=CH-. ^{13}C NMR: 2.6 (s) 3H-CH_3, 7.7 d (H_b) CH=CH_b-Ph, 6.8 (d) 1H CH_a=CH-Ph, 6.9-8.4 (m) 11H Ar-H.

TABLE-1
MELTING POINT AND YIELD (%) OF
COMPOUNDS **1**, **2a-2c**, **3a-3c**, **4a-4f**, **5a-5c**, **6a-6f**

Compd.	R	R_1	m.p. (ºC)	Yield (%)	R_f
1	–	–	–	–	–
2a	H	–	80	70	0.52
2b	$–OCH_3$	–	152	75	0.39
2c	$–NO_2$	–	158	70	0.29
3a	H	–	152	75	0.85
3b	$–OCH_3$	–	182	75	0.79
3c	$–NO_2$	–	212	70	0.73
4a	H	Br	122	40	0.68
4b	$–OCH_3$	Br	125	48	0.64
4c	$–NO_2$	Br	122	48	0.49
4d	H	I	140	48	0.89
4e	$–OCH_3$	I	170	45	0.68
4f	$–NO_2$	I	198	45	0.76
5a	H	–	137	80	0.81
5b	$–OCH_3$	–	192	82	0.72
5c	$–NO_2$	–	224	80	0.73
6a	H	Br	160	60	0.78
6b	$–OCH_3$	Br	186	60	0.86
6c	$–NO_2$	Br	202	60	0.89
6d	H	I	265	60	0.81
6e	$–OCH_3$	I	220	65	0.70
6f	$–NO_2$	I	252	60	0.68

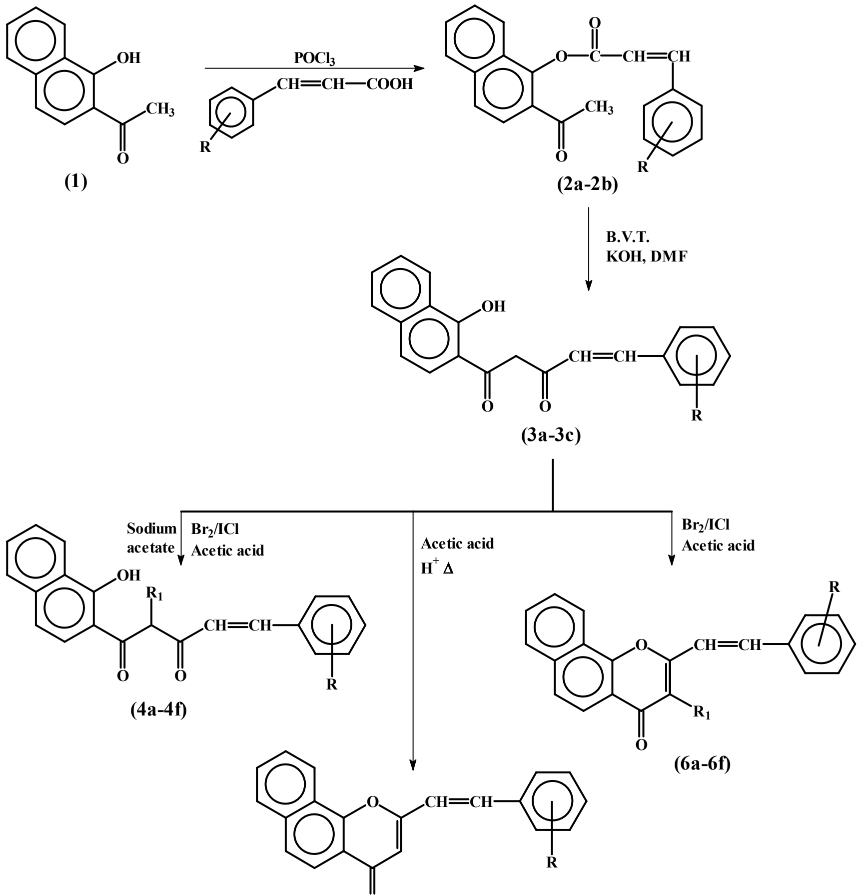
Compound 3a: IR: 3433 s -O-H *str.*, 2827 m CH_2 *sym. str.*, 1627-1585 s –COCH=CH– *str.*, 1469 s, >CH_2 *str.*, 1352 s Ph-OH *str.*, 1266 s >C-O *str.*, 961 s, -CH=CH- *trans str.* ^{13}C NMR: 13.8 (s) 1H-O-H, 14.65 (s) 1H enolic -OH, 7.7 d 1H, Ph=CH_b-CH, 6.6 (d) 1H Ph =CH- CH_a, 6..3.5 1H C-H 7.2-7.6 m 11H Ar-H. ^{13}C: C_1 194.86, C_2 97.12, C_3 173.48, C_4 138.96, C_5 136.51, C_6 134.38, C_7 125.42, C_8 127.51, C_9 128.49, C_{10} 61.62, C_{11} 123.46, C_{12} 126.93, C_{13} 121.86, C_{14} 122.99, C_{15} 129.41, C_{16} 118.11, C_{17} 111.75, C_{18} 124.71, C_{19} 129.60.

Compound 4a: IR: 3055 v -OH *str.*, 1627-1577 s, –COCH=CH– *str.*, 1332 m Ph-OH *str.*, 1269 m C-O *str.*, 964 s, *trans* -CH=CH- *str.*, 542 m, C-Br *str.* ^{13}C NMR: 14.66 (s) 1H enolic OH, 13.89 (s) 1H O-H, 7.76 d 1H, CH_A=CH, 7.25 (d) 1H CH_B, 6.0-8.4 m 11H Ar-H.

Compound 4d: IR: 3055 v O-H *str.*, 1627-1577 s, –COCH=CH– *str.*, 1332 m O-H` *str.*, 1263 m Ph-C-O *str.*, 962 s, *trans* -CH=CH- *str.*, 489 m, C-I *str.* ^{13}C NMR: 14.6 (s) 1H enolic OH, 13.88 (s) 1H OH, 7.7 d 1H, CH_A, 7.29 (d) 1H CH_B, 6.0-8.4 m 11H Ar-H.

Compound 5a: IR: 3020 m -CH=CH- *str.*, 3058 m Ar-CH=CH *str.*, 1639 s $(Ar)_2CO$, 1392 s, γ-pyron ring 1199 s –C–CO–C– *str.*, 1085 s -C-O-C *asym. str.*, 962 m *trans* -CH=CH- *str*. ^{13}C NMR: 8.14 d 1H CH_A, 6.88 d 1H CH_B, 6.4 s 1H >C-HC, 6.0-8.6 m 11H Ar-H. ^{13}C: C_1 153.10, C_2 136.49, C_3 178.20, C_4 111.71, C_5 129.02, C_6 129.18, C_7 123.95, C_8 122.33, C_9 122.23, C_{10} 120.20, C_{11} 129.89, C_{12} 134.94, C_{13} 160.89, C_{14} 128.19, C_{15} 125.07, C_{16} 135.98, C_{17} 127.04, C_{18} 127.70, C_{19} 120.75.

Compound 6b: IR: 3060 m -CH=CH- *str.*, 1693 m >C=O *str.*, conjugation 1629 s C=C *str.*, conj. 1388 m γ-pyron ring 1205-1178 m –C–CO–C– *str.*, 1089 m C-O-C *asym. str.*, 966 s *trans* -CH=CH- *str.*, 565 m C-Br *str.* ^{13}C NMR: 3.8 (s) 3H-O-CH_3, 8.17 d 1H CH_A, 7.94 d 1H CH_B, 6.0-8.0 m 11H Ar-H.



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