Asian Journal of Chemistry Vol. 22, No. 5 (2010), 3362-3368

Synthesis of 1-Phenyl Naphthalene and Pericarbonyl Lignans

SUJATA DEO, FARHIN INAM, R.P. MAHASHABDE* and A.N. JADHAV
Chemistry Department, Institute of Science, Nagpur-440 001, India
Email: rachana_mahashabde@rediffmail.com

The approach towards synthesis of 1-phenyl naphthalene and pericarbonyl lactone by cyclization of Perkin condensation product, ∝-arylidene β-benzoyl propionic acid with polyphosphoric acid and concentrated sulphuric acid can be achieved in one step.

Key Words: Synthesis, 1-Phenyl naphthalene, Pericarbonyl lignans.

INTRODUCTION

Synthesis of 1-phenyl naphthalene has been subject of great interest, as it is an important intermediate for synthesis of cyclo lignans and also for their physiological properties[1]. Haworth *et al.*[2] synthesized Taiwanin-C & and Block Stevenson[3] obtained Justicidin B and Justicidin-E with 1-phenyl naphthalene system.

To prepare pericarbonyl lactone[4] β-benzoyl propionic acid was used which has two reactive methylene groups and a carboxylic functional group which could lead to the basic skeleton of lignan. The carboxyl group would yield part of furan ring and the oxo group could be reduced.

EXPERIMENTAL

Conversion of ∝-arylidene β-benzoyl propionic acid to 1-phenyl naphthoic acid (7): Treatment of ∝-arylidene β-benzoyl propionic acid (**4**) with conc. H_2SO_4 or PPA at 100 ºC for 1 h gave precipitate on crushed ice which was identified as 1-phenyl naphthoic acid (**7**).

Infrared spectra showed absorption at 1670 cm^{-1} for carboxylic acid group. Structure also supported by NMR studies. Above reactions takes place by enolization followed by removal of hydrogen and hydroxyl group (Table -4).

Conversion of ∝-arylidene β-benzoyl propionic acid to pericarbonyl lactone (8): ∝-Arylidene β-benzoyl propionic acid (**4**) was treated with aq. formaldehyde and sodium hydroxide to give product identified as ∝-arylidene β-methylene β-benzoyl propionic acid (**5**).

The IR spectra of **5** showed broad band at 1660 cm^{-1} for carbonyl group. NMR spectra for 2 methylene protons showed singlet at 6.060 and 7.85 singlet for olefinic proton.

The compound **5** was treated with conc. H_2SO_4 at 0 ºC for 24 h and mixture was poured on ice when 1-aryl naphthalene carboxylic acid lactone (**8**) was obtained which was isolated and crystallized to give yellow solid. IR spectra showed absorption at 1760 cm^{-1} indicating presence of 5 membered lactone ring. NMR spectra were also consistent to the structure assigned to them.

TABLE-1

Aryl aldehyde (β-Aroyl propionic acid)	Butenolide (m.f.)	Yield, % (m.p., ºC)	UV λ_{max}, nm (log €)	IR (cm^{-1})	NMR δ Ar, H, R
Veratraldehyde (β-Benzoyl propionic acid)	**3a** ($C_{19}H_{16}O_4$)	73.3 (125)	249 (4.21) 392 (4.32) 486 (4.24)	1772 1762	-
Veratraldehyde (4-Methoxy β-benzoyl propionic acid)	**3b** ($C_{20}H_{18}O_5$)	82.7 (172)	-	-	7.25-6.91, 6.78, 6.03
Piperenol (β-Benzoyl propionic acid)	**3c** ($C_{18}H_{12}O_4$)	85.4 (166)	252 (4.12) 484 (4.46)	1772 1762	7.85-6.91, 6.78, 6.03
Piperenol (4-Methoxy β-benzoyl propionic acid)	**3d** ($C_{19}H_{14}O_5$)	76.1 (115)	-	-	7.95-6.90, 6.70, 6.05
Vanillin (β-Benzoyl propionic acid)	**3e** ($C_{18}H_{14}O_4$)	85.6 (147)	252 (4.18) 393 (4.26)	1772 1760	-
Vanillin (4-Methoxy β-benzoyl propionic acid)	**3f** ($C_{19}H_{16}O_3$)	72.2 (188)	-	-	-
3,4,5-Trimethoxy benzaldehyde (β-Benzoyl propionic acid)	**3g** ($C_{21}H_{19}O_4$)	88.9 (168)	249 (4.20) 394 (4.03) 405 (4.11)	1765	-
3,4,5-Trimethoxy benzaldehyde (4-Methoxy β-benzoyl propionic acid)	**3h** ($C_{22}H_{21}O_5$)	84.0 (177)	-	-	
Benzaldehyde (β-Benzoyl propionic acid)	**3i** ($C_{17}H_{12}O_2$)	70.0 (153)	248 (4.55) 390 (3.79)	1792 1762	8.01-7.42 7.06
Benzaldehyde (4-Methoxy β-benzoyl propionic acid)	**3j** ($C_{18}H_{14}O_3$)	69.1 (155)	-	-	-

Similarly, the compound **4** was treated with polyphosphoric acid at 100 ºC for 1 h, when same lactone (**8**) was obtained (Table-4).

Conversion of ∝-arylidene β-benzoyl propionic acid to 1-phenyl naphthalene system (9): ∝-Arylidene β-benzoyl propionic acid (**4**) was converted to its ester by CH_2N_2 to give methyl ∝-arylidene β-benzoyl propionic acid (**6**) which was further cyclized by PPA and conc. H_2SO_4 as discussed above when 1-phenyl-3-carbomethoxy naphthalene (**9**) was isolated. The IR indicated presence of aryl ester at 1720 cm^{-1} (Table-4).

Condensation of β-benzoyl propionic acid and aryl aldehyde (veratraldehyde): β-Benzoyl propionic acid (**1**) and veratraldehyde (**2a**) were reactived with acetic anhydride and a drop of pyridine for 3 h. The hot reaction mixture was poured in cold water with stirring and then acidified with conc. HCl. The yellow mass obtained was filtered and crystallized with benzene to give ∝-veratralidene (3,4-dimethoxy benzelidene) γ-phenyl-δ,β-butenolide (**3a**), m.p. 125 ºC.

Conversion of ∝-veratralidene γ-phenyl-δ,β-butenolide to ∝-veratralidene β-benzoyl propionic acid: ∝-Veratralidene γ-phenyl-δ,β-butenolide (**3a**) was a reacted for 5 h with alcoholic sodium carbonate solution (prepared by dissolving 5 g anhydrous sodium carbonate in 20 mL methanol and 30 mL water). The resulting mixture was filtered cooled and acidified with conc. HCl to get a brown precipitate

which was crystallized with aqueous methanol and was identified as ∝-veratralidene β-benzoyl propionic acid (**4a**), m.p. 169 ºC.

TABLE-2

∝-Arylidene β-benzoyl propionic acid	eq. wt. Found (req.)	m.p., ºC (m.f.)	UV λ_{max}, nm (log €)	IR (cm^{-1})	NMR δ
(**4a**) $R_1 = R_2 = OCH_3$, $R_3 = H$, $R^1 = H$	323 (326)	169 ($C_{19}H_{20}O_4$)	233 (4.70) 274 (3.99) 398 (3.85)	1681	3.65-3.89 (s, 6H), 4.25 (s, 2H, CH_2), 6.89-8.10 (m, 8H-olefinic and aromatic proton)
(**4b**) $R_1 = R_2 = R^1 = OCH_3$, $R_3 = H$	349 (356)	192 ($C_{20}H_{20}O_6$)	-	1681	-
(**4c**) $R_1 = R_2 = O - CH_2 - O$, $R_3 = H$, $R^1 = H$	307 (310)	203 ($C_{18}H_{14}O_4$)	237 (4.42) 280 (4.13) 302 (4.05)	1682	-
(**4d**) $R_1 = R_2 = O- CH_2-O$, $R_3 = H$,$R^1 = OCH_3$	335 (340)	208 ($C_{19}H_{16}O_6$)	-	1680	-
(**4e**) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = H$, $R^1 = H$	317 (312)	207 ($C_{18}H_{16}O_4$)	233 (4.39) 289 (4.17)	1681	-
(**4f**) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = R^1 = OCH_3$	339 (342)	211 ($C_{10}H_{18}O_6$)	230 (4.20) 290 (4.12)	1682	3.68 and 3.95 (s, 6H, OCH_3), 4.28 (s, 2H, CH_2), 7.19 (s, 1H, OH) 6.90-8.10 (m, 8H-olefinic and aromatic proton)
(**4g**) $R_1 = R_2 = R_3 = OCH_3$, $R^1 = H$	354 (356)	198 ($C_{21}H_{20}O_6$)	-	1682	-
(**4h**) $R_1 = R_2 = R_3 = OCH_3$, $R^1 = OCH_3$	382 (387)	209 ($C_{21}H_{23}O_7$)	-	1685	-
(**4i**) $R_1 = R_2 = R_3 = H$, $R^1 = H$	263 (265)	171 ($C_{17}H_{13}O_3$)	244 (4.45) 264 (4.26)	1680	-
(**4j**) $R_1 = R_2 = R_3 = H$, $R^1 = OCH_3$	293 (296)	177 ($C_{18}H_{16}O_4$)	245 (4.28) 275 (4.30) 296 (4.05)	1681	-

Conversion of ∝-veratralidene β-benzoyl propionic acid to ∝-veratralidene, β-methylene, β-benzoyl propionic acid: To a solution of ∝-veratralidene β-benzoyl propionic acid (**4a**) in 10 % aq. NaOH solution was added 40 % formalin solution and was left overnight. It was then cooled and dried with sodium sulphate. Evaporation of solvent gave a gum like solid which was crystallized from benzene petroleum ether and identified as ∝-veratralidene, β-methylene β-benzoyl propionic acid (**5a**), m.p. 125 ºC.

Conversion of ∝-veratralidene β-benzoyl propionic acid to methyl ∝-veratralidene, β-benzoyl propionic acid: To a suspension of ∝-veratralidene β-benzoyl propionic acid (**4a**) in ether was added a solution of CH_2N_2 in ether (it was prepared from 2 g nitrosomethylene and 3 g NaOH, at 0 ºC excess of CH_2N_2 was decomposed by adding glacial acetic acid). The ether solution was washed with water sodium bicarbonate solution and dried (anhydrous sodium sulphate). Evaporation of solvent led to a yellow oil which was crystallized from methanol and identified as methyl ∝-veratralidene β-benzoyl propionic acid (**6a**), m.p. 96 ºC.

TABLE-3

∝-Arylidene β-methylene β-benzoyl propionic acid	eq. wt. Found (req.)	m.p., ºC (m.f.)	UV λ_{max}, nm (log €)	IR (cm^{-1})	NMR δ
(5a) $R_1 = R_2 = OCH_3$, $R_3 = H$, $R^1 = H$	332 (338)	125 ($C_{20}H_{18}O_5$)	235 (4.21) 282 (4.08)	1660	3.82 and 3.90 (s, 6H, $2OCH_3$) 6.06 (s,2H, $-C=CH_2$) 6.8-8.0 (m, 9h, aromatic and olefinic protons)
(5b) $R_1 = R_2 = R^1 = OCH_3$, $R_3 = H$	364 (369)	126 ($C_{21}H_{11}O_6$)	240 (4.22) 292 (4.08)	1680	5.99-6.02 (d, 2H, $-C+CH_2$), 6.15 (s, 2H, $-OCH_2O-$), 6.93-8.0 ((m, 9h, aromatic and olefinic protons)
(5c) $R_1 = R_2 = O-CH_2-O$, $R_3 = H$, $R^1 = H$	317 (322)	201 ($C_{19}H_{14}O_4$)	258 (4.67) 304 (4.09)	1660	-
(5d) $R_1 = R_2 = O-CH_2-O$, $R_3 = H$, $R^1 = OCH_3$	335 (337)	198 ($C_{20}H_{17}O_5$)	-	1680	-
(5e) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = H$, $R^1 = H$	320 (323)	176 ($C_{19}H_{15}O_5$)	-	1670	-
(5f) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = R^1 = OCH_3$	348 (354)	201 ($C_{20}H_{18}O_6$)	-	1660	-
(5g) $R_1 = R_2 = R_3 = OCH_3$, $R^1 = H$	363 (369)	195 ($C_{21}H_{21}O_6$)	-	-	-
(5h) $R_1 = R_2 = R_3 = OCH_3$, $R^1 = OCH_3$	396 (400)	201 ($C_{22}H_{24}O_7$)	-	-	-

Substitutions

a) $R_1 = R_2 = OCH_3$, $R_3 = H$, $R^1 = H$

b) $R_1 = R_2 = R^1 = OCH_3$, $R_3 = H$

c) $R_1 = R_2 = O-CH_2-O$, $R_3 = H$, $R^1 = H$

d) $R_1 = R_2 = O-CH_2-O$, $R_3 = H$, $R^1 = OCH_3$

e) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = H$, $R^1 = H$

f) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = R^1 = OCH_3$

g) $R_1 = R_2 = R_3 = OCH_3$, $R_1 = H$

h) $R_1 = R_2 = R_3 = OCH_3$, $R_1 = OCH_3$

i) $R_1 = R_2 = R_3 = H$, $R^1 = H$

j) $R_1 = R_2 = R_3 = H$, $R^1 = OCH_3$

Cyclization of ∝-veratralidene β-benzoyl propionic acid with polyphosphoric acid: ∝-Veratralidene β-benzoyl propionic (**4a**) acid was refluxed with PPA at 100 ºC for 1 h. The mixture was poured on crushed ice when the solid precipitated. It was crystallized with aq. ethanol and identified as 1-phenyl-6,7-dimethoxy naphthoic acid (**7a**), m.p. 217 ºC.

Cyclization with conc. H_2SO_4: ∝-Veratralidene β-benzoyl propionic acid (**4a**) was treated with conc. H_2SO_4 at 0 ºC for 24 h. The solution was poured in crushed ice, when precipitate separated which was crystallized from benzene pet. ether and identified as 1-phenyl-6,7-dimethoxy naphthoic acid (**7a**), m.p. 217 ºC.

TABLE-4

Lactone	eq. wt. Found (Req.)	m.p. (ºC)	m.f.	UV λ_{max}, nm (log €)	IR (cm^{-1})	NMR δ
(**7a**) $R_1 = R_2 = OCH_3$, $R_3 = H$, $R^1 = H$	305 (308)	217	$C_{19}H_{16}O_5$	235 (4.21) 282 (4.08)	1680	3.8 and 4.0 (s, 6H, $2OCH_3$), 7.2 (s, 1H, C_8-H), 7.35 (s, 1H, C_5-H), 7.43-7.85 (m, 5H, phenyl) and 8.45 (s, 1H, C_4-H)
(**7b**) $R_1 = R_2 = R^1 = OCH_3$, $R_3 = H$	320 (322)	179	$C_{20}H_{18}O_4$	240 (4.30) 288 (4.18)	1682	–
(**7c**) $R_1 = R_2 = O - CH_2 - O$, $R_3 = H$, $R^1 = H$	303 (304)	240	$C_{19}H_{12}O_4$	238 (4.25) 282 (4.10)	1680	–
(**7d**) $R_1 = R_2 = O - CH_2$-O,R_3=H,$R^1 = OCH_3$	315 (318)	242	$C_{20}H_{14}O_4$	-	1680	–
(**7e**) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = H$, $R^1 = H$	291 (294)	179	$C_{18}H_{14}O_4$	-	1681	4.1 (s, $1OCH_3$), 4.5 (s, 1H, OH, aromatic protons), 7.0 (s, 1H, C_8-H), 7.0-8.8 (m, aromatic-protons), 7.5 (m, 5H, phenyl)
(**7f**) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = R^1 = OCH_3$	322 (324)	212	$C_{19}H_{16}O_5$	-	1680	–
(**7g**) $R_1 = R_2 = R_3 = OCH_3$, $R^1 = H$	333 (336)	223	$C_{20}H_{16}O_5$	-	1683	3.8-3.9,3.95 (s, 9H, $3OCH_3$), 6.5-8.5 (m, aromatic protons), 7.5 (m, 5H, phenyl)
(**7h**) $R_1 = R_2 = R_3 = OCH_3$,$R^1 = OCH_3$	366 (368)	216	$C_{21}H_{20}O_6$	-	1680	–
(**8a**) $R_1 = R_2 = OCH_3$, $R_3 = H$, $R^1 = H$	-	205	$C_{20}H_{16}O_4$	258 (4.69) 314 (4.02)	1760	3.85 and 4.06 (s, 6H, $2OCH_3$), 5.22 (s, 2H, lactone CH_2), 7.16 (s, 1H, C_8-H), 7.37 (s, 1H,C_5-H), 7.6 (br. s, 5H, phenyl) and 8.36 (s, H, C_4-H)
(**8b**) $R_1 = R_2 = R^1 = OCH_3$, $R_3 = H$	-	230	$C_{21}H_{18}O_5$	260 (4.71) 320 (4.12)	1761	3.90, 4.01, 4.25 (s, 9H, $3OCH_3$), 5.30 (s, 2H, lactone CH_2), 7.1-7.7 (m, 6H, aromatic), 8.4 (s, 1H, C_4-H)
(**8c**) $R_1 = R_2 = O - CH_2 - O$, $R_3 = H$, $R^1 = H$	-	211	$C_{19}H_{12}O_4$	258 (4.60) 312 (4.12)	1762	5.23 (s, 2H, lactone CH_2), 6.10 (s, 2H, $-OCH_2O$), 7.13-7.4 (d, 6H aromatic), 8.28 (s, H, C_4-H)
(**8d**) $R_1 = R_2 = O - CH_2 - O$,$R_3 = H$,$R^1 = OCH_3$	-	215	$C_{20}H_{16}O_5$	-	1763	–
(**8e**) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = H$, $R^1 = H$	-	210	$C_{20}H_{16}O_4$	-	1761	3.83 (s, 3H, $1OCH_3$), 5.20 (s, 2H, lactone CH_2), 7.04, 7.30 (m, 7H and 1H, OH aromatic), 8.25 (s, 1H, C_4-H)
(**8f**) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = R^1 = OCH_3$	-	220	$C_{21}H_{19}O_5$	-	1761	–
(**8g**) $R_1 = R_2 = R_3 = OCH_3$, $R^1 = H$	-	235	$C_{21}H_{19}O_5$	-	1762	3.90, 4.01, 4.25 (s, 9H, $3OCH_3$), 5.30 (s, 2H, lactone CH_2), 7.1-7.7 (m, 6H, aromatic), 8.4 (s, 1H, C_4-H)
(**8h**) $R_1 = R_2 = R_3 = OCH_3$, $R^1 = OCH_3$	-	240	$C_{22}H_{19}O_6$	-	-	–
(**9a**) $R_1 = R_2 = OCH_3$, $R_3 = H$, $R^1 = H$	-	124	$C_{20}H_{18}O_4$	257 (4.71) 306 (4.05)	1720	3.85, 3.96, 4.03 (s, 9H, CO_2, CH_3, OCH_3), 7.24and 7.30 (s, sh), C_3-H and C_8-H), 7.85 (s, sh, phenyl) 7.9 (d, $J = 2$ H_2, 1H, C_4-H), 8.47 (d, $J = 2$ H_2, C_2-H)
(**9b**) $R_1 = R_2 = R^1 = OCH_3$, $R_3 = H$	-	126	$C_{21}H_{23}O_5$		1720	–
(**9c**) $R_1 = R_2 = O - CH_2 - O$, $R_3 = H$, $R^1 = H$	-	171	$C_{21}H_{14}O_4$	258 (4.67) 304 (4.09) 342 (3.51)	1720	4.02 (s, 3H, OCH_3), 5.94) s, 2H, OCH_2O-), 7.32 and 7.38 (5 (sh) 2H, C_5-H and C_8-H), 7.60 (s, sh, phenyl), 8.04 (d, $J = 2$, H_2, 1H, 2H) and 8.86 (d, $J = 2$ H_2, 1H, C_4-H)
(**9d**) $R_1 = R_2 = O - CH_2 - O$,$R_3 = H$,$R^1 = OCH_3$	-	182	$C_{22}H_{17}O_5$	260 (4.91) 308 (3.39)	1720	–
(**9e**) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = H$, $R^1 = H$	-	152	$C_{19}H_{18}O_4$	-	1720	–
(**9f**) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = R^1 = OCH_3$	-	163	$C_{20}H_{21}O_5$	-	1720	–
(**9g**) $R_1 = R_2 = R_3 = OCH_3$, $R^1 = H$	-	132	$C_{21}H_{22}O_5$	-	1720	–
(**9h**) $R_1 = R_2 = R_3 = OCH_3$, $R^1 = OCH_3$	-	136	$C_{22}H_{25}O_6$	-	1720	–

Cyclization of ∝-veratralidene β-methylene β-benzoyl propionic acid with polyphosphoric acid: ∝-Veratralidene, β-methylene β-benzoyl propionic acid (**5a**) was refluxed with PPA at 100 ºC for 1 h. The mixture was poured on crushed ice when the solid precipitated. It was crystallized with aq. ethanol and identified as 1-veratryl naphthalene-3-carboxylic acid lactone (**8a**), m.p. 205 ºC.

Cyclization with conc. H_2SO_4: ∝-Veratralidene, β-methylene β-benzoyl propionic acid (**5a**) was treated with conc. H_2SO_4 at 0 ºC for 24 h. The solution was poured in crushed ice, when precipitate separated which was crystallized from benzene pet. ether and identified as 1-veratryl naphthalene-3-carboxylic acid lactone (**8a**), m.p. 205 ºC.

Cyclization of methyl ∝-veratralidene β-benzoyl propionic acid with polyphosphoric acid: Methyl ∝-veratralidene β-benzoyl propionic acid (**6a**) was refluxed with PPA at 100 ºC for 1 h. The mixture was poured on crushed ice when the solid precipitated. It was crystallized with aq. ethanol and identified as 1-phenyl-3-carbomethoxy-6,7-dimethoxy naphthalene (**9a**), m.p. 124 ºC.

Cyclization with conc. H_2SO_4: Methyl ∝-veratralidene β-benzoyl propionic acid (**6a**) was treated with conc. H_2SO_4 at 0 ºC for 24 h. The solution was poured in crushed ice, when precipitate separated which was crystallized from benzene pet. ether and identified as 1-phenyl 3-carbomethoxy, 6-7-dimethoxy naphthalene (**9a**), m.p. 124 ºC.

Substitutions

a) $R_1 = R_2 = OCH_3$, $R_3 = H$, $R^1 = H$
b) $R_1 = R_2 = R1 = OCH_3$, $R_3 = H$
c) $R_1 = R_2 = O\text{-}CH_2\text{-}O$, $R_3 = H$, $R^1 = H$
d) $R_1 = R_2 = O\text{-}CH_2\text{-}O$, $R_3 = H$, $R^1 = OCH_3$
e) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = H$, $R^1 = H$
f) $R_1 = OCH_3$, $R_2 = OH$, $R_3 = R^1 = OCH_3$
g) $R_1 = R_2 = R_3 = OCH_3$, $R^1 = H$
h) $R_1 = R_2 = R_3 = OCH_3$, $R^1 = OCH_3$
i) $R_1 = R_2 = R_3 = H$, $R^1 = H$
j) $R_1 = R_2 = R_3 = H$, $R^1 = OCH_3$

RESULTS AND DISCUSSION

Perkin condensation of β-benzoyl propionic acid (**1**) with aryl aldehyde (**2**) yielded butenolide[5] (**3**) which finally lead to ∝-arylidene β-benzoyl propionic acid[6] (**4**). The system thus obtained contained the required skeleton to prepare pericarbonyl lactone and 1-phenyl naphthalene system.

∝-Arylidene β-benzoyl propionic acid (**4**) was treated with different reagents like CH_2N_2 and formalin to get its ester and formylated products **5** and **6**, respectively.

Earlier attempts[7] to prepare pericarbonyl lactone system[8] from **5** were attempted in two steps. In the first step, **5** was cyclized by acetic acid and hydrochloric

acid and the cyclized product obtained from **5** was hydrolyzed followed by treatment with hydrochloric acid to get 1-phenyl 3-carboxylic acid lactone (**8**).

However, the synthesis of pericarbonyl lactone from **5** was achieved in one step with polyphosphoric acid and conc. H_2SO_4 which were found to be remarkable cyclization reagents in these reactions. With the view to cyclize ∝-arylidene β-benzoyl propionic acid (**4**) and its derivatives ∝-arylidene β-methylene β-benzoyl propionic acid (**5**) and methyl ∝-arylidene β-benzoyl propionic acid (**6**), they were treated with polyphosphoric acid (PPA) and conc. H_2SO_4.

Conclusion

The synthesis of pericarbonyl lactone (**8**) from (**5**) was achieved in one step with polyphosphoric acid and conc. H_2SO_4 which were found to be remarkable cyclization reagents in these reactions. In system (**5**) there is hyperconjugation at CH_2. And cyclization takes place by keto-enol tautomerism. The aromatic atmosphere spread is more on s-*cis* butadiene than s-*trans* orientation. Though the s-*trans* is more, stable here s-*cis* has more chance to exit. Hence the facile cyclization *via* keto-enol tautomerization which in turn existed due to hyperconjugation which is possible due to methylene. All these intermediate structures drives the reaction towards aryl lactonization via cyclization, by removal of H and OH and simultaneous tautomerism at the COOH and CH positive centre. The above discussion leads to formation of pericorbonyl lactone (**8**). The synthesis of **7** from **4** and **9** from **6** takes place involving keto-enol tautomerism followed by removal of H and OH.

ACKNOWLEDGEMENTS

The authors are greatful to Dr. M.M. Gadegone, Director, Institute of Science, Nagpur for providing the necessary research facilities. Thanks are also due to C.S.I.R. for spectral analysis.

REFERENCES

1. S.P.B. Ovenden, J. Yu, S.S. Wan, G. Sberna, R.M. Tait, D. Rhodes, S. Cox, J. Coates, N.G. Walsh and B.M. Meurer-Grimes, *Phytochemistry*, **65**, 3255 (2004).
2. R.D. Haworth and G. Sheldrick, *J. Chem. Soc.*, (1935).
3. R. Stevenson and E. Block, *J. Chem. Soc.*, 711 (1971).
4. C. David, Harrowven, Mark Bradley, J Lois Castro and Stuart R Flanagan, *Tetrahedron Lett.*, **42**, (2001).
5. A.I. Scott, Pergamon Press, London, p. 79 (1969).
6. V.R. Pasarkar, Ph.D. Thesis, Nagpur University, India (1977).
7. S. Takano, S. Otaki and K. Oyasawara, *Tetrahedron Lett.*, **26**, (1985).
8. P.W. Agnihotri, V.R. Pasarkar and G. Bagawant, *J. Indian Chem. Soc.*, **59**, 869 (1982).

(*Received*: 27 February 2009; *Accepted*: 11 January 2010) AJC-8279