

Synthesis of Dibenzoylmethanes as Intermediates for Flavone Synthesis by a Modified Baker-Venkataraman Rearrangement

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1-Polyoxyphenyl-3-(2,6-dioxyphenyl)propane-1,3-diones have been synthesized as intermediates for flavone synthesis by condensation of 2-(2,6-dioxybenzoyloxy)polyoxyacetophenone in the presence of phase transfer catalyst. The average yields of 1-polyoxyphenyl-3-phenylpropane-1,3-diones, 1-polyoxyphenyl-3-(2-benzyloxyphenyl)propane-1,3-diones and 1-polyoxy-3-(2,6-dibenzyloxyphenyl)propane-1,3-diones were 79%, 74% and 71%, respectively. The bulkiness of the benzyloxy groups or methoxy groups exerted steric hindrance and reduced the yield. Nevertheless, the yields were higher than the previously reported ones.

Key words: 1,3-Diphenylpropane-1,3-diones, Intermediates for flavone synthesis, Phase transfer catalysis

INTRODUCTION

The Baker-Venkataraman rearrangement of 2-benzoyloxyacetophenones is a key reaction step for synthesis of flavone derivatives. However, it is a disadvantage that one usually needs strong reaction conditions for this rearrangement. Baker (Baker, 1933) and Venkataraman (Mahal *et al.*, 1933, 1934) used potassium carbonate, sodium amide, sodium ethoxide or metallic sodium as base. Farkas and coworkers (Farkas *et al.*, 1968) synthesized 1-(2-hydroxy-5,6-dimethoxyphenyl)-3-(2,6-dimethoxyphenyl)-1,3-propanedione, an intermediate for the synthesis of zapotin from *Casimiroa edulis*, in the presence of NaH at 90°C and for 4 hrs. The difficulty in the enolate formation of the acetyl group in a polyoxygenated acetophenone which could be due to electron rich oxy group in the benzene ring might be a reason for retarding the reaction. Beside this electronic effect, another reason for lowering the yield is a hydrolysis of the sensitive methoxy groups caused by the strong reaction condition and the long reaction time. So the use of a phase transfer catalyst, accelerating the nucleophilic reactions in an inert solvent and at a low temperature (Weber *et al.*, 1977), could be advantageous for such a reaction. Recently we have synthesized various kind of 2-(polyoxybenzoyloxy)-polyoxyacetophenones as starting materials for synthesis of the dibenzoylmethanes (Song *et*

al., 1994). These acetophenones are expected to undergo a smooth intramolecular Claisen condensation under a phase transfer catalytic conditions. Tetrabutylammonium fluoride was proved to be suitable and effective phase transfer catalyst for the condensation of dibenzoylmethanes.

MATERIALS AND METHODS

Materials

Tetrabutylammonium fluoride was purchased from Aldrich Chemical Co. Solvents and chemicals used in this procedure were of reagent grade.

Apparatus

Melting points were determined on a Electrothermal 9100 (Germany) and were uncorrected. IR spectra were recorded on a IR Report-100 (Jasco., Japan). ¹H-NMR spectra were taken on JNM-EX90 (JEOL., Japan) spectrometer using TMS as an internal standard.

General Synthetic methods

0.008 mol of the acetophenone was dissolved in 20 ml of benzene. 0.0008 mol of tetrabutylammonium fluoride and 0.01 mol of KOH powder were added to this solution. The mixture was stirred for 30 min at room temperature. The reaction mixture was washed with 20 ml of water three times and the solvent was evaporated. The residue was recrystallized in

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ethanol or methanol.

1,3-diphenylpropane-1,3-diones

1-(2-hydroxyphenyl)-3-phenylpropane-1,3-dione (1): Yield 85%; yellow crystal; mp. 119-121°C; IR(KBr) ν_{\max} cm^{-1} 3400, 3080, 1613; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 4.69 (2H, s, H-COCH₂CO), 6.89-7.68 (6H, m, H-3,4,5,3',4',5'), 7.80 (1H, dd, J=8.7, 2.2 Hz, H-6), 8.10-8.21 (2H, m, 2',6'), 11.98 (1H, s, H-OH).

1-(2-hydroxy-4-methoxyphenyl)-3-phenylpropane-1,3-dione (2): Yield; 83%, yellow crystal; mp. 101-103°C; IR(KBr) ν_{\max} cm^{-1} 3380, 3088, 2971, 1610; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 3.85 (3H, s, H-OCH₃), 4.56 (2H, s, H-COCH₂CO), 6.45-6.56 (3H, H-3,5,6), 7.25-7.58 (3H, m, H-3',4',5'), 7.69 (1H, d, J=8.9 Hz, H-6), 7.86-7.98 (2H, m H-2',6'), 12.57 (1H, s, H-OH).

1-(2-hydroxy-5-methoxyphenyl)-3-phenylpropane-1,3-dione (3): Yield 83%; yellow crystal; mp. 99-100°C; IR(KBr) ν_{\max} cm^{-1} 3390, 3089, 2987, 1609; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 3.84 (3H, s, H-OCH₃), 4.59 (2H, s, H-COCH₂CO), 6.90-7.21 (3H, m, H-3,4,6), 7.47-7.60 (3H, m, H-3',4',5'), 7.89-8.00 (2H, m, H-2',6'), 11.64 (1H, s, H-OH).

1-(2-hydroxy-6-methoxyphenyl)-3-phenylpropane-1,3-dione (4): Yield 70%; yellow crystal; mp. 96-98°C; IR(KBr) ν_{\max} cm^{-1} 3390, 3090, 2990, 1610; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 3.87 (3H, s, H-OCH₃), 4.60 (2H, s, H-COCH₂CO), 6.58-6.87 (3H, m, H-3,4,5), 7.21-7.78 (3H, m, H-3',4',5'), 7.81-8.01 (2H, m, H-2',6'), 12.30 (1H, s, H-OH).

1-(2-hydroxy-4,6-dimethoxyphenyl)-3-phenylpropane-1,3-dione (5): Yield 73%; yellow crystal; mp. 128-129°C; IR(KBr) ν_{\max} cm^{-1} 3390, 3087, 2980, 1608; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 3.85 (3H, s, H-OCH₃), 3.90 (3H, s, H-OCH₃), 4.60 (2H, s, H-COCH₂CO), 6.18 (1H, d, J=2.3 Hz, H-5), 6.30 (1H, d, J=2.3 Hz, H-3), 7.10-7.42 (3H, m, H-3',4',5'), 7.82-7.92 (2H, m, H-2',6'), 12.01 (1H, s, H-OH).

1-(2-hydroxy-3,4-dimethoxyphenyl)-3-phenylpropane-1,3-dione (6): Yield 78%; yellow crystal; mp. 119-121°C; IR(KBr) ν_{\max} cm^{-1} 3385, 3090, 2989, 1612; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 3.82 (3H, s, H-OCH₃), 3.87 (3H, s, H-OCH₃), 4.70 (2H, s, H-COCH₂CO), 6.60 (1H, d, J=8.9 Hz, H-5), 7.12-7.42 (3H, m, H-3',4',5'), 7.65 (1H, d, J=8.9 Hz, H-6), 7.89-7.99 (2H, m, H-2',6'), 12.34 (1H, s, H-OH).

1-(2-hydroxy-3,4,6-trimethoxyphenyl)-3-phenylpropane-1,3-dione (7): Yield 70%; yellow crystal; mp. 110-111°C; IR(KBr) ν_{\max} cm^{-1} 3400, 3090, 2974, 1614; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 3.84 (3H, s, H-OCH₃), 3.87 (3H, s, H-OCH₃), 3.99 (3H, s, H-OCH₃), 4.58 (2H, s, H-COCH₂CO), 6.30 (1H, s, H-5), 7.07-7.38 (3H, m, H-3',4'

,5'), 7.86-7.97 (2H, m, H-2',6'), 12.24 (1H, s, H-OH).

1-(2-hydroxyphenyl)-3-(2-benzyloxyphenyl)propane-1,3-dione (8): Yield; 73%, yellow crystal; mp. 144-146°C; IR(KBr) ν_{\max} cm^{-1} 3380, 3078, 2978, 1610; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 4.65 (2H, s, H-COCH₂CO), 5.21 (2H, s, H-CH₂-Ph), 7.08-7.58 (11H, m, H-3,4,5,3',4',5', -CH₂-Ph), 7.76 (1H, dd, J=8.7, 2.2 Hz, H-6), 7.95 (1H, dd, J=8.8, 2.2 Hz, H-6'), 12.02 (1H, s, H-OH).

1-(2-hydroxy-4-methoxyphenyl)-3-(2-benzyloxyphenyl)propane-1,3-dione (9): Yield 73%; yellow crystal; mp. 97-99°C; IR(KBr) ν_{\max} cm^{-1} 3385, 3090, 2978, 1616; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 3.86 (3H, s, H-OCH₃), 4.60 (2H, s, H-COCH₂CO), 5.21 (2H, s, H-CH₂-Ph), 6.48 (1H, d, J=2.3 Hz, H-3), 6.87 (1H, d, J=2.3 Hz, H-5), 7.15-7.67 (8H, m, H-3',4',5', -CH₂-Ph), 7.80 (1H, d, J=8.9 Hz, H-6), 8.04 (1H, dd, J=8.8, 2.2 Hz, H-6').

1-(2-hydroxy-5-methoxyphenyl)-3-(2-benzyloxyphenyl)propane-1,3-dione (10): Yield 80%; yellow crystal; mp. 131-132°C; IR(KBr) ν_{\max} cm^{-1} 3390, 3084, 2975, 1618; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 3.80 (3H, s, H-OCH₃), 4.70 (2H, s, H-COCH₂CO), 5.20 (2H, s, H-CH₂-Ph), 6.80-7.52 (11H, m, H-3,4,6,3',4',5', -CH₂-Ph), 8.05 (1H, dd, J=8.8, 2.2 Hz, H-6'), 12.12 (1H, s, H-OH).

1-(2-hydroxy-6-methoxyphenyl)-3-(2-benzyloxyphenyl)propane-1,3-dione (11): Yield 63%; yellow crystal; mp. 123-124°C; IR(KBr) ν_{\max} cm^{-1} 3400, 3089, 2988, 1614; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 3.90 (3H, s, H-OCH₃), 4.59 (2H, s, H-COCH₂CO), 5.23 (2H, s, H-CH₂-Ph), 6.78-7.47 (11H, m, H-3,4,5,3',4',5', -CH₂-Ph), 7.98 (1H, dd, J=8.8, 2.2 Hz, H-6'), 12.20 (1H, s, H-OH).

1-(2-hydroxy-4,6-dimethoxyphenyl)-3-(2-benzyloxyphenyl)propane-1,3-dione (12): Yield 75%; yellow crystal; mp. 113-114°C; IR(KBr) ν_{\max} cm^{-1} 3380, 3050, 2978, 1618; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 3.89 (3H, s, H-OCH₃), 3.92 (3H, s, H-OCH₃), 4.62 (2H, s, H-COCH₂CO), 5.21 (2H, s, H-CH₂-Ph), 6.21 (1H, d, J=2.3 Hz, H-5), 6.30 (1H, d, 2.3 Hz, H-3), 6.92-7.52 (8H, m, H-3',4',5', -CH₂-Ph), 8.00 (1H, dd, 8.8, 2.2 Hz, H-6'), 12.32 (1H, s, H-OH).

1-(2-hydroxy-3,4-dimethoxyphenyl)-3-(2-benzyloxyphenyl)propane-1,3-dione (13): Yield 78%; yellow crystal; mp. 154-156°C; IR(KBr) ν_{\max} cm^{-1} 3390, 3095, 2988, 1615; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 3.82 (3H, s, H-OCH₃), 3.98 (3H, s, H-OCH₃), 4.65 (2H, s, H-COCH₂CO), 5.19 (2H, s, H-CH₂-Ph), 6.85 (1H, d, J=8.9 Hz, H-5), 6.90-7.42 (8H, m, H-3',4',5', -CH₂-Ph), 8.11 (1H, dd, J=8.8, 2.2 Hz, H-6'), 12.42 (1H, s, H-OH).

1-(2-hydroxy-3,4,6-trimethoxyphenyl)-3-(2-benzyloxyphenyl)propane-1,3-dione (14): Yield 78%; yellow crystal; mp. 148-150°C; IR(KBr) ν_{\max} cm^{-1} 3400, 3089, 2978, 1619; $^1\text{H-NMR}$ (CDCl_3) δ (ppm) 3.82 (3H, s, H-OCH₃), 3.88 (3H, s, H-OCH₃), 3.92 (3H, s, H-OCH₃),

4.64 (2H, s, H-COCH₂CO), 5.20 (2H, s, H-CH₂-Ph), 6.30 (1H, s, H-5), 7.00-7.48 (8H, m, H-3',4',5', -CH₂-Ph), 8.04 (1H, dd, J=8.8, 2.2 Hz, H-6'), 12.35 (1H, s, H-OH).

1-(2-hydroxyphenyl)-3-(2,6-dibenzoyloxyphenyl)propane-1,3-dione (15): Yield 71%; yellow crystal; mp. 110-112°C; IR(KBr) ν_{\max} cm⁻¹ 3400, 3082, 2988, 1622; ¹H-NMR(CDCl₃) δ (ppm) 4.61 (2H, s, H-COCH₂CO), 5.20 (4H, s, H-CH₂-Ph \times 2), 6.65 (2H, d, J=8.8 Hz, H-2',6'), 7.14-7.48 (14H, m, H-3,4,5,4', -CH₂-Ph \times 2), 7.80 (1H, dd, J=8.7, 2.2 Hz, H-6), 12.20 (1H, s, H-OH).

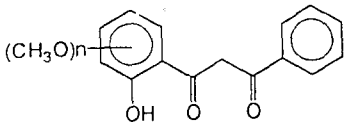
1-(2-hydroxy-4-methoxyphenyl)-3-(2,6-dibenzoyloxyphenyl)propane-1,3-dione (16): Yield 70%; yellow crystal; mp. 98-99°C; IR(KBr) ν_{\max} cm⁻¹ 3400, 3008, 2990, 1625; ¹H-NMR(CDCl₃) δ (ppm) 3.80 (3H, s, H-OCH₃), 4.58 (2H, s, H-COCH₂CO), 5.20 (4H, s, H-CH₂-Ph \times 2), 6.42 (1H, d, J=2.3 Hz, H-3), 6.68 (2H, d, J=8.8 Hz, H-2',6'), 6.80 (1H, d, J=2.3 Hz, H-5), 7.14-7.48 (11H, m, H-4', -CH₂-Ph \times 2), 7.84 (1H, d, J=8.9 Hz, H-6), 12.24 (1H, s, H-OH).

1-(2-hydroxy-5-methoxyphenyl)-3-(2,6-dibenzoyloxyphenyl)propane-1,3-dione (17): Yield 74%; yellow crystal; mp. 105.3-106.7°C; IR(KBr) ν_{\max} cm⁻¹ 3390, 3088, 2987, 1620; ¹H-NMR(CDCl₃) δ (ppm) 3.82 (3H, s, H-OCH₃), 4.70 (2H, s, H-COCH₂CO), 5.21 (4H, s, H-CH₂-Ph \times 2), 6.65 (1H, d, J=2.2 Hz, H-3), 6.70 (2H, d, J=8.8 Hz, H-2',6'), 6.82 (1H, d, J=2.2 Hz, H-6), 7.20-7.48 (11H, m, H-4'-CH₂-Ph \times 2), 12.26 (1H, s, H-OH).

1-(2-hydroxy-6-methoxyphenyl)-3-(2,6-dibenzoyloxyphenyl)propane-1,3-dione (18): Yield 70%; yellow crystal; mp. 107-108°C; IR(KBr) ν_{\max} cm⁻¹ 3395, 3093, 2985, 1625; ¹H-NMR(CDCl₃) δ (ppm) 3.80 (3H, s, H-OCH₃), 4.69 (2H, s, H-COCH₂CO), 5.19 (4H, s, H-CH₂-Ph \times 2), 6.72 (2H, d, J=8.8 Hz, H-2',6'), 7.00-7.45 (14H, m, H-3,4,5,4', -CH₂-Ph \times 2), 12.16 (1H, s, H-OH).

1-(2-hydroxy-4,6-dimethoxyphenyl)-3-(2,6-dibenzoyloxyphenyl)propane-1,3-dione (19): Yield 74%; yellow

Table I. Yield and physical data of 1-polyoxyphenyl-3-phenylpropane-1,3-diones (1-7)



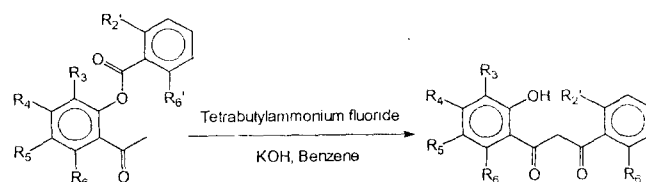
| Compd. | Color | mp.(°C) | Yield(%) |
|--------|------------------|---------|----------|
| 1 | Yellowish needle | 119-121 | 85 |
| 2 | Yellowish needle | 101-103 | 83 |
| 3 | Yellowish needle | 99-100 | 83 |
| 4 | Yellowish needle | 96- 98 | 70 |
| 5 | Yellowish needle | 128-129 | 73 |
| 6 | Yellowish needle | 122-123 | 78 |
| 7 | Yellowish needle | 110-111 | 70 |

crystal; mp. 111-112°C; IR(KBr) ν_{\max} cm⁻¹ 3390, 3090, 2990, 1622; ¹H-NMR(CDCl₃) δ (ppm) 3.58 (3H, s, H-OCH₃), 3.64 (3H, s, H-OCH₃), 4.65 (2H, s, H-COCH₂CO), 5.20 (4H, s, H-CH₂-Ph 2), 6.00 (1H, d, 2.2 Hz, H-3), 6.28 (1H, d, 2.2 Hz, H-5), 6.60 (2H, d, J=8.8 Hz, H-2',6'), 7.14-7.43 (11H, m, H-4', -CH₂-Ph \times 2), 12.28 (1H, s, H-OH).

1-(2-hydroxy-3,4-dimethoxyphenyl)-3-(2,6-dibenzoyloxyphenyl)propane-1,3-dione (20): Yield 72%; yellow crystal; mp. 107-108°C; IR(KBr) ν_{\max} cm⁻¹ 3395, 3091, 2984, 1625; ¹H-NMR(CDCl₃) δ (ppm) 3.70 (3H, s, H-OCH₃), 3.78 (3H, s, H-OCH₃), 4.62 (2H, s, H-COCH₂CO), 5.20 (4H, s, H-CH₂-Ph \times 2), 6.37 (1H, d, J=8.7 Hz, H-5), 6.72 (2H, d, J=8.8 Hz, H-2',6'), 7.12 (1H, d, J=8.7 Hz, H-6), 7.16-7.50 (11H, m, H-4', -CH₂-Ph \times 2), 12.28 (1H, s, H-OH).

1-(2-hydroxy-3,4,6-trimethoxyphenyl)-3-(2,6-dibenzoyloxyphenyl)propane-1,3-dione (21): Yield 72%; yellow crystal; mp. 128-129°C; IR(KBr) ν_{\max} cm⁻¹ 3390, 3084, 2978, 1622; ¹H-NMR(CDCl₃) δ (ppm) 3.76 (3H, s, H-OCH₃), 3.79 (3H, s, H-OCH₃), 3.83 (3H, s, H-OCH₃), 4.67 (2H, s, H-COCH₂CO), 5.20 (4H, s, H-CH₂-Ph \times 2), 6.25 (1H, s, H-5), 6.64 (2H, d, J=8.8 Hz, H-2',6'), 7.12-7.40 (11H, m, H-4', -CH₂-Ph \times 2), 12.27 (1H, s, H-OH).

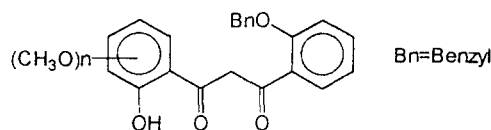
1-(2,6-dihydroxy-3,4,5-trimethoxyphenyl)-3-(2,6-dibenzoyloxyphenyl)propane-1,3-dione (22): Yield 70%; yellow oil; IR ν_{\max} cm⁻¹ 3328(OH), 3089, 2987, 1624;



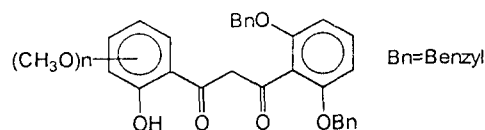
Scheme 1. Synthesis of 1,3-diphenylpropane-1,3-diones

1. R₃=R₄=R₅=R₆=R₂'=R₆'=H
2. R₃=R₅=R₆=R₂'=R₆'=H, R₄=OCH₃
3. R₃=R₄=R₆=R₂'=R₆'=H, R₅=OCH₃
4. R₃=R₄=R₅=R₂'=R₆'=H, R₆=OCH₃
5. R₃=R₆=R₂'=R₆'=H, R₄=R₆=OCH₃
6. R₅=R₆=R₂'=R₆'=H, R₃=R₄=OCH₃
7. R₅=R₂'=R₆'=H, R₃=R₄=R₆=OCH₃
8. R₃=R₄=R₅=R₆=R₆'=H, R₂'=OBn
9. R₃=R₅=R₆=R₆'=H, R₄=OCH₃, R₂'=OB
10. R₃=R₄=R₆=R₆'=H, R₅=OCH₃, R₂'=OBn
11. R₃=R₄=R₅=R₆'=H, R₆=OCH₃, R₂'=OBn
12. R₃=R₅=R₆'=H, R₄=R₆=OCH₃, R₂'=OBn
13. R₅=R₆=R₆'=H, R₃=R₄=OCH₃, R₂'=OBn
14. R₅=R₆'=H, R₃=R₄=R₆=OCH₃, R₂'=OBn
15. R₃=R₄=R₅=R₆=H, R₂'=R₆'=OBn
16. R₃=R₅=R₆=H, R₄=OCH₃, R₂'=R₆'=OBn
17. R₃=R₄=R₆=H, R₅=OCH₃, R₂'=R₆'=OBn
18. R₃=R₄=R₅=H, R₆=OCH₃, R₂'=R₆'=OBn
19. R₃=R₅=H, R₄=R₆=OCH₃, R₂'=R₆'=OBn
20. R₅=R₆=H, R₃=R₄=OCH₃, R₂'=R₆'=OBn
21. R₅=H, R₃=R₄=R₆=OCH₃, R₂'=R₆'=OBn
22. R₃=R₄=R₅=OCH₃, R₆=OH, R₂'=R₆'=OBn

* Bn=Benzyl

Table II. Yield and physical data of 1-(polyoxyphenyl)-3-(2-benzoyloxyphenyl)propane-1,3-diones (**8-14**)

| Compd. | Color | mp.(°C) | Yield(%) |
|-----------|------------------|---------|----------|
| 8 | Yellowish needle | 144-146 | 73 |
| 9 | Yellowish needle | 97- 99 | 73 |
| 10 | Yellowish needle | 131-132 | 80 |
| 11 | Yellowish needle | 123-124 | 63 |
| 12 | Yellowish needle | 113-114 | 75 |
| 13 | Yellowish needle | 154-156 | 78 |
| 14 | Yellowish needle | 148-150 | 78 |

Table III. Yield and physical data of 1-(polyoxyphenyl)-3-(2,6-dibenzoyloxy-phenyl)propane-1,3-diones (**15-22**)

| Compd. | Color | mp.(°C) | Yield(%) |
|-----------|------------------|---------|----------|
| 15 | Yellowish needle | 110-112 | 71 |
| 16 | Yellowish needle | 98- 99 | 70 |
| 17 | Yellowish needle | 105-106 | 74 |
| 18 | Yellowish needle | 107-108 | 70 |
| 19 | Yellowish needle | 111-112 | 74 |
| 20 | Yellowish needle | 107-108 | 72 |
| 21 | Yellowish needle | 128-129 | 72 |
| 22 | Yellowish oil | | 70 |

$^1\text{H-NMR}(\text{CDCl}_3)$ δ (ppm) 3.71 (3H, s, H-OCH₃), 3.75 (3H, s, H-OCH₃), 3.80 (3H, s, H-OCH₃), 4.68 (2H, s, H-COCH₂CO), 5.22 (4H, s, H-CH₂-Ph \times 2), 6.65 (2H, d, $J=8.8$ Hz, H-2',6'), 7.10-7.41 (11H, m, H-4'H-CH₂-Ph \times 2), 12.20 (1H, s, H-OH), 12.68 (1H, s, H-OH).

RESULTS AND DISCUSSION

The Baker-Venkataraman condensation of 2-benzoyloxyacetophenones to 1,3-diphenylpropane-1,3-diones could be carried out in high yield (70-85%) by using tetrabutylammonium fluoride as phase transfer catalyst.

And the reaction times (0.5-3 hrs) was shorter than other reactions (Baik et al., 1988). As seen in Table I and Scheme 1, the yields of 1-(polyoxyphenyl)-3-phenylpropane-1,3-diones from 2-benzoyloxyacetophenone were 79% in average. But presence of a methoxy group in C-6 of 2-benzoyloxy-6-methoxy-acetophenone as starting material lowered the yields of 4, 5 and 7. Steric effect of the methoxy group in C-6 would be the cause for lowering the yields.

As seen in Table II, introduction of a benzoyloxy group in C-2' severely reduced the yields of the corresponding 1,3-diones. The average yield of 1-(polyoxyphenyl)-3-(2-benzoyloxyphenyl)propane-1,3-diones was 74%. It is lower than average 79% of 1-(2-hydroxyphenyl)-3-phenylprop-1,3-diones (Table I). These results could be explained by steric hinderance and deactivation of ester carbonyl function by 1'-Benzoyloxy group. Polyoxygenation of phenyl rings (Table III, scheme I) of the acetophenones lowered the yields of the 1, 3-diones (15-22), owing to the steric and electronic effects. However, the average yield of present reactions (Table III) was still higher than the yield of previous studies (Baik et al., 1988).

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