One pot synthesis of 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-diones by modified Baker–Venkataraman transformation using microwave irradiation

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Reaction of 2-hydroxyacetophenones with aromatic acid anhydrides in the presence of anhydrous barium hydroxide in dimethyl sulfoxide using microwave irradiation gives 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-diones directly in a single pot reaction in high yields.

Keywords: 2-hydroxyacetophenones, aromatic acid anhydrides, microwave irradiations, 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-diones

1-(2-Hydroxyphenyl)-3-phenylpropane-1,3-diones constitute an important class of compounds[1] of natural occurrence and are also used as intermediates for the synthesis of flavones,[2] coumaran-3-ones,[3] isoxazoles,[4] pyramidines[5] and pyrazolines[6] which possess a broad spectrum of pharmacological activities.[7] The most convenient method for synthesis of these compounds involves base-catalysed Baker–Venkataraman rearrangement of 2-aroyloxyacetophenones. The various bases which have been used for this purpose include pulverised potassium hydroxide in dry pyridine,[8] potassium carbonate in a biphase medium using phase transfer catalysis,[9] sodamide,[10] sodium hydride,[11] and under UV irradiation.[12]

We now report an highly efficient procedure for the preparation of the title compounds (I Scheme 1) which involves the reaction of a 2-hydroxyacetophenone with an aromatic acid anhydride in the presence of anhydrous barium hydroxide in dimethyl sulfoxide medium under microwave irradiation (M.W.). The intermediate 2-aroyloxyacetophenones formed initially undergo rearrangement as soon as they are formed yielding the required β-diketones in a single pot reaction in high yields. The same reactions when repeated under ordinary thermal conditions, took much longer times (60 min) and yields were also poor.

The validity of above procedure was shown by preparing differently substituted 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-diones (Table 1) and the identity of the compounds was confirmed from their ^{1}H NMR and IR spectra and melting point comparison with literature values.

Experimental

The reactions were carried out in a domestic microwave oven (Samsung, output energy 900 W, frequency 2450 MHz, with temperature control arrangement model No. CE118KF) using 30% power for all the experiment maintaining the oven temperature at 40 °C.

General procedure for preparation of 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-diones **I(a–g)**

A solution of 2-hydroxyacetophenone (1 mmol) aromatic acid anhydride (1 mmol) anhydrous barium hydroxide (0.2 g) in dimethyl sulfoxide (1 ml) as taken in a 20 ml beaker covered with an inverted glass and funnel was subjected to microwave irradiation. Completion of the reaction was checked by TLC. The reaction mixture was diluted with ice cold water and the yellow solid that separated out was filtered and crystallised from methanol.

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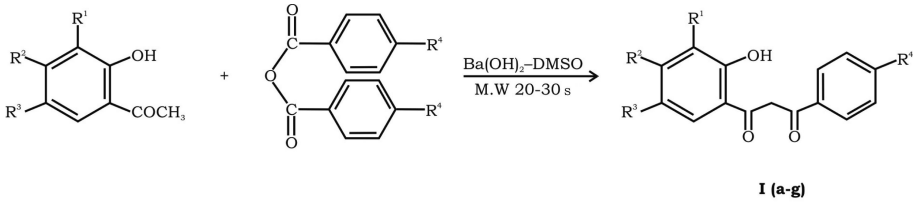

Scheme 1

Table 1 Synthesis of 1-(2-hydroxyphenyl)-3-phenylpropane-1,3-diones (I) under microwave irradiation

Product I (Scheme)	R^1	R^2	R^3	R^4	Method A		Method B		M.p./°C	Lit. M.p./°C
					Time /s	Yield /%	Time /min	Yield /%		
a	H	H	H	H	20	89	40	70	118–119	117–120[12]
b	H	H	H	OCH_3	30	80	50	65	107–109	110[13]
c	H	H	CH_3	H	25	86	45	60	79–81	83–84[14]
d	H	H	CH_3	OCH_3	25	90	55	75	92–93	94[15]
e	H	OCH_3	H	H	25	85	45	65	101–102	102[16]
f	H	OCH_3	H	OCH_3	25	85	50	60	105–107	107–108[17]
g	OCH_3	OCH_3	H	OCH_3	30	80	60	60	130–131	132[18]

Method A, Microwave irradiation.
Method B, Δ at 100°C on a water bath.

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References

1 J.N. Roitman, K. Mann and E. Wolenweber, *Photochemistry*, 1992, **31**, 985.
2 J. Staunton, H.D. Barton and W.D. Ollis, *Comprehensive Organic Chemistry,* Vol 4, Pergamon Press, London, 1979, 659.
3 O. Prakash, S. Goyal, S. Pahuja and S.P. Singh, *Synth. Commun.,* 1990, **20**, 1409.
4 M.M. Chincholkar and V.S. Jamode, *Indian J. Chem.,* 1979, **17B**, 510.
5 A.N. Thool and B.J. Ghiya, *J. Indian Chem. Soc.,* 1988, **65**, 522.
6 M.G. Joshi and K.N. Wadodkar, *Indian J. Chem.,* 1982, **21B**, 689.
7 J.M. Cassady, W.H. Baird and C. Chang, *J. Nat. Prod.,* 1990, **53**, 22; B. Havsteen, *Biochem. Pharmac.,* 1983, **32**, 1141.
8 H.S. Mahal and K. Venkataraman, *Curr. Sci.,* 1933, **4**, 214.
9 P.K. Jain, J.K. Makrandi and S.K. Grover, *Synthesis*, 1982, 221.
10 S.V. Kostanecki and J. Tambor, *Chem. Ber.,* 1900, **33**, 330.
11 I. Hirao, M. Yamaguchi and M. Hamada, *Synthesis,* 1984, 1076.
12 V. Bansal, P.K. Singh and R.N. Khanna, *Indian J. Chem.,* 1996, **35B**, 586.
13 W. Baker and F. Glocking, *J. Chem. Soc.,* 1950, 2759.
14 P.N. Wadodkar and M.G. Marathey, *Indian J. Chem.*, 1972, **10**, 145.
15 D.M. Fitzgerld, J.F.O/. Sullivan, E.M. Philbin and T.S. Wheelar, *J. Chem. Soc.,* 1955, 860.
16 H. Schmid and C.W. Bernholzer, *Helv. Chim. Acta.,* 1954, **37**, 1706.
17 N.C. Goomer and A. Bannerji, *Synthesis*, 1980, 874.
18 I.C. Badhwar, K.S. Kang and K. Venkataraman, *J. Chem Soc.,* 1932, 1107.