J. Chem. Research (S), 1998, 280–281†

Highly Efficient and Single Step Synthesis of 4-Phenylcoumarins and 3,4-Dihydro-4-phenylcoumarins Over Montmorillonite K-10 Clay, Under Microwave Irradiation†

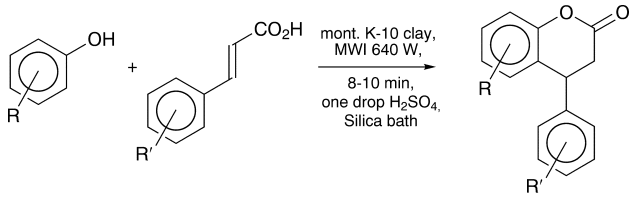
Jasvinder Singh,* Jasamrit Kaur, Sandeep Nayyar and Goverdhan L. Kad

Department of Chemistry, Panjab University, Chandigarh-160 014, India

A simple, elegant and one-pot synthesis of 3,4-dihydro-4-phenylcoumarins, 4-phenylcoumarins and their derivatives by making use of solid support, montmorillonite K-10 clay in conjunction with microwave irradiation is described.

Coumarins and dihydrocoumarins are an important class of organic compounds, used in the pharmaceutical industry and as intermediates in the synthesis of useful pesticides and bioactive compounds. A number of syntheses of coumarins are available which offer a variety of intermediates and reaction conditions.[1–7] Some of the problems which arise with these have been avoided by employing solid supports under microwave conditions.[8–10]

We have found that some 3,4-dihydro-4-phenylcoumarins and 4-phenylcoumarins can be obtained in a single step and in good yield. Phenol (or its derivatives) and cinnamic acid (or its derivatives) impregnated on activated montmorillonite K-10 clay (by heating under vacuum for 2 h), when subjected to microwave irradiation (MWI), in an open vessel and employing optimized conditions of 640 W power output in a domestic microwave oven, for 8–10 min, furnished 3,4-dihydro-4-phenylcoumarin and its derivatives **1**–**5**, Scheme 1. The results of this reaction are summarized in Table 1.



1–5

Scheme 1

The methodology adopted has a few advantages (i) no solvent is required and (ii) since an open vessel is used there is no question of excessive accumulation and consequent danger of explosion. The exact role of the microwave radiation is not known, that is whether it provides a thermal effect or in some way decreases the activation barrier, so that the reaction proceeds quickly. Montmorillonite KSF-clay predoped with or without $ZnCl_2$ was also used, however greater exposure time to MWI was required. When a mixture of phenol, cinnamic acid and one drop of H_2SO_4 was refluxed in dimethylformamide for 10 h, with or without K-10 clay, no reaction was observed.

Table 1 Reaction between phenols and cinnamic acids to form 3,4-dihydro-4-phenylcoumarins

Compound	R	R′	Solid support	*t*/min	Yield (%)	^{13}C NMR (δ)/phase on DEPT	300 MHz ^{1}H NMR (δ)	ν_{max}/cm^{-1}	Mass spectrum *m*/*z* M$^+$/%	Mp (lit.)/ °C
1	H	*p*-OMe	K-10	8	85	167.827/– 37.21/ – ve 39.90/ + ve	2.94–3.09 (m, 2 H) 4.28–4.32 (t, 1 H) 3.79 (s, 3 H)	1760, 1160, 1240	254/100	98[a]
2	*m*-OH	H	KSF/$ZnCl_2$ (no acid)	20	79	167.001/– 36.54/ – ve 38.93/ + ve	2.83–3.00 (m, 2 H) 4.06–4.24 (t, 1 H) 6.45 (br s, OH)	1760, 1210, 3200–3400	240/24	140–142 (140[1])
			K-10	8	75	38.93/ + ve	6.45 (br s, OH)		240/22	
3	*m*-OMe	H	K-10	8	81	167.741/– 37.404/ – ve 40.192/ + ve	2.96–3.10 (m, 2 H) 4.26–4.31 (t, 1 H) 3.80 (s, 3 H)	1760, 1130, 1220	254/100	110–114 (112[1])
4	H	*m*,*p*-OCH_2O-	K-10	10	65	167.683/– 37.32/ – ve 39.89/ + ve	2.94–3.09 (m,2 H) 4.25–4.29 (t, 1 H) 5.95 (s, 2 H)	1770, 1230, 1260	268/100	118[b]
5	H	H	K-10	10	82	167.645/– 37.063/ – ve	2.98–3.13 (m, 2 H) 4.32–4.37 (t,1 H)	1780, 1140, 1240	224/65	80–82 (83[1])
			KSF (no acid)	22	74	40.749/ + ve				

[a]Found: C, 75.43; H, 5.59. $C_{16}H_{14}O_3$ requires C, 75.58; H, 5.55%. [b]Found: C, 71.69; H, 4.55. $C_{16}H_{12}O_4$ requires C, 71.64; H, 4.51%.

*To receive any correspondence.

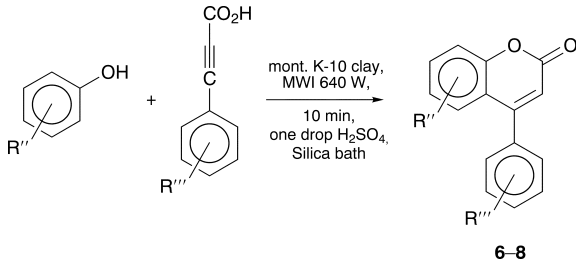
†This is a **Short Paper** as defined in the Instructions for Authors, Section 5.0 [see *J. Chem. Research (S)*, 1998, Issue 1]; there is therefore no corresponding material in *J. Chem. Research (M)*.

Table 2 Reactions of phenols and phenylpropynoic acid to form coumarins

Compound	R″	R‴	*t*/min	Yield (%)	Main peak in 300 MHz ^{1}H NMR (δ)	ν_{max}/cm^{-1}	Mass spectrum *m/z* M$^+$/%	Mp (lit.)/ °C
6	H	H	10	69.5	6.42 (s, 1 H)	1710, 1620, 1240	222/60	102–104(105[13])
7	*m*-OMe	H	10	55.0	6.28 (s, 1 H)	1700, 1630, 1220	252/54	138[a]
8	H	*p*-OMe	10	67.0	6.20 (s, 1 H)	1690, 1620, 1260	252/46	101–103[b]

[a]Found: C, 76.29, H, 4.51. $C_{16}H_{12}O_3$ requires C, 76.18; H, 4.79%. [b]Found: C, 76.06, H, 4.70. $C_{16}H_{12}O_3$ requires C, 76.17; H, 4.77%.

Similarly, when phenol (or its derivatives) and phenylpropynoic acid (or its derivatives) were subjected to MWI in the presence of montmorillonite K-10 clay with one drop of H_2SO_4 and placed in a silica bath, coumarins **6**–**8** (Scheme 2) were obtained in good yield as shown in Table 2.



6–8

Scheme 2

The results of the spectral data were compared with the data for analogs or similar systems.[11] The most relevant resonance in the ^{13}C NMR spectrum is at δ 167–168, corresponding to the carbonyl carbon. Condensation reactions involving resorcinol or its monomethyl ether with cinnamic acid, resulting in products **2**, **3** and **7**, proceed at the 4 not at the 2 position: thus the product available through this route will exclusively be the 7- and not the 5-substituted derivative.[12]

Experimental

Montmorillonite K-10 clay was purchased from Fluka.

Typical Procedure.—To activated montmorillonite K-10 clay (2 g) in a 100 ml Erlenmeyer flask was added a mixture of freshly distilled phenol (0.50 g, 5.3 mmol) and recrystallized *p*-methoxycinnamic acid (0.94 g, 5.3 mmol) dissolved in CH_2Cl_2 (5 ml) along with one drop of concentrated H_2SO_4. The solvent was evaporated and the resultant free-flowing solid placed on a silica bath and subjected to MWI at 640 W for 10 min. Dichloromethane (20 ml) was added, the reaction mixture filtered and the filtrate washed with saturated $NaHCO_3$ solution, brine and dried over Na_2SO_4. Evaporation of the solvent *in vacuo* yielded the product, 1.05 g (82%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.29–7.26 (d, $J = 4$, 1 H), 7.11–7.08 (t, $J = 4$, 4 H), 6.99–6.97 (d, $J = 4$, 1 H), 6.89–6.86 (d, $J = 4$, 2 H), 4.32–4.28 (t, $J = 6$ Hz, 1 H), 3.79 (s, 3 H) and 3.09–2.94 (m, 2 H). Mass spectrum (*m/z*, % base): 255/24 (M$^+$+1), 254/100 (M$^+$), 253/5 (M$^+$−1), 149/4 and 148/17. ^{13}C NMR ($CDCl_3$/phase on DEPT): δ 167.827, 159.005, 151.681, 132.240, 128.643/+ve, 128.310/+ve, 126.250, 124.659/+ve, 117.097/+ve, 114.502/+ve, 55.320/+ve, 39.900/+ve and 37.210/−ve. IR (CCl_4, cm^{-1}): 1760, 1240, 1160 and 750–710.

We are grateful to the CSIR, New Delhi, for providing financial assistance for this work.

Received, 11th November 1997; Accepted, 27th January 1998
Paper E/7/08103K

References

1 J. D. Simpson and H. Stephen, *J. Chem. Soc*., 1956, 1382.
2 P. Sebok, J. Jeko, T. Timar and J. Cs. Jaszberenyi, *Tetrahedron Lett*, 1992, **33**, 2791.
3 J. E. Pickett and P. C. Van Dort, *Tetrahedron Lett*., 1992, **33**, 1161.
4 A. J. Hoefnagel, E. A. Gunnewegh, R. S. Downing and H. Van Bekkum, *J. Chem. Soc., Chem. Commun*., 1995, 225.
5 L. Crombie, R. C. F. Jones and C. J. Palmer, *J. Chem. Soc., Perkin. Trans. 1*, 1987, 317.
6 S. Setha and R. Phadke, *Org. React*. (*N.Y.*), 1953, **7**, 1.
7 D. D. Chaudhari, *Chem. Ind*., 1983, 568.
8 G. L. Kad, J. Kaur, P. Bansal and J. Singh, *J. Chem. Res*. (*S*), 1996, 188.
9 G. L. Kad, I. R. Trehan, J. Kaur, S. Nayyar, A. Arora and J. S. Brar, *Indian J. Chem., Sect. B*, 1996, **35**, 734.
10 V. Singh, J. Singh, K. P. Kaur and G. L. Kad, *J. Chem. Res*. (*S*), 1997, 58.
11 K. K. Chan, *Tetrahedron*, 1977, **33**, 899.
12 N. S. Narasimhan and R. S. Mali, *Synthesis*, 1983, 957.
13 F. Bergmann, M. Weizmann, E. Dimant, J. Patai and J. Szmuskowicz, *J. Am. Chem. Soc*., 1948, **70**, 1612.