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Highly Efficient and Single Step Synthesis of 4-Phenylcoumarins and 3,4-Dihydro-4phenylcoumarins Over Montmorillonite K-10 Clay, Under Microwave Irradiation[†] Jasvinder Singh.^{*} Jasamrit Kaur, Sandeep Navyar and

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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.



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 ZnCl₂ was also used, however

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 $^{1}\text{H NMR}$ (δ)	$v_{\rm max}/{\rm cm}^{-1}$	Mass spectrum <i>m/z</i> M ⁺ /%	Mp (lit.)/ °C
1	Н	<i>p</i> -OMe	K-10	8	85	167.827/-	2.94–3.09 (m. 2 H)	1760, 1160, 1240	254/100	98ª
						37.21/-ve	4.28–4.32 († 1 H)			
						39.90/+ve	3.79 (s, 3 H)			
2	<i>m</i> -OH	Н	KSF/ZnCl ₂ (no acid)	20	79	167.001/-	2.83–3.00 (m 2 H)	1760, 1210, 3200–3400	240/24	(140-142)
			(no dola)			36.54/-ve	4.06-4.24	0200 0100		(110)
						38.93/ + ve	6.45 (br s, OH)			
			K-10	8	75	38.93/ + ve	6.45 (br s, OH)		240/22	
3	<i>m</i> -OMe	Н	K-10	8	81	167.741/-	2.96–3.10 (m, 2 H)	1760, 1130, 1220	254/100	110–114 (112 ¹)
						37.404/-ve	À.26–4.31 (t, 1 H)			, , , , , , , , , , , , , , , , , , ,
л	ы		K 10	10	65	40.192/ + ve	3.80 (s, 3 H)	1770 1220	269/100	110 ^b
4	п	<i>ш,р</i> -ОСП <u>2</u> О-	K-10	10	05	107.003/-	(m,2 H)	1260	200/100	110
						37.32/-ve	4.25-4.29			
						39.89/+ve	(I, I H) 5.95 (s, 2 H)			
5	Н	Н	K-10	10	82	167.645/-	2.98 - 3.13	1780, 1140,	224/65	80 - 82
						37.063/-ve	(III, 2 H) 4.32–4.37	1240		(03)
			KCE	າາ	7/	40.749/ 1.00	(t,1 H)			
			(no acid)	~~	/ 7	+0.7+3/ + Ve				

^aFound: C, 75.43; H, 5.59. C₁₆H₁₄O₃ requires C, 75.58; H, 5.55%. ^bFound: C, 71.69; H, 4.55. C₁₆H₁₂O₄ 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)*. 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 2 Reactions of phenols and phenylpropynoic acid to form coumarins

Compound	R″	R‴	<i>t</i> /min	Yield (%)	Main peak in 300 MHz ¹ H NMR (δ)	$v_{\rm max}/{\rm cm}^{-1}$	Mass spectrum <i>m/z</i> 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	<i>m</i> -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

^aFound: C, 76.29, H, 4.51. C₁₆H₁₂O₃ requires C, 76.18; H, 4.79%. ^bFound: C, 76.06, H, 4.70. C₁₆H₁₂O₃ 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.



The results of the spectral data were compared with the data for analogs or similar systems.¹¹ The most relevant resonance in the ¹³C 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 CH₂Cl₂ (5 ml) along with one drop of concentrated H₂SO₄. 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

NaHCO₃ solution, brine and dried over Na₂SO₄. Evaporation of the solvent *in vacuo* yielded the product, 1.05 g (82%). ¹H NMR (300 MHz, CDCl₃): 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. ¹³C NMR (CDCl₃)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 (CCl₄, cm⁻¹): 1760, 1240, 1160 and 750–710.

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