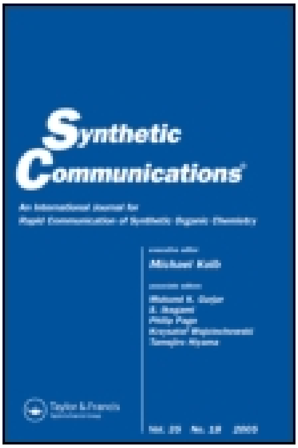

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SYNTHESIS OF CINNAMIC ACIDS CATALYZED BY EXPANSIVE GRAPHITE UNDER ULTRASOUND

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SYNTHESIS OF CINNAMIC ACIDS CATALYZED BY EXPANSIVE GRAPHITE UNDER ULTRASOUND

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ABSTRACT

Knoevenagel condensation of malonic acid with aromatic aldehydes catalysed by expansive graphite results cinnamic acids in 65–98% yields under ultrasound irradiation.

Reported applications for cinnamic acids and its derivatives include: used as a light penetration inhibitor in sunscreen formulations;[1] for the preparation of herbicidal compositions;[2] used as a substrate in the formation of photopolymers,[3] used as a raw material in the synthesis of heterocyclic color complexes[4] and antitumor agents *et al.*[5,6]

The Knoevenagel condensation of various aromatic aldehydes with malonic acid to give cinnamic acids has been extensively studied using base catalysts like ammonia, primary and secondary amines, particularly piperidine, pyridine, pyridine with a trace of piperidine and other secondary and tertiary amine.[7,8] It has been reported using acidic catalysts for the condensation such as sulfuric acid,[9,10] sulfuric acid–acetic acid.[11] However, both bases and acids, as homogenous catalysts, are difficult to be recovered and easily polluted the environment.

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Ultrasound has been increasingly used in organic synthesis.[12–15] Herein, we wish to report the efficient condensation between malonic acid and various aromatic aldehydes catalysed by expansive graphite under ultrasound.

$$\underset{\mathbf{1(a\text{-}j)}}{\mathrm{ArCHO}} + \underset{\mathbf{2}}{\mathrm{CH_2(CO_2H)_2}} \xrightarrow[43\ ^{\circ}\mathrm{C},\, \mathrm{CH_3CO_2C_2H_5}]{\text{graphite, u.s.}} \underset{\mathbf{3(a\text{-}j)}}{\mathrm{ArCH{=}CHCOOH}}$$

Scheme

As shown in the Scheme and Table, the ultrasound technique represented a better procedure in terms of the higher yield, milder reaction condition, easier workup. For example, 4-nitrocinnamic acid and 3-nitrocinnamic acid was previously prepared in yield 73% and 75% respectively, catalysed by piperidine, after standing for 24 h at rt, continuous heating for 7 h at 90°C.[8] Whereas under ultrasonication, 4-nitrocinnamic acid and 3-nitrocinnamic acid were obtained in a 98% and 89% yield at 43°C for 6–7 h. The catalyst, expansive graphite, can be easily removed by filtration and can be reused only by dried. Meanwhile, the present procedure also got a good result on molar scale for **1a**. It is worth noting that a prolonged period

Table. Preparation of Cinnamic Acids Catalysed by Expansive Graphite Under Ultrasound

Entry	Ar	Time (h)/ temp (°C)	Yield[a] (%)	m.p. (°C) (lit.)
a	2-furyl	3.5/41	77	135–136(136)[16]
		3.5–5/43	84[b]	135–136
b	4-ClC_6H_4	3.5/43	84	248–249(249–250)[18]
c	3-ClC_6H_4	6.0/43	98	162–163(162–163)[18]
d	4-$O_2NC_6H_4$	6.0/43	98	284–286(283–286)[8]
e	3-$O_2NC_6H_4$	7.0/43	89	199–200(198–201)[8]
f	4-$CH_3OC_6H_4$	10.0/43	81	170(170–172)[8]
g	4-$(CH_3)_2NC_6H_4$	9.0/43	85	214–215(216)[17]
h	4-OH-3-$MeOC_6H_3$	10.0/43	98	168–169(169)[16]
i	4-$CH_3C_6H_4$	10.0/43	65	196–197(198)[16]
j	3,4-$(OCH_2O)C_6H_3$	10.0/43	97	238–239(240)[16]

[a] Isolated yield based on aldehyde.

[b] The reaction was done on molar scale.

of ultrasonication did not increase the product yields. On the contrary, the products were polymerized.

In conclusion, we have established a practical condensation procedure for the synthesis of cinnamic acids catalysed by expansive graphite under ultrasound irradiation. The operational simplicity, use of inexpensive, non-corrosive and reusable catalyst, high yields and non-pollution can make this procedure a useful and attractive alternative to the currently available methods.

EXPERIMENTAL

Liquid aldehydes were purified by distillation prior to use. Melting points were uncorrected. IR spectra were recorded on Bio-Rad FTS-40 spectrometer (KBr). ^{1}H NMR spectra were measured on VXR-300S spectrometer, using TMS as internal standard and using $CDCl_3$ as solvent. Sonication was performed in Shanghai Branson-CQX ultrasonic cleaner with a frequency of 25 kHz and a nominal power 500 W. The reaction flask was located at the maximum energy area in the cleaner and the temperature of water bath was controlled by addition or removal of water.

Preparation of Expansive Graphite

A mixture of concentrated sulfuric acid (98%, 20 g), nitric acid (65%, 10 g), natural flake graphite (10 g) and potassium permanganate (0.7 g) was stirred at rt for 30 min. The expansive graphite was filtered, washed with water until pH = 6–7 and dried at 60°C for 1 h.

General Procedure

To a 50 ml Pyrex flask was charged with substituted aromatic aldehyde (**1**, 0.1 mol), malonic acid (**2**, 0.15 ml), expansive graphite (1.02 g), and ethyl acetate (20 ml). The mixture was irradiated in the water bath of an ultrasonic cleaner at the temperature for the period as indicated in the Table (sonication was continued until aldehyde disappeared, as indicated by TLC). The catalyst was separated by filtration and washed with ethyl acetate, the solvent was evaporated under reduced pressure until the crystal appeared. After cooling in an ice water bath, the formed product was collected by filtration and washed with water. The authenticity of the products was established by their melting points, IR and ^{1}H NMR spectra.

The procedure on molar scale was followed with furfural (1.00 mol), malonic acid (1.50 mol), expansive graphite (10.2 g), and ethyl acetate (400 ml) in a 1000 ml Pyrex flask. The mixture was irradiated in the water bath of an ultrasonic cleaner at 43°C for 3.5 h (sonication was continued until aldehyde disappeared, as indicated by TLC). The following procedure was the same as stated in the general workup.

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