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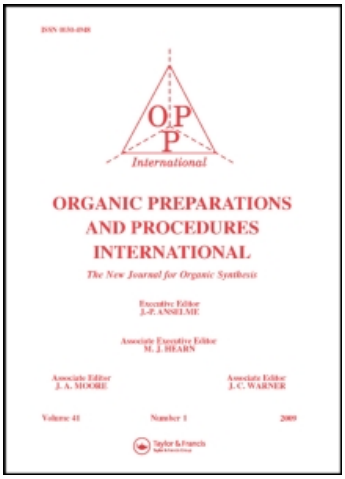

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SILICA GEL CATALYZED PREPARATION OF CINNAMIC ACIDS UNDER MICROWAVE IRRADIATION

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SILICA GEL CATALYZED PREPARATION OF CINNAMIC ACIDS UNDER MICROWAVE IRRADIATION

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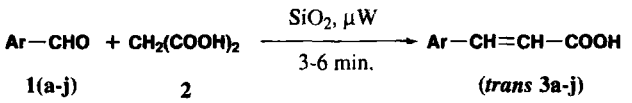
Microwave irradiation has become a very useful tool in organic synthesis and a great number of classical organic reactions have been successfully carried out utilizing the microwave dielectric heating technique.[1] Further, with the growing importance of inorganic solid supports in organic synthesis, numerous organic transformations have been reported using microwave heating with reactants adsorbed on inorganic supports such as SiO_2, Al_2O_3, clay etc.[2] These catalysts are fairly inexpensive and their application under solvent-free conditions can be highly advantageous due to the environmentally benign chemical processes they offer such as cleaner and faster reactions with an opportunity for easy separation and recycling of the catalysts.



1(a-j) **2** (*trans* **3a-j**)

There have been a number of reports on the condensation of carbonyl functionality with a variety of active methylene compounds using inorganic solid supports.[3] However, application of such non-conventional methods for the condensation of malonic acid with carbonyl compounds is scarce. In continuation of our ongoing program to develop environmentally benign solid-phase reactions[4] using inorganic supports and microwave activation, we present here a microwave-promoted condensation of malonic acid with aromatic aldehydes under solvent free (dry) conditions.

trans-Cinnamic acids (**3a-j**) were formed when the equimolar mixture of aromatic aldehydes (**1a-j**) and malonic acid, adsorbed on SiO_2, were irradiated with a microwave output of 600 watts. All the reactions were conducted in open Erlenmeyer flasks and the temperature of the reaction mass

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reached a maximum in the range 110-120° during irradiation. The products were isolated in moderate to high yields by extracting the reaction mass with ethyl acetate and evaporation of the solvent *in vacuo*. The crude products thus obtained, were purifed by flash chromatography and all products were characterized by IR, ^{1}H NMR spectroscopy and also by comparison of their melting points with the reported data for authentic samples. The condensations proceeded only to a minor extent (15-20% yield in 2 hours) when conducted under conventional conditions using an oil bath at 120°, which confirms the rate augmentation during microwave irradiation. The catalyst recovered during workup could be effectively reused after activation without any apparent loss of activity. However, aromatic ketones (e. g. acetophenone) did not yield α,β-unsaturated acid under these conditions. It may be of interest to mention that the literature methods for the thermal condensation of aromatic aldehydes and malonic acid using Al_2O_3,[6a] zeolite,[6b] pyridinium acetate,[6c] give arylidene malonic acids without any decarboxylation.

Table 1. Microwave-assisted Preparation of *trans*-Cinnamic Acids (**3a-j**)[a]

Entry	Ar	Reaction time (min.)	Yield[b] (%)	Melting Point (°C) Observed	Lit.[5]
1a	C_6H_5	4	83	135-137	135-136
1b	4-$NO_2C_6H_4$	4	86	285-286	286
1c	3-BrC_6H_4	4	84	177-178	179
1d	4-ClC_6H_4	4	80	248-249	249-250
1e	4-$CH_3C_6H_4$	6	71	194-196	196-198
1f	4-$CH_3OC_6H_4$	5	76	170-172	173-175
1g	2,4-$Cl_2C_6H_3$	5	80	232-234	233-235
1h	4-HOC_6H_4	5	78	213-215	214-215
1i	3,4-$(HO)_2C_6H_5$	5	76	223-224	225
1j	3,4-$(CH_3O)_2C_6H_3$	4	78	182-183	183

a) All products are identified by IR, ^{1}H NMR spectral analysis. b) Yield after chromatography.

In summary, the microwave promoted condensation of malonic acid with aromatic aldehydes catalyzed by SiO_2, is a rapid and clean general method for the preparation of cinnamic acids in good yields. This condensation and decarboxylation proceeds well with neutral catalyst, in the absence of any base, under solvent free (dry) conditions. Other merits such as simple workup and easy isolation procedure, the use of inexpensive catalyst that can be readily recovered and reused, makes this procedure an environmentally friendly and attractive alternative to conventional methods of synthesis.

EXPERIMENTAL SECTION

Microwave irradiations were carried out using a commercial microwave oven (BPL, BMO 700T) operating at a frequency 2450 MHz. Melting points (uncorrected) were recorded on a Buchi 510 appa-

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ratus. IR and ^{1}H NMR spectra were recorded on NICOLET-740 and Gemini 200 instruments, respectively. Chromatography grade SiO_2 (Aldrich 230-400 mesh), was activated at 140° for 3 hrs prior to use.

Microwave-assisted Preparation of Cinnamic acids. Typical Procedure.- Malonic acid (1.04 g, 10 mmol) and benzaldehyde (1.06 g, 10 mmol) were mixed with activated SiO_2 (5 g) in an agate mortar and the resulting fine powder was placed a pyrex Erlenmeyer flask and irradiated at a microwave output of about 600 watts for 4 minutes. The reaction mixture was cooled to room temperature and charged directly on a silica gel column (mesh 100-200 Å). Elution with ethyl acetate:n-hexane, 3:7) afforded the pure cinnamic acid (1.2 g, 83%), mp. 135-137°.

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