

Note

Friedel-Craft reaction in dry media under microwave irradiation

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Received 7 May 2007; accepted (revised) 3 October 2007

Friedel-Craft reaction on aromatic and hetero aromatic compounds in dry media under microwave irradiation has been carried out successfully using acid washed montmorillonite K10 clay as well as TLC grade silica gel as heterogeneous catalyst. Both the catalysts are found to be almost equally efficient. This method enhances the rate of the reaction, increases yields and purity of products and leads to the development of an economic and eco-friendly procedure.

Keywords: Friedel-Craft reaction, microwave irradiation, solid-phase synthesis, Montmorillonite K10 Clay

The solvent-free organic reactions assisted by microwaves in particular, have gained special attention¹⁻³ in recent years. The use of microwave activation in organic synthesis can increase the purity of the resulting products, enhance the chemical yield and shorten the reaction time. Solvent-free reaction leads to a clean, eco-friendly and economic technology.

Friedel-Craft reaction is a very versatile method for alkylation and acylation of aromatic and hetero aromatic compounds. Traditional Friedel-Craft reaction employs AlCl_3 as catalyst in higher than stoichiometric quantities. This process leads to pollution related to the disposal of catalyst and generation of highly acidic effluent and needs to be replaced by a green process.

Some modifications of Friedel-Craft reaction have already been reported⁴⁻⁷. Alkylation of N-protecting group free indole with vinyl ketone using iron salt catalyst has been reported by Tshiyuki *et al.*⁸. Venu Gopal *et al.* have reported the vapour phase alkylation of indole with methanol over zeolites⁹. 4-(Methylthio)-acetophenone, the important intermediate for the synthesis of Rofecoxib which has selective COX-2 inhibition has been prepared by heterogeneous catalyst¹⁰. A conceptually new regioselective and highly *syn*-stereoselective intramolecular Friedel-

Craft type O-alkylation of phenol with aryl epoxide by the use of appropriately substituted aryl borates has also been reported¹¹. In the present work, the use of Lewis acid and solvent have been successfully avoided by using solid acids under the influence of microwave irradiation. Acid washed silica gel and montmorillonite K10 were used as heterogeneous catalyst. The result of the reactions is summarized in **Table I**. Benzoyl chloride, in absence of a second substrate, gave anthraquinone whereas benzyl chloride gave anthracene. Dihydroanthracene is perhaps first formed by a Friedel-Craft reaction which readily eliminates two hydrogen atoms under the reaction conditions to form anthracene. Reaction of pyridine with benzoyl chloride gave two products (monitored by TLC) out of which only one could be isolated and it was found to be 4-benzoylpyridine. Both the catalysts were found to be almost equally efficient. This method has advantages such as shorter reaction time, better yield and purity, simpler work-up and environmental acceptability.

Experimental Section

Microwave oven reactions were carried out in a Samsung domestic microwave oven with microwave energy output of 1250 W. Melting points were determined in Cintex melting point apparatus and are uncorrected. IR spectra were recorded as KBr pellets on a Shimadzu IR-435 spectrometer, ^1H NMR spectra in CDCl_3 were recorded on a Perkin-Elmer R-32 (90 MHz) instrument.

Preparation of catalyst

Montmorillonite K10 clay and TLC-grade silica gel were washed with 1:1 HCl solution through a small column and dried.

General procedure for Friedel-Craft reaction

Substrate **1** (20 mmol) and substrate **2** (20 mmol) were mixed with the acidified Montmorillonite K-10 clay (2 g) and the mixture was subjected to microwave irradiation for specified time (**Table I**). After completion of the reaction (monitored by TLC), the mixture was cooled to RT. The product was isolated by extracting with the appropriate solvent and

Table I — Friedel-Craft reaction under microwave irradiation in dry media

Compd	Substrate (1)	Substrate (2)	Product (3)	Reaction time (min)	Yield (%)	
					Mont.K10	Silica gel
a	Benzene	Benzoyl chloride	Benzophenone*	1	82	80
b	Benzene	Acetyl chloride	Acetophenone**	2	68	65
c	Benzoyl chloride	Benzoyl chloride	Anthraquinone***	1	80	80
d	Benzene	Benzyl chloride	Diphenylmethane**	1.5	65	62
e	Benzyl chloride	Benzyl chloride	Anthracene***	1.5	70	65
f	Pyridine	Benzoyl chloride	4-Benzoylpyridine*	2	60	56
g	Indole	Methyl iodide	3-methyl indole*	3	73	71

* Purified by recrystallization
 ** Purified by TLC
 *** Purified by sublimation

purified either by recrystallisation from a suitable solvent or TLC as indicated in **Table I**.

Each reaction was repeated using silica gel and the results are compared.

Benzophenone, 3a. Gave orange precipitate with Brady's reagent, m.p. 48°C, Mixed m.p. with authentic sample was undepressed.

Acetophenone, 3b. Semi-solid, gave orange precipitate with Brady's reagent.

Anthraquinone, 3c. m.p. 284°C, mixed m.p. with authentic sample was undepressed.

Diphenylmethane, 3d (Ref. 12). Liquid, miscible with alcohol and ether, gave orange colour with AlCl_3 . ^1H NMR (CDCl_3): δ 2.3 (s, 2H, CH_2), 6.1-6.2 (m, 4H, ArH), 6.5-6.6 (m, 6H, ArH).

Anthracene, 3e. m.p. 215-17°C. Mixed m.p. with authentic sample was undepressed.

4-Benzoylpyridine, 3f (Ref. 13). m.p. 68-70°C. IR (KBr): 1650 cm^{-1} ; ^1H NMR (CDCl_3): δ 7.2 (d, 2H, C_2 and $\text{C}_6\text{-H}$), 7.5-7.7 (m, 5H, ArH), 8.3 (d, 2H, C_3 and $\text{C}_5\text{-H}$).

3-Methylindole, 3g (Ref. 14). m.p. 95°C. ^1H NMR (CDCl_3): δ 2.0 (s, 3H, CH_3), 3.5 (bs, 1H, NH), 6.0 (s, 1H, C_2H), 6.6-6.8 (m, 4H, ArH).

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