

Cu–Mg (24: 76) alloy: an efficient catalyst for Friedel–Crafts acylation of arenes

Krishnappa Manjula, Vaderapura P. Jayashankara and Mohamed A. Pasha*

Department of Studies in Chemistry, Central College Campus, Bangalore University, Bangalore-560 001, India

Friedel–Crafts acylation of different arenes was carried out in the presence of Cu–Mg (24:76) alloy under microwave irradiation and solvent-free conditions. Different substrates undergo acylation predominantly at the *para*-position. An efficient, simple, selective Friedel–Crafts acylation reaction affords good yields of the products and the catalyst could be easily recovered and recycled.

Keywords: Friedel–Crafts acylation, arenes, benzoyl chloride, Cu–Mg (24:76)

The Friedel–Crafts acylation of aromatic compounds is one of the most established and useful reactions carried out industrially.¹ Pharmaceuticals, perfumery and flavor chemicals, dyes, plastics, antioxidants, stabilisers, fungicides, *etc.* are prepared by this reaction.² Catalytic Friedel–Crafts acylation have been achieved by various methods. Recently, Zn³ and ZnO⁴ have emerged to promote Friedel–Crafts acylation reaction. The catalytic Friedel–Crafts acylation reactions have got their own advantages and limitations. For example, higher selectivity, easier work up and environmental safety are some of the advantages. Disadvantages are use of excess acid catalyst, unsatisfactory yields, cumbersome methodologies, flammability or risk of explosion of the reagents and cost of the reagents. Thus, the search for new catalysts and methods is still of practical importance.

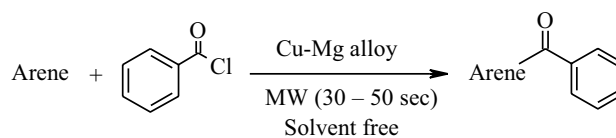
Microwaves on the other hand accelerate the chemical reactions in solvents as well as under solvent-free conditions, and have witnessed an explosive growth. Microwave irradiation often leads to shorter reaction time, increased yields and easier work up matching with ‘green chemistry’ protocols. The availability of several publications clearly indicates the impact of microwave-assisted reactions in organic synthesis.⁵

In order to promote the Friedel–Crafts acylation reaction of aromatic compounds with benzoyl chloride, we have used Cu–Mg (24:76) alloy, and the corresponding acylated product is obtained in high yields under microwave irradiation and solvent-free conditions as shown in Scheme 1.

Results and discussion

In our laboratory we have shown that, reduction of different functional groups using metals/metal salts and/or ammonium salts is possible and simple metals such as Al, Zn, Sn and Sb can replace expensive and complex reducing agents for the reduction under different reaction conditions.^{6–9} Now, our interest is in the use of metals in conjunction with microwave irradiation. Recently we have reported synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones/thiones using catalytic amount of ZnCl₂ *via* Biginelli reaction under microwave condition.⁸ In this paper we report a simple, efficient and selective method for the preparation of aromatic ketones by solvent-free Friedel–Crafts acylation reaction of aromatic compounds with benzoyl chloride in the presence of Cu–Mg (24:76) alloy under microwave irradiation. In order to find a suitable catalyst, we worked with three different alloys namely: Cu–Mg (24:76), Cu–Zn (50:50) and Al–Ni (50:50) alloys under solvent-free condition and found that, alloys can promote the Friedel–Crafts acylation of aromatic compounds to afford the corresponding acylated products in satisfactory yields as shown in Table 1.

Out of the three selected catalysts, Cu–Mg (24:76) alloy which is non-toxic, inexpensive and commercially available



Scheme 1

Table 1 Friedel–Crafts acylation of chlorobenzene with benzoyl chloride using different alloys under microwave irradiation.

Entry	Alloy	Reaction temp./°C	Time/s	Yield/%
1	Cu–Mg (24:76)	100–103	30	70
2	Cu–Zn (50:50)	107–109	35	64
3	Al–Ni (50:50)	115–117	45	60

has been used earlier for a number of reactions.^{10a–c} Now, we have shown that it is active towards the Friedel–Crafts acylation. The results of Friedel–Crafts acylation of aromatic compounds catalysed by Cu–Mg (24:76) alloy under microwave irradiation are presented in Table 2. All of the aromatic compounds reacted very rapidly within 30–50 s. The reactions are clean and easy acylation of unactivated benzenes such as chlorobenzene also takes place to afford the corresponding aromatic ketone in acceptable yields (Table 2, entry 2). Acylation occurs exclusively at the position *para* to group presented in the arene. We report here only the major isomer, which has been isolated by column chromatography.

We have examined recovery and reuse of the catalyst and found that, the yields of the product in the second and third uses of the catalyst were almost same as that in the first use. In every case >90 % of Cu–Mg alloy was recovered by filtration, washing with water and drying at 120 °C (Table 3).

From the above discussions, it is clear that, Cu present in the alloy may react with acyl chloride to generate respective acylium ion, which may participate in Friedel–Crafts reaction leaving behind copper chloride. Mg present (1: 3 ratio) in the alloy probably converts the copper chloride into copper metal, which catalyses the reaction in further cycles. It is also possible that, catalytic amount of copper chloride is sufficient to bring about this reaction.

In conclusion, we have described an efficient solvent-free protocol for Friedel–Crafts acylation of aromatic compounds using non-toxic and inexpensive Cu–Mg powder. The simple procedure, good product yields, short reaction time as well as easy recovery and reuse of the catalytic system is expected to contribute to the development of more benign acylation of aromatics with acyl chloride.

Experimental

All aromatic compounds and benzoyl chloride are purchased from s. d fine chem, BDH/MERCK and the solvents were distilled before use.

* Correspondent. E-mail: m_af_pasha@yahoo.co.in

Table 2 Friedel–Crafts acylation of substituted aromatic compounds with benzoyl chloride in presence of Cu–Mg alloy under microwave irradiation

Entry	Substrate	Product	Reaction temp./°C ^x	Time/s	Yield/% ^c	M.p (°C)
						Found/Reported
1	Benzene	Benzophenone	67–68	35	70	46–47/46–48 ^b
2	Chlorobenzene	4-Chlorobenzophenone	100–103	30	68	74–76/75–77 ^b
3	Toluene	4-Methylbenzophenone	78–80	40	65	56–58/56.5–57 ^a
4	Biphenyl	4-Benzoylbiphenyl	96–98	50	70	101/101–103 ^b
5	Anthracene	9-Anthraphenone	70–73	40	65	146–148/148 ³
6	2-Xylene	3,4-Dimethylbenzophenone	60–63	45	60	73/71–74 ^b
7	Naphthalene	2-Benzoylnaphthalene	68–70	35	65	80–82/82 ³
8	1,2-Dichlorobenzene	3,4-Dichlorobenzophenone	58–60	40	64	103/101–104 ^b

^xReaction temperature was measured by immersing a glass thermometer into the reaction mixture immediately after exposure to microwave irradiation.

^aAldrich Handbook of Fine Chemicals, 2000–2001.

^bLancaster Research Chemicals, 2002–2003.

^cYield of isolated product.

Table 3 Repeated use of Cu–Mg alloy for acylation of toluene with benzoyl chloride under microwave irradiation^a

Number of uses	Time/s	Yield/% ^b	Recovery of Cu–Mg/%
1	40	65	95
2	50	62	92
3	60	58	90

^aMolar ratio of toluene, benzoyl chloride and Cu–Mg alloy is 1: 1: 0.5

^bYield of isolated product

Alloys present in our chemical store were subjected to analysis for composition by JSM-840A Scanning Microscope. All the reactions were carried out using a conventional (unmodified) household microwave oven (LG, Little Cheff, MS-230V, ~50 Hz). Reactions were monitored on TLC by comparison with the authentic samples. Melting points were taken in open capillaries using paraffin bath and are uncorrected.¹¹ Yields refer to the isolated products after purification by silica gel chromatography. The IR spectra of the products were recorded on NICOLET 400D FT-IR spectrophotometer.

General procedure for conversion of aromatic compounds to aromatic ketones under Microwave irradiation:

A mixture of benzene (0.078 g, 1 mmol) and Cu–Mg (0.044 g, 0.5 mmol) was taken in a Pyrex cylindrical tube; benzoyl chloride (0.140 g, 1 mmol) was added, homogenised and irradiated in a commercial microwave oven (320 W). At the end of irradiation (35 sec), the mixture was cooled to room temperature and extracted with EtOAc or Et₂O. The organic layer was dried over sodium sulfate and the solvent was removed under vacuum. The crude product

(benzophenone) was purified by silica gel column chromatography using 5 % EtOAc in light petroleum as eluent to get benzophenone (0.13 g, 70 %).

The authors thank Metallurgy Department, Indian Institute of Science, Bangalore for determining the alloy compositions.

Received 12 August 2005; 19 December 2005

Paper 05/3431

References

- J.E. Hofmann and A. Schriesheim, *Friedel-Crafts and Related Reactions*, G.A. Olah (ed.), J. Wiley and Sons, New York, 1964, **2**, 597.2.
- G.A. Olah, *Friedel-Crafts Chemistry*, J. Wiley & Sons, New York, 1973.
- S. Paul, P. Nanda, R. Gupta and A. Loupy, *Synthesis*, 2003, **18**, 2877.
- H.M. Sarvari and H. Sharghi, *J. Org. Chem.*, 2004, **69**, 6953.
- (a) P. Lidstrom, J. Tierney, B. Wathey and J. Westman, *Tetrahedron*, 2001, **57**, 9225; (b) P. Perreux and A. Loupy, *Tetrahedron*, 2001, **57**, 9199.
- D. Nagaraja and M.A. Pasha, *Tetrahedron Lett.*, 1999, **40**, 7855.
- (a) M.A. Pasha and V.P. Jayashankara, *Indian J. Chem.*, 2004, **43B**, 2464; (b) M.A. Pasha and V.P. Jayashankara, *Ultrason. Sonochem.*, 2006, **13**, 42; (c) M.A. Pasha and V.P. Jayashankara, *J. Chem. Res (S)*, 2004, **4**, 282; (d) M.A. Pasha and V.P. Jayashankara, *Ultrason. Sonochem.*, 2005, **12**, 433.
- M.A. Pasha, N. Ramachandraswamy and V.P. Jayashankara, *Indian J. Chem.*, 2005, **44B**, 823.
- M.A. Pasha and V.P. Jayashankara, *Synth. React. Inorg. Met-Org. Nano-met. Chem.*, 2005, **35**, 477.
- (a) L. Burris, R.K. Steunenber and W.E. Miller, *AIChE Sympo. Series*, 1987, **83**, 254,135; (b) R.K. Steunenber, R.D. Pierce and L. Burns, *Series III, Process Chem.*, Pergamon Press, Oxford, New York, 1969, **4**, 461; (c) N.R. Chellew and R.K. Steunenber, *Nucl. Appl.*, 1967,142.
- A.I. Vogel, *A Text Book of Practical Organic Chemistry*, 5th edn, Longman Group Ltd, London, 1989, p.77.