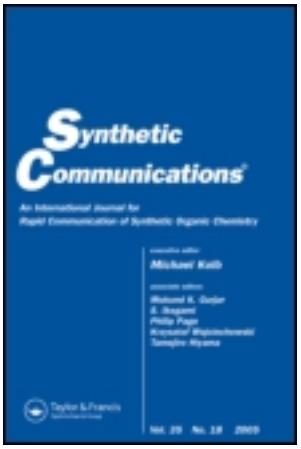


Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

# Convenient Method for the Friedel-Crafts Acylation of Benzene Derivatives Using Silver Nitrate as Catalyst

K. M. Lokanatha Rai [a], Ebraheem Abdu Musad [a], R. L. Jagadish [b] & K. N. Shivakumar [a]

[a] Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore, India

[b] Department of Polymer Science, Sir. M. V. P. G. Centre, Tubinakere, Mandya, India

Published online: 03 Mar 2011.

To cite this article: K. M. Lokanatha Rai , Ebraheem Abdu Musad , R. L. Jagadish & K. N. Shivakumar (2011) Convenient Method for the Friedel-Crafts Acylation of Benzene Derivatives Using Silver Nitrate as Catalyst, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:7, 953-955, DOI: 10.1080/00397911003707139

To link to this article: http://dx.doi.org/10.1080/00397911003707139

*Synthetic Communications*®, 41: 953–955, 2011

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911003707139

Taylor & Francis
Taylor & Francis Group

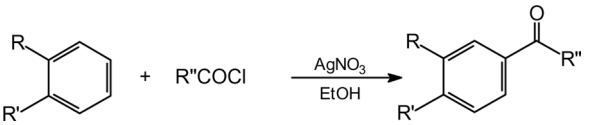


# CONVENIENT METHOD FOR THE FRIEDEL–CRAFTS ACYLATION OF BENZENE DERIVATIVES USING SILVER NITRATE AS CATALYST

**K. M. Lokanatha Rai,[1] Ebraheem Abdu Musad,[1] R. L. Jagadish,[2] and K. N. Shivakumar[1]**

[1]*Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore, India*
[2]*Department of Polymer Science, Sir. M. V. P. G. Centre, Tubinakere, Mandya, India*

## GRAPHICAL ABSTRACT




**Abstract** *Friedel–Crafts acylation of benzene derivatives such as anisole, toluene, and xylene has been successively carried out using silver nitrate as the catalyst in the presence of an eco friendly solvent (ethyl alcohol). Both benzoyl chloride and acetyl chloride reacted smoothly under the conditions to afford the corresponding ketones in good yield.*

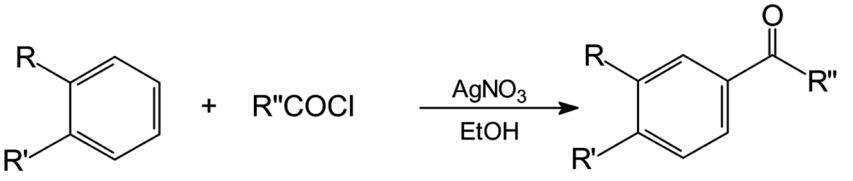
**Keywords** Catalyst; Friedel–Crafts; silver nitrate

Friedels–Crafts acylation or alkylation reactions are fundamental and some of the most important processes in organic synthesis as well as in industrial chemistry.[1] These reactions are generally carried out using $AlCl_3$ as Lewis acid in the presence of solvents such as $CS_2$ and nitrobenzene. Various reagents used to acylate or alkylate the hydrocarbon under Friedel–Crafts conditions include $SnCl_4$, $FeCl_3$, $ZnCl_2$, ZnO, hafnium(IV) triflate,[2] ytterbium(II) triflate,[3] titanium(IV) chloride triflate,[4] and bismuth(III)triflate.[5] The results obtained in these reagents are usually good, but one has to do the reaction under drastic conditions. In addition to this, tedious workup procedures and use of large amount of acid, which may induce environmental pollution, remain as severe problems to overcome, especially in large-scale industrial processes.

Under these circumstances, development of more efficient and powerful catalysts is strongly demanded. In this article, we report the Friedel–Crafts acylation

Received December 8, 2009.

Address correspondence to K. M. Lokanatha Rai, Department of Studies in Chemistry, University of Mysore, Manasagangotri, Mysore 570006, India. E-mail: kmlrai@yahoo.com




1 2 3(a-g)

**Scheme 1.** (a) R=R′=H, R″=Ph; (b) R=H, R′=$OCH_3$, R″=Ph; (c) R=R′=$CH_3$, R″=Ph; (d) R=H, R′=$OCH_3$, R″=$CH_3$; (e) R=R′=$CH_3$, R″=$CH_3$; (f) R=H, R′=$CH_3$, R″=$CH_3$; and (g) R=R′=H, R″=$CH_3$.



of benzene, toluene, anisole, and o-xylene using silver nitrate as catalyst in an ecofriendly solvent, ethanol. This method has distinct advantages over the other existing methods although the reagent is costlier: it has mild reaction conditions, shorter reaction time, easy workup procedure, and excellent yields.

Most alkyl halides, when in contact with alcoholic silver nitrate, precipitate silver chloride, but no reaction occurs when there is aryl halide in the place of alkyl halides. Recently Ajay Kumar et al.[6] observed that reaction of chloramine-T with alcoholic silver nitrate followed by addition of alkenes afforded aziridine derivatives. The probable path for the formation of aziridine involves the generation of highly reactive nitrene intermediate, which may be formed by eliminating AgCl from chloramine-T. These results prompted us to utilize silver nitrate as catalyst for Friedel–Crafts acylation, keeping in mind that reaction of acyl halide with silver nitrate generates reactive carbocation and we wanted to make it general method for the synthesis of aryl ketones.

In a typical synthesis, equimolar quantities of benzene and acetyl chloride in alcohol were treated with an equimolar quantity of well-powdered silver nitrate with stirring at room temperature (Scheme 1). It was then stirred for 2–3 h. On the usual workup, it yields 80 to 85% of acetophenone. Formation of ketones (**3**) were confirmed by comparing the synthesized molecules with the standard samples (e.g., acetophenone and benzophenone) and others prepared by conventional method using thin-layer chromatography (TLC) and also by taking respective boiling points and melting points (Table 1). Further, the products were confirmed by infrared (IR) and NMR studies.

**Table 1.** Synthesis of benzophenone

| Entry | R | R′ | R″ | Yield (%) |
|---|---|---|---|---|
| **3a** | H | H | Ph | 84 |
| **3b** | H | $OCH_3$ | Ph | 80 |
| **3c** | $CH_3$ | $CH_3$ | Ph | 74 |
| **3d** | H | $OCH_3$ | $CH_3$ | 84 |
| **3e** | $CH_3$ | $CH_3$ | $CH_3$ | 71 |
| **3f** | H | $CH_3$ | $CH_3$ | 79 |
| **3g** | H | H | $CH_3$ | 82 |

## EXPERIMENTAL

Melting points were recorded in open capillaries using a Thomus Hoover apparatus and were uncorrected. The compounds were routinely checked for their purity by TLC using silica gel-G as adsorbent. IR spectra were recorded on a Shimadzu Fourier transform (FT) 8300 spectrometer. $^1$H NMR spectra were recorded on a Jeol 60-MHz FT NMR spectrometer using $CDCl_3$ as solvent.

### Typical Procedure for the Preparation of Benzophenone (3a)

A mixture of benzene (0.66 g, 8.5 mmol), benzoyl chloride (1.44 g, l0.3 mmol), and silver nitrate (1.69 g, 10 mmole) in ethanol (10 ml) was stirred using a magnetic stirrer for 2 h. The precipitated silver chloride in the reaction was filtered off. The filtrate was extracted into ether and washed with 10% NaOH ($3 \times 20$ ml) and water. After drying over anhydrous sodium sulfate, the ethereal layer was evaporated in vacuo. The resultant residue dissolved in chloroform (2 ml) was poured into a flask containing petroleum ether, and crystals of benzophenone were obtained. Recrystallization from alcohol produces pure crystals of benzophenone in 83% (0.6 g), mp = 44–46 °C.



## ACKNOWLEDGMENT

The project was supported by the AstraZeneca Research Foundation of India, Bangalore, India.

## REFERENCES

1. Olah, A. In *Friedel–Crafts and Related Reactions*; Interscience: New York, 1964; Vol. III, Part 1; Heaney, H. In *Comprehensive Organic Synthesis*; B. M. Trost (Ed.); Pergamon Press: Oxford, 1991; p. 733.
2. Hachiya, I.; Morikawi, M.; Kobayashi, S. Catalytic Friedel–Crafts acylation reactions using hafnium triflate as a catalyst in lithium perchlorate–Nitromethane. *Tetrahedron Lett.* **1995**, 409.
3. Kobashi, S.; Hachiya, I. Lanthanide triflates as water-tolerant lewis acids: Activation of commercial formaldehyde solution and use in the aldol reaction of silyl enol ethers with aldehydes in aqueous media. *J. Org. Chem.* **1994**, *59*, 3590.
4. Izume, T.; Shijna, I.; Hulaiyama, T. An efficient esterification reaction between equimolar amounts of free carboxylic acids and alcohols by the combined use of octamethylcyclotetrasiloxane and a catalytic amount of titanium(IV) chloride tris(trifluoromethanesulfonate). *Chem. Lett.* **1995**, 141.
5. Laurent-Robert, H.; Leroux Dubae, J. Enhancement of dienophilic and enophilic reactivity of the glyoxylic acid by bismuth(III) triflate in the presence of water. *Synth. Lett.* **1998**, 1138.
6. Ajaykumar, K.; Rai, K. M. L.; Umesha, K. B. A new approach for the transformation of alkenes to pyrrolines via aziridine intermediates. *Tetrahedron* **2001**, 57, 6993–6996.