

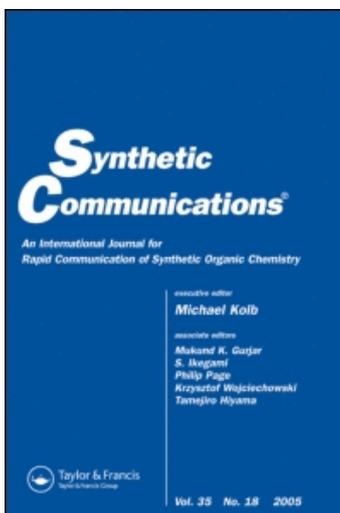
This article was downloaded by:

On: 27 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Synthetic Communications

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597304>

### Highly Efficient and Novel Method for Synthesis of 1,3,5-Triarylbenzenes from Acetophenones

Kiran Phatangare<sup>a</sup>; Vikas Padalkar<sup>a</sup>; Devidas Mhatre<sup>a</sup>; Ketan Patil<sup>a</sup>; Atul Chaskar<sup>ab</sup>

<sup>a</sup> C. K. Thakur Research Centre, Navi Mumbai, India <sup>b</sup> Department of Chemistry, Material and Engineering Chemistry, "Giulio Natta" Politecnico di Milano, Milan, Italy

**To cite this Article** Phatangare, Kiran , Padalkar, Vikas , Mhatre, Devidas , Patil, Ketan and Chaskar, Atul(2009) 'Highly Efficient and Novel Method for Synthesis of 1,3,5-Triarylbenzenes from Acetophenones', *Synthetic Communications*, 39: 22, 4117 – 4121

**To link to this Article:** DOI: 10.1080/00397910902885533

**URL:** <http://dx.doi.org/10.1080/00397910902885533>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## Highly Efficient and Novel Method for Synthesis of 1,3,5-Triarylbenzenes from Acetophenones

Kiran Phatangare,<sup>1</sup> Vikas Padalkar,<sup>1</sup> Devidas Mhatre,<sup>1</sup> Ketan Patil,<sup>1</sup>  
and Atul Chaskar<sup>1,2</sup>

<sup>1</sup>C. K. Thakur Research Centre, Navi Mumbai, India

<sup>2</sup>Department of Chemistry, Material and Engineering Chemistry,  
“Giulio Natta” Politecnico di Milano, Milan, Italy

**Abstract:** Heteropolyacid–phosphomolybdic acid has been found to be an efficient and recyclable catalyst for cyclotrimerization of acetophenones into 1,3,5-triarylbenzenes in good yields.

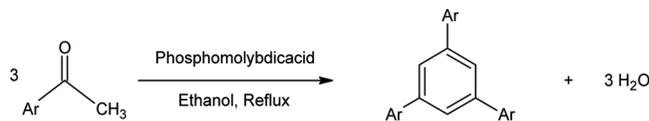
**Keywords:** Acetophenones, heteropolyacid, 1,3,5-triarylbenzenes

1,3,5-Triarylbenzenes gained importance because of their uses in electrode and electroluminescent devices, such as photocopiers and laser printers,<sup>[1–3]</sup> resist materials,<sup>[4]</sup> and conducting polymers.<sup>[5]</sup> Triarylbenzenes have been made by condensation of aryl acetones in various acidic media, such as HCl, H<sub>2</sub>SO<sub>4</sub>, TiCl<sub>4</sub>, SiCl<sub>4</sub>, AlCl<sub>3</sub>, SnCl<sub>4</sub>, para toluene sulfonic acid (PTSA), Bi(OTf)<sub>3</sub> · 4H<sub>2</sub>O, BiCl<sub>3</sub>, FeCl<sub>3</sub>, and Amberlyst-15, which are widely used for this transformation.<sup>[6–16]</sup> However, in spite of their potential utility, these methods typically suffer from one or more disadvantages, such as high cost, use of a stoichiometric amount of catalyst, moisture sensitivity, specialized handling, tedious workup, and nonrecyclability of the catalyst.

In recent decades, heteropolyacids (HPAs) as catalysts have become important in pharmaceutical and fine chemical industries.<sup>[17]</sup> HPAs are more active catalysts than conventional inorganic and organic acids for

Received December 10, 2008.

Address correspondence to Atul Chaskar, C. K. Thakur Research Centre, Navi Mumbai 410206, India. E-mail: achaskar@rediffmail.com



**Scheme 1.** Cyclotrimerization of acetophenone.

various reactions in solution.<sup>[18]</sup> Solid HPAs have gained importance because of easy workup procedures, minimization of waste, mild reaction conditions, cleaner products, enhancement in selectivity, and improved reaction rates. They are noncorrosive and environmentally benign, because they can be recycled and reused.<sup>[19]</sup>

Thus, considering the advantage and applications of HPAs and as part of our ongoing project to explore the catalytic activities of HPAs in organic transformations,<sup>[20,21]</sup> we attempted the convenient and practical synthesis of 1,3,5-triarylbenzenes using phosphomolybdic acid (Scheme 1).

To compare catalytic efficiency of phosphomolybdic acid with different acid catalysts, the cyclotrimerization of acetophenone with 5–10 mol% of acid catalyst in ethanol at reflux temperature was investigated. Results are shown in Table 1.

The results mentioned in Table 1 demonstrate the effective use of phosphomolybdic acid for the cyclotrimerization reaction. The

**Table 1.** Effect of different acid catalysts on percentage yield of cyclotrimerization of acetophenone

Entry	Acid catalyst	Mole (%)	Time (h)	Yield (%) <sup>b</sup>
1	HCl	10	11	45
2	H <sub>2</sub> SO <sub>4</sub>	10	9	52
3	TiCl <sub>4</sub>	10	24	50
4	SiCl <sub>4</sub>	10	24	60
5	AlCl <sub>3</sub>	10	15	69
6	SnCl <sub>4</sub>	10	24	55
7	<i>p</i> -TSA	10	17	40
8	Bi(OTf) <sub>3</sub>	10	8	62
9	BiCl <sub>3</sub>	10	24	20
10	FeCl <sub>3</sub>	10	15	65
11	Amberlyst-15	10	15	52
12	Phosphomolybdic acid	5	5	87

<sup>a</sup>Reaction conditions: ArCOME (5 mmol), HPA (0.1 mmol), ethanol (4 ml), reflux.

<sup>b</sup>Isolated yield.

**Table 2.** Cyclotrimerization of different acetophenones into 1,3,5-triarylbenzenes using phosphomolybdic acid as a solid acid catalyst<sup>a</sup>

Entry	Ar	Time (h)	Yield (%) <sup>b</sup>
1	Ph	5	87
2	2-Me-C <sub>6</sub> H <sub>4</sub>	7	68
3	2-MeO-C <sub>6</sub> H <sub>4</sub>	6.5	70
4	3-Me-C <sub>6</sub> H <sub>4</sub>	6.2	72
5	3-MeO-C <sub>6</sub> H <sub>4</sub>	6	75
6	3-F-C <sub>6</sub> H <sub>4</sub>	7	78
7	3-Cl-C <sub>6</sub> H <sub>4</sub>	8	73
8	4-Me-C <sub>6</sub> H <sub>4</sub>	6	88
9	4-Ph-C <sub>6</sub> H <sub>4</sub>	4	92
10	4-Cl-C <sub>6</sub> H <sub>4</sub>	5.5	76
11	4-F-C <sub>6</sub> H <sub>4</sub>	9	80
12	4-Br-C <sub>6</sub> H <sub>4</sub>	8	72
13	4-I-C <sub>6</sub> H <sub>4</sub>	4.2	78
14	4-MeO-C <sub>6</sub> H <sub>4</sub>	4.6	90
15	4-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub>	12	30

<sup>a</sup>Reaction conditions: ArCOMe (5 mmol), HPA (0.1 mmol), ethanol (4 ml), reflux.

<sup>b</sup>Isolated yield.

cyclotrimerization of different acetophenones was carried out by refluxing the acetophenone with 5 mol% HPA in ethanol at reflux temperature to obtained product in good yield (Table 2).

## CONCLUSION

In conclusion, phosphomolybdic acid as a HPA catalyst has proved to be a useful, efficient, and recyclable catalyst for cyclotrimerization of acetophenones. The present protocol has several advantages over reported literature methods from economical and environmental points of view, such as operational simplicity, short reaction time, mild reaction condition, good yield of the product, and recyclability of catalyst.

## EXPERIMENTAL

All commercial reagents were used as received without purification, and all solvents were of reagent grade. The reaction was monitored by thin-layer chromatography (TLC) using 0.25-mm Merck silica-gel

60 F<sub>254</sub> precoated plates, which were visualized with ultraviolet (UV) light. Melting points were observed using open capillaries. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a VXR 300-MHz instrument, using tetramethylsilane (TMS) as an internal standard.

### General Procedure for Conversion of Acetophenone into 1,3,5-Triphenylbenzene

Acetophenone (5 mmol) and phosphomolybdic acid (0.1 mmol) were added to ethanol (4 ml), and the reaction mixture was stirred for 5 h at reflux temperature. After completion of reaction, as indicated by TLC, the solvent was removed under pressure. The solid product was washed with water and recrystallized using a mixture of ethanol and dichloromethane (1:1). The aqueous part was concentrated to isolate the phosphomolybdic acid. Yield 87%, mp 172–174°C.

### Data

<sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.18 (3H, s); 7.72 (6H, m); 7.50 (6H, m); 7.42 (3H, m) ppm. <sup>13</sup>CNMR (CDCl<sub>3</sub>): δ 142, 141, 129, 127.5, 127.3, 125 ppm. MS (EI, 70 eV) 306 (M<sup>+</sup>), 289, 232, 154, 136.

### ACKNOWLEDGMENTS

The authors are grateful to the University Grants Commission, New Delhi, the University of Mumbai for financial support, and to Dr. S. T. Gadade, principal, C. K. Thakur College, for providing laboratory and other facilities.

### REFERENCES

1. Horgan, A. M. Composite layered photoreceptor. US patent 4081274, 1978; *Chem. Abstr.* **1978**, 89, 120873.
2. Lindeman, S. V.; Struchkov, Y. T.; Michailov, V. N.; Resanov, A. L. Synthesis and crystal structure of 1,3,5-tris[4-(phenylethynyl)phenyl]benzene. *Izu. Akad. Nauk. Ser. Khim* **1994**, 1986; *Chem. Abstr.* **1995**, 123, 32717.
3. Aslam, M.; Aguilar, D. A. Trimerization process for preparing 1,3,5-tris(4'-hydroxyphenyl)benzenes. WO patent 9314065, 1993; *Chem. Abstr.* **1993**, 119, 270793.
4. Ikadai, J.; Yoshida, H.; Obshita, J.; Kunai, A. Facile synthesis of polycyclic aromatic hydrocarbons via a trisaryne equivalent. *Chem. Lett.* **2005**, 34, 56.

5. (a) Pepin-Donat, B.; Geyer, A.; Viallat, A. Structural and transport properties in solid-state conducting gels: Influence of the crosslink density. *Polymer* **1998**, *39*, 6673; (b) Robourt, E.; Pepin-Donat, B.; Dinh, E. Routes towards three-dimensional fully conjugated conducting polymers, 1: Preparation of the kit of monomers. *Polymer* **1995**, *36*, 399.
6. Lyle, R. E.; Dewitt, E. J.; Nichols, M. M.; Cleland, W. Acid catalysed condensations, I: 1,3,5-triarylbenzenes. *J. Am. Chem. Soc.* **1953**, *75*, 5959.
7. Jing, X.; Xu, F.; Zhu, Q.; Ren, X.; Yan, C.; Wang, L.; Wang, J. Novel method for the synthesis of 1,3,5-triarylbenzenes from ketones. *Synth. Commun.* **2005**, *35*, 3167.
8. Plater, M. J.; Praveen, M. A new synthesis of truxenone. *Tetrahedron Lett.* **1997**, *38*, 1081.
9. Li, Z.; Sun, W. H.; Jin, X.; Shao, C. Triple self-condensation of ketones yielding aromatics promoted with titanium tetrachloride. *Synlett* **2001**, 1947.
10. Iranpoor, N.; Zeynizaded, B.  $\text{TiCl}_3(\text{OTf})$  catalyses the efficient conversion of acetophenones to 1,3,5-triarylbenzenes. *Synlett* **1998**, 1079.
11. Lorette, N. B. Ketone condensations using a sulfonic acid ion exchange resin. *J. Org. Chem.* **1957**, *22*, 346.
12. Odell, A. F.; Hines, C. W. The pyrosulfates of sodium and potassium as condensing agents. *J. Am. Chem. Soc.* **1913**, *35*, 82.
13. Elmorsy, S. S.; Pelter, A.; Smith, K. The direct production of tri- and hexa-substituted benzenes from ketones under mild conditions. *Tetrahedron Lett.* **1991**, *32*, 4175.
14. Plater, M. J.; McKay, M.; Jackson, T. Synthesis of 1,3,5-tris[4-(diarylamino)phenyl]benzene and 1,3,5-tris(diarylamino)benzene derivatives. *J. Chem. Soc., Perkin Trans. 1* **2000**, 2695.
15. Elmorsy, S. S.; Pelter, A.; Smith, K.; Hursthouse, M. B.; Ando, D. Investigations of the tetrachlorosilane-ethanol-induced self-condensations of ketones. *Tetrahedron Lett.* **1992**, *33*, 821.
16. Ono, F.; Ishikura, Y.; Tada, Y.; Endo, M.; Sato, T. Efficient conversion of acetophenones into 1,3,5-triarylbenzenes catalyzed by bismuth(III) trifluoromethanesulfonate tetrahydrate. *Synlett* **2008**, 2365.
17. Okuhara, T.; Mizuno, N.; Misono, M. Catalytic chemistry of heteropoly compounds. *Adv. Catal.* **1996**, *41*, 113.
18. Drago, R. S.; Dias, J. A.; Maier, T. O. An acidity scale for Brønsted acids including  $\text{H}_3\text{PW}_{12}\text{O}_{40}$ . *J. Am. Chem. Soc.* **1997**, *119*, 7702.
19. Schwegler, M. A.; Van Bekkum, H.; De Munck, N. Heteropolyacids as catalysts for the production of phthalate diesters. *Appl. Catal.* **1991**, *74*, 191.
20. Chaskar, A.; Yadav, A.; Langi, B.; Murugappan, A.; Bodkhe, A. Heteropoly acids as heterogeneous catalysis for  $\alpha$ -thiocyanation of ketones. *Adv. Synth. Catal.* (Communicated).
21. Chaskar, A.; Padalkar, V.; Phatangare, K.; Patil, K.; Bodkhe, A.; Langi, B. Heteropoly acids as a useful recyclable heterogeneous catalyst for the facile and highly efficient aza-cope rearrangement of N-allylanilines. *Appl. Catal. A: General* **2009**, *359*, 84.