Brønsted acid-surfactant (BAS) catalysed cyclotrimerization of aryl methyl ketone

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Abstract

A Brønsted acid-surfactant catalysed and simple, mild, metal catalyst free and chemo-selective method has been developed for synthesis of 1, 3, 5-triaryl benzenes from aryl methyl ketones. The advantages of this protocol subsume green and sustainable reaction medium, mild reaction conditions, easy product recovery and its good yields.

Keywords:
1, 3, 5-Triaryl benzenes
Aryl methyl ketones
Brønsted acid-surfactant catalyst (BASC)
Dodecylbenzenesulfonic acid (DBSA)

1. Introduction

Polyphenylenes are always considered as important and interesting class of compounds due to their various useful characteristics and applications. 1, 3, 5-triaryl benzenes have been extensively employed as intermediates of buckminster fullerene synthesis and also for the synthesis of conjugated star polyaromatics, and pharmaceuticals\textsuperscript{1}. These compounds also play role as thermally stable materials and hence used as resisting materials\textsuperscript{7}/conducting polymers\textsuperscript{3}. Besides, this 1, 3, 5-triaryl benzenes are useful as electroluminescent materials\textsuperscript{4,5} in OLEDs\textsuperscript{6,7}, electrode devices\textsuperscript{8}, etc.

Owing to these facts 1, 3, 5-triarylbenzenes are synthesized by applying numerous strategies and using different methodologies. The most general approach of 1,3,5-triarylbenzene synthesis is triple condensation of aryl methyl ketones\textsuperscript{9} and alkynes by incorporating different catalysts such as transition metal complexes (Nb\textsuperscript{10},...
Co\textsuperscript{11}, Ir\textsuperscript{12}, Pd\textsuperscript{13}, Rh\textsuperscript{14}), acids (HCl\textsuperscript{15}, SiCl\textsubscript{4}\textsuperscript{16}, TiCl\textsubscript{4}\textsuperscript{17}, TiCl\textsubscript{3}(OTf)\textsuperscript{18}) and solid acids\textsuperscript{19}. Alternative methods include cross-coupling reactions involving 1,3,5-trihalobenzenes with organometallic moieties, catalysed by metals\textsuperscript{20}. Whereas, these days the more modern and recent method practiced for production of 1, 3, 5-triarylbenzenes is by using PTSA (TsOH.H\textsubscript{2}O)\textsuperscript{21}. However, in spite of their potential utility, many of these methodologies are associated with some drawbacks such as use of organic solvents and metal catalysts, harsh reaction conditions, non-recyclability of the catalyst, lower yields presumably due to the deactivation of catalyst by the water formed during the course of reaction. Considering these facts there is utmost need to develop a green methodology which could be water tolerant.

In recent years dodecylbenzenesulfonic acid (DBSA) has emerged as an ecofriendly catalyst and/or medium in organic reactions. It has received great deal of attention as a mild brønsted acid and surfactant for an array of organic transformations owing to its easy and inexpensive availability, non-toxicity, environmental benign nature, easy biodegradable nature, along with moisture and air tolerance characteristics.\textsuperscript{22,23} DBSA, an anionic surfactant, forms micelles in water. The micelles, comprising of hydrophilic and hydrophobic parts not only act as an acid catalyst but also enhance the solubility of organic substrates.

With regards to our interest in developing synthetic methodology using miceller media\textsuperscript{24,25} promoted us to investigate the utility of micelles as catalyst as well as reaction medium for triple condensation of aryl methyl ketone which readily led to corresponding 1,3,5-triaryl benzene (Scheme 1).

\begin{equation}
\text{Ph} - \text{O} \xrightarrow{\text{DBSA-H}_2\text{O, 130-135 °C}} \text{Ph} \text{Ph} \text{Ph}
\end{equation}

Scheme 1. Cyclotrimerization of aryl methyl ketone

2. Results and discussion

An initial attempt for cyclotrimerization of acetophenone was performed in brønsted acid surfactant dodecylbenzenesulfonic acid (DBSA) and 1, 3, 5- triphenyl benzene was obtained in excellent yield. The brønsted acid surfactant first promotes sequence of aldol reactions and formed cyclophloroglucinol which on further dehydration yielded 1, 3, 5- triphenyl benzene. The equilibrium position occurs between cyclophloroglucinol and 1, 3, 5- triphenyl benzene in one stage and the water molecules generated during the reaction were removed from the micellar solution by hydrophobic interior of micelles, resulting into the enhancement in reaction rate (Scheme 2).

Inspired by above obtained results, we subsequently carried out cyclotrimerization of various substituted acetophenones. To our surprise all the products were obtained in good to excellent yields. Electron donating groups lower the yields as compared to electron withdrawing groups. In case of halides, the yields increased with decreasing electronegativity.
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\(^{a}\)Cyclotrimerization of aryl methyl ketones.
3. Experimental

All commercial reagents were used as received without purification and all solvents were of reagent grade. The reaction was monitored by TLC using 0.25 mm E-Merck silica gel 60 F254 precoated plates, which were visualized with UV light. Melting points were taken in open capillaries. The IR spectra were recorded on a PerkinElmer 257 spectrometer using KBr discs. $^1$H NMR and $^{13}$C NMR spectra were recorded on a VXR-300 MHz instrument using TMS as an internal standard.

Typical procedure

A mixture of acetophenone (3 mmol) and dodecylbenzenesulfonic acid (3 mmol) was stirred at 130-135 °C for 10 h. After completion of reaction as indicated by TLC, the reaction mixture was extracted with ethyl acetate (2 x 15 mL). The combined organic layer was washed with water, dried over magnesium sulphate, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography with hexane: ethyl acetate (9:1) as eluent to get pure compound.

Representative spectral data

1, 3, 5-Triphenyl benzene: (1)

Mp. 170-171 °C;

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$: 7.82 (s, 3H), 7.73 (d, 6H, $J = 7.48$ Hz), 7.51 (t, 6H, $J = 7.44$ Hz), 7.42 (t, 3H, $J = 7.2$ Hz);

$^{13}$C NMR (CDCl$_3$) $\delta$: 142.4, 141.2, 128.9, 127.6, 127.4, 125.2;

IR $\nu$ (KBr): 3080, 3032, 3056, 1594, 1575, 1496, 1411, 1076, 1027, 910, 872, 765, 750, 690, 626, 610, 503, 487 cm$^{-1}$; FAB-MS $m/z$: 319 (55), 306 (25), 228 (26), 154 (47), 136 (93), 107 (33), 89 (36), 57 (100);

HRMS-FAB (m/z): [M]$^+$ calcd for C$_{24}$H$_{18}$, 306.1409; found, 306.1407

1, 3, 5-Tris(4′-bromophenyl)benzene: (6)
Mp. 253-255 °C;

$^1$H NMR (300 MHz, CDCl$_3$) δ: 7.69 (s, 3H), 7.61 (d, 6H, $J = 8.44$ Hz), 7.53 (d, 6H, $J = 8.48$ Hz);

$^{13}$C NMR (CDCl$_3$) δ: 141.5, 139.6, 132.0, 128.9, 125.0, 122.1;

IR ν (KBr): 3081, 3057, 3032, 2921, 1594, 1575, 1496, 1411, 1076, 1027, 872, 765, 750, 690, 610, 503 cm$^{-1}$;

HRMS-FAB (m/z): [M]$^+$ calcd for C$_{24}$H$_{15}$Br$_3$, 539.8724; found, 539.8733.

4. Conclusion

As final points, the synthesis of 1, 3, 5- triaryl benzenes from a range of aryl methyl ketones has been accomplished using easily available, inexpensive and relatively non-corrosive DBSA surfactant in water as a catalyst and reaction medium. We anticipate that this eco-friendly and environmental benign protocol will be of wide synthetic and commercial interest and utility.

References


