

Synthesis of symmetric 1,3,5-triarylbenzenes[†]

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A facile and efficient method for synthesis of symmetric 1,3,5-triarylbenzenes is presented; six symmetric 1,3,5-triarylbenzenes was obtained from their corresponding substituted acetophenones in the presence of thionyl chloride in anhydrous ethanol.

Keywords: symmetric 1,3,5-triarylbenzenes, acetophenones

The properties of molecules or molecular complexes with a high degree of symmetry are of interest in a large number of research areas.¹ 1,3,5-Triarylbenzenes are a class of important C₃-symmetry compounds in the manufacture of electrode and electroluminescent devices. Recently, a family of three-dimensional dendrimers consisting of hyperbranched chains prepared by multiplicative growth from symmetric triphenylbenzene has attracted much attention.² Moreover, molecular nonlinear optics (NLO) material,³ Langmuir Monolayers³ and conjugated conducting oligomers² have also led to a surge of interest in the nature of the excited state of these symmetric compounds. Branched functionalised benzenoid compounds are versatile organic intermediates for the synthesis of C₆₀, pharmaceuticals, sensitizers for photographic processes as well as for preparation of conjugated star polyaromatics.⁴ In order to synthesise these conjugated star polyaromatics, it became necessary to seek an efficient method for synthesis of functionalised 1,3,5-triarylbenzenes. The general method for synthesising these symmetric 1,3,5-triarylbenzenes is catalysis of the triple condensation of aryl methyl ketones. The reported condensation reagents involve strong acids,^{5,9} aluminum chloride, beryllium chloride,² samarium trichloride,⁶ tetrachlorosilane⁷ and TiCl₃(OTf).⁸ However, the literature methods involve the use of high temperatures, high pressures or long reaction times, which often result in poor yields and low purity of the product.⁵ They are inconvenient for synthesis of 1,3,5-triarylbenzenes. In our development of new methods for synthesis of 1,3,5-triarylbenzenes, we have found that thionyl chloride is a good catalyst. But as a rule, thionyl

chloride has been used as a chlorinisation reagent in the organic synthesis reactions or industry. We wish to report here the efficient synthesis of symmetric 1,3,5-triaryl benzenes from acetophenones in the presence of thionyl chloride in anhydrous ethanol.

Using thionyl chloride-anhydrous ethanol as the catalyst system, six symmetric 1,3,5-triarylbenzenes have been obtained from corresponding aryl methyl ketones under mild conditions with good yields (Scheme 1).

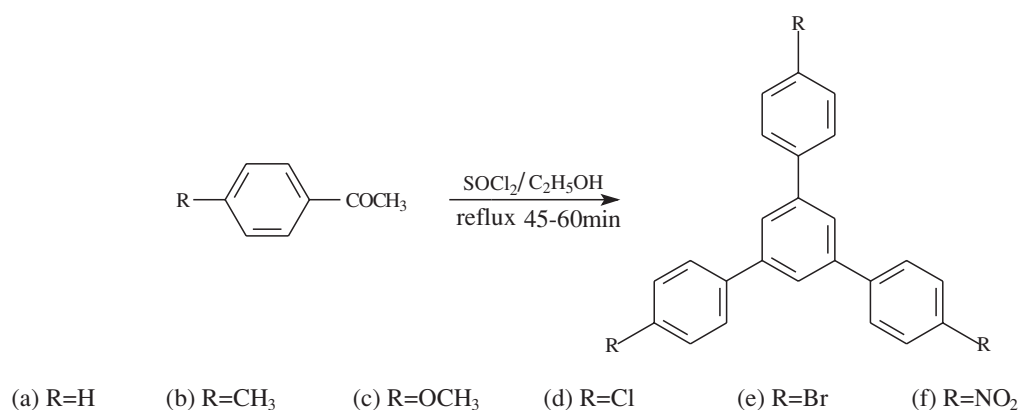
The reaction conditions and results are summarised in Table 1.

Table 1 Synthesis of symmetric 1,3,5-triaryl benzenes

Entry	Product	Time/min	Yield/%
1	a	60	85
2	b	60	57
3	c	60	66
4	d	45	74
5	e	45	72
6	f	45	79

We also attempted to change the catalyst by using TiCl₄ and PCl₃ in the presence of anhydrous ethanol to catalyse the reaction, but did not gain the target compounds. Furthermore, we found that the ethanol is indispensable in the catalyst system. Moreover the by-product HCl also accelerates the reaction.⁹

In this paper, the efficient and simple synthesis of symmetric 1,3,5-triarylbenzenes from acetophenones in the presence of thionyl chloride in anhydrous ethanol has been reported. Unlike many other literature methods, thionyl chloride-anhydrous ethanol can catalyse the synthesis of



Scheme 1 The synthesis of symmetric 1,3,5-triarylbenzenes.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M)*.

1,3,5-triarylbenzenes under mild conditions. At the same time, we believe that this reaction also expands the application of thionyl chloride in organic synthesis. A detailed mechanism and further applications of this reaction are under study in our laboratory.

Experimental

General procedure for preparation of symmetric 1,3,5-triarylbenzenes: To a stirred mixture of the ketone (15mmol) and anhydrous ethanol (75mmol), thionyl chloride (25mmol) was added. The mixture was heated at reflux for 45–60 min. After completion of the reaction, saturated Na₂CO₃ was added and the mixture was filtered. The solid was washed twice successively with water (30ml), anhydrous ethanol (20ml) and ethyl ether (20ml). The crude products were purified by recrystallisation.

Spectra data of a-f: **Compound a:** m.p.: 172–174°C (m.p.⁴: 173°C); IR (KBr): 1590, 1570 (m, Ar), 750 (s, Ar) cm⁻¹; ¹H NMR (CDCl₃): δ7.78–7.35 (m, 18H, ArH);

Compound b: m.p.: 178–180°C (m.p.⁴: 177–178°C); IR (KBr): 2900 (s, CH₃), 1560 (m, Ar), 800 (s, Ar) cm⁻¹; ¹H NMR (CDCl₃): δ7.78–7.24 (m, 15H, ArH), 2.4 (s, 9H, CH₃) ppm; MS: *m/z* (%): 348 (M⁺, 100);

Compound c: m.p.: 146–147°C (m.p.⁶: 142–144°C); IR (KBr): 2900 (s, CH₃), 1510 (m, Ar), 820 (s, Ar) cm⁻¹; ¹H NMR (CDCl₃): δ7.78–6.88 (m, 15H, ArH), 3.9 (s, 9H, CH₃) ppm; MS: *m/z* (%): 396 (M⁺, 100);

Compound d: m.p.: 227–229°C (m.p.⁶: 227–229°C); IR (KBr): 1590, 1500 (m, Ar), 1020 (s, Ar-Cl), 800 (s, Ar) cm⁻¹; ¹H NMR (CDCl₃): δ7.78–7.39 (m, 15H, ArH) ppm; MS: *m/z* (%): 410 (M⁺, 100);

Compound e¹⁰: m.p.: 246–248°C; IR (KBr): 1580, 1480 (m, Ar), 810 (s, Ar) cm⁻¹; ¹H NMR (CDCl₃): δ7.79–7.41 (m, 15H, ArH) ppm; MS: *m/z* (%): 544 (M⁺+H, 100);

Compound f: m.p.: 325–327°C (m.p.⁶: 325–327°C); IR (KBr): 1630, 1550 (m, Ar), 800 (s, Ar) cm⁻¹; ¹H NMR (CDCl₃): δ7.79–7.25 (m, 15H, ArH) ppm; MS: *m/z* (%): 441 (M⁺, 100);

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