

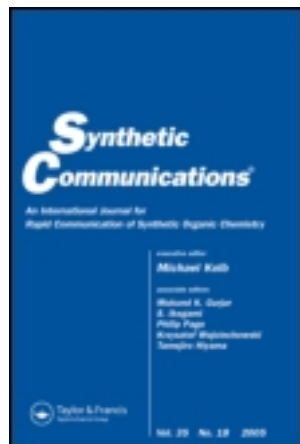
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Novel Method for the Synthesis of 1,3,5-Triarylbenzenes from Ketones

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Abstract: Treatment of aryl ketones with p-toluenesulfonic acid and a catalytic amount of tin tetrachloride anhydrous (5%) in 1-pentanol gives good yields of 1,3,5-triarylbenzenes.

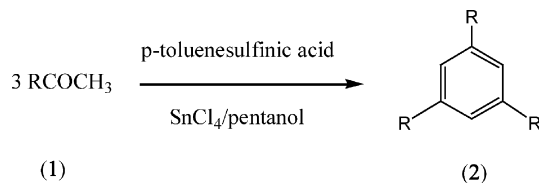
Keywords: Tin tetrachloride, 1,3,5-triarylbenzene, p-toluenesulfonic acid

INTRODUCTION

Triaryl benzenes are an important class of compounds in electrode and electroluminescent devices. A simple method yielding these compounds involves the triple condensation of aryl methyl ketones (**1**), as shown in Scheme 1. The reported methods of inducing condensation involve primarily one of three catalysts: a sulfuric acid and sodium pyrosulfate mixture, hydrogen chloride and/or hydrochloric acid, or aniline and aniline

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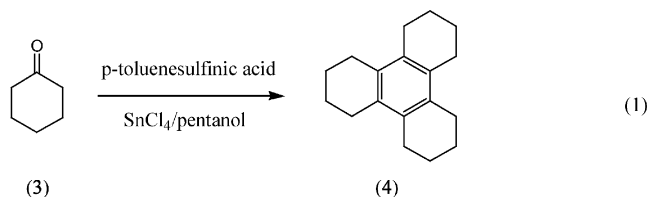
Scheme 1. R = (a) C₆H₅; (b) 4-MeC₆H₄; (c) 4-MeOC₆H₄; (d) 4-ClC₆H₄; (e) 4-BrC₆H₄; (f) -Me and (g) 4-NO₂C₆H₄.

hydrochloride^[1–3] In isolated cases other catalysts were used, such as beryllium chloride, sodium ethoxide, and sulfoacetic acid.^[4–6] The most satisfactory results were obtained using acidic catalysts. They are both inconvenient and unsuitable for synthesis of all but the simplest compounds.

We therefore sought a more efficient and more general method to convert (1) into (2) and now report that interaction of compounds (1a–1e) with one equivalent of p-toluenesulfonic acid and a catalytic amount of tin tetrachloride, anhydrous (5%), in 1-pentanol at reflux temperature gave different yields of (2a–2e) regardless of whether the starting ketone contained electron-withdrawing or electron-donating groups. The results are given in Table 1.

Clearly, p-TsOH/SnCl₄ is a potent reagent for the triple condensation of ketones to yield benzenoids. Table 1 shows that the yields of ketones containing electron-withdrawing groups are much lower than those of the ketones containing electron-donating groups. The precise nature of the reagents responsible for the condensation is not known. Our further investigations of scope and pathway of this reaction will be reported separately.

We then examined the reactions of cyclohexanone (3) (Eq. (1)). In this case, it gave the desired triannulated benzene (4) in yields of 79%.

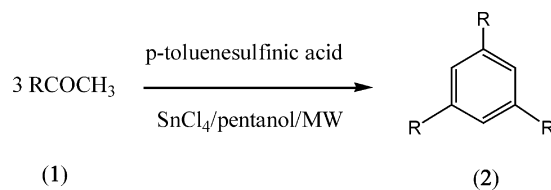


To improve the yield of the triarylbenzenes, we tried the reaction under microwave-induced conditions instead of refluxing (Scheme 2). The results are given in Table 2.

Clearly, the use of a microwave oven is convenient when compared to other experimental conditions and the reaction proceeds efficiently in a shorter period of time and with higher yields. In conclusion, the SnCl₄/p-TsOH/pentanol condition we found is effective enough to catalyze

Table 1. Yield of triarylbenzenes from aryl methyl ketones

Entry	<i>t</i> (h)	<i>T</i> (°C)	Yield (%) (2)	Mp (°C)
1a	4	110	82	172
1b	4	110	85	179–180
1c	5.5	110	77	143
1d	7	120	72	246
1e	7	120	74	263
1f	3	40	66	—
1g	24	150	<30	153



Scheme 2. R = (a) C₆H₅; (b) 4-MeC₆H₄; (c) 4-MeOC₆H₄; (d) 4-ClC₆H₄; (e) 4-BrC₆H₄; (f) -Me and (g) 4-NO₂C₆H₄.

the triple condensation of not only aryl methyl ketones but also cyclohexenone. Microwave-induced versions of the condensation reaction are more convenient because of the short reaction time and better yields of the products. The further elaboration of in situ generated triarylbenzenes into useful products in one-pot procedures using microwave irradiation is currently being investigated.

Table 2. Yield of triarylbenzenes from aryl methyl ketones under microwave-induced conditions

Entry	<i>t</i> (min) ^a	Power (W)	Yield (%) (2)	Mp (°C)
3a	3 × 1	400	86	172
3b	3 × 1	400	84	179–180
3c	3 × 1	400	88	143
3d	3 × 1.5	400	80	246
3e	3 × 1.5	400	85	263
3f	3 × 0.5	300	73	—
3g	3 × 3	400	55	153

^aNumber of irradiations for a given time; 2 × 3 indicates 2 irradiations of 3 min each.

EXPERIMENTAL

Melting points were measured on a Kofler apparatus and are uncorrected. MS measurements were performed on ZAB-HS spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker AM-500 and AM-400 instruments. Chemical shifts refer to TMS on the δ scale.

The p-toluenesulfonic acid (1.72 g, 10 mmol) was added to a stirred solution of (**1c**) (1.50 g, 10 mmol) in dry 1-pentanol (10 mL). Then, the catalytic amount of tin tetrachloride anhydrous (5%) was added slowly by a syringe to the mixture. The mixture was stirred for 5.5 h at 110°C and then

Table 3. Analytical data for the compound **2a–2g**^a and compound **4**^b

Compound	^1H NMR	MS	^{13}C NMR (100 M)	Mp (°C)
2a	7.81 (3H, s), 7.72 (6H, m), 7.50 (6H, m), 7.41 (3H, m)	306 (M ⁺); 289; 232; 154; 136	142.4, 141.2, 128.8, 127.5, 127.4, 125.2	172
2b	7.13 (3H, s), 7.59 (6H, m), 7.27 (6H, m), 2.42 (9H, s)	—	142.2, 138.4, 137.2, 129.5, 127.2, 124.6, 21.1	179–180
2c	7.73 (3H, s), 7.59 (6H, d, $J = 7.8$), 7.29 (6H, d, $J = 7.8$), 2.42 (9H, s)	—	160.9, 137.6, 128.9, 128.4, 125.2, 114.6, 56.0	143
2d	7.70 (3H, s), 7.60 (6H, d, $J = 8.4$), 7.46 (6H, d, $J = 8.4$)	—	141.8, 139.2, 134.0, 129.1, 128.5, 125.0	246
2e	7.66 (3H, s), 7.49 (6H, d, $J = 8.4$), 7.37 (6H, d, $J = 8.4$)	—	137.6, 135.6, 132.3, 129.6, 125.2, 122.0	263
2g	8.25 (6H, d, $J = 8.5$), 7.66 (3H, s), 7.74 (6H, d, $J = 8.5$)	—	147.3, 142.7, 137.6, 128.3, 125.2, 124.1	153
4	2.57 (12H, m), 1.77 (12H, m)	240 (M ⁺); 225; 212; 199; 183	132.6, 26.8, 23.1	216

^aTrimethylbenzene (**2f**) is easily detected by TLC.

^bAll the spectra data are in good agreement with those of the literature report.^[1]

poured into ethanol (20 mL), stirred, and filtered. Crystallization from EtOH and CH₂Cl₂ (1 : 1) gave (**2c**) (1.15 g), mp 143°C, yield 72%.

All the analytical data for the compounds (**2a–2g**) and compound (**4**) are given in Table 3.

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