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Note

New method for the synthesis of 1,3,5-triarylbenzenes

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Adsorbed on clayfen together with *p*-toluenesulfonic acid and catalytic amount of tin tetrachloride anhydrous (5%), aryl ketones are readily turned to 1,3,5-triarylbenzenes in good yields upon exposure to microwaves under solvent-free conditions. A new method for the synthesis of poly substituted benzene is developed, which is simple and rapid.

Keywords: 1,3,5-triarylbenzenes, *p*-toluenesulfonic acid, tin tetrachloride anhydrous, clayfen

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Triaryl benzenes are a class of important compounds in the electrode and electroluminescent devices. A simple method yielding these compounds involves the triple condensation of aryl methyl ketones **1**, as in Equation (1). The reported methods of inducing condensation involve primarily one of three catalysts: sulfuric acid and sodium pyrosulfate mixture, hydrogen chloride and/or hydrochloric acid, or aniline and aniline hydrochloride[1-3]. In isolated cases other catalysts were used, such as beryllium chloride, sodium ethoxide, and sulfoacetic acid[4-6]. Recently, lots of catalyzers, such as thionyl chloride, silicon tetrachloride, copper chloride, titanium tetrachloride and so on, were reported in this field[7]. It will be noted that the most satisfactory results were obtained using an acidic catalyst. They are both inconvenient and unsuitable for the synthesis of all but the simplest compounds.

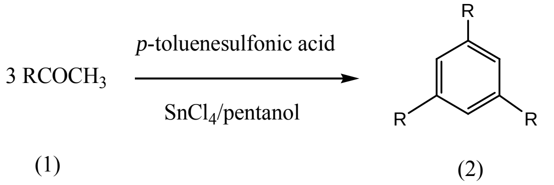
Results and Discussion

A more efficient and more general method was employed to convert **1** into **2**, and the interaction of compounds **1a-e** with one equivalent of *p*-toluenesulfonic acid and catalytic amount of tin tetrachloride, anhydrous(5%) in 1-pentanol at reflux temperature gave different yields of **2a-e**. The results are given in **Table I**.

Clearly, *p*-TsOH/$SnCl_4$ is a potent reagent for the triple condensation of ketones to yield benzenoids. The precise nature of the reagents responsible for the condensation is not known.

Further investigations of scope and pathway of this reaction will be reported separately.

Table I — Yield of triarylbenzenes from aryl methyl ketones

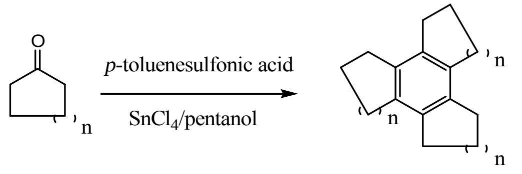


(1)

(1) (2)

R = (a) C_6H_5 ; (b) 4-MeC_6H_4; (c) 4-$MeOC_6H_4$; (d) 4-ClC_6H_4; (e) 4-BrC_6H_4; (f) Me; (g) 4-$NO_2C_6H_4$

Entry	t (hr)	T (°C)	Yield of **2** (%)	m.p. (°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

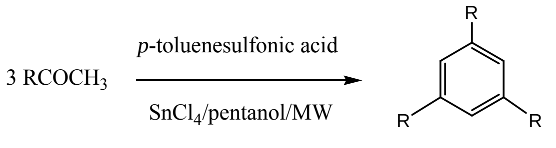


(2)

(**3a**), n=1
(**3b**), n=2

(**4a**), n=1
(**4b**), n=2

Table II — Yield of triarylbenzenes from aryl methyl ketones under microwave-induced condition



(3)

(1) (2)

R = (a) C_6H_5; (b) 4-MeC_6H_4; (c) 4-$MeOC_6H_4$; (d) 4-ClC_6H_4; (e) 4-BrC_6H_4; (f) –Me; (g) 4-$NO_2C_6H_4$

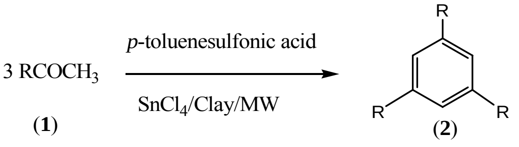
Entry	t (min)[a]	Power (W)	Yield of **2** (%)	m.p. (°C)
3a	3 × 1	400	86	172
3b	3 × 1	400	84	179-180
3c	3 × 1	400	88	143
3d	3 × 1.5	400	80	246
3e	3 × 1.5	400	85	263
3f	3 × 0.5	300	73	-
3g	3 × 3	400	55	153

[a] Number of irradiations for a given time; 2 × 3 indicates 2 irradiations of 3 min duration each.

The reactions of cyclohexanone and cyclopentanone was examined (Eqn. 2). In this case, gave the desired triannulated benzene **4** and in yield of 79 and 77% respectively.

In order to improve the yield of the triarylbenzenes, the reaction was carried out under microwave-induced

Table III —Yield of triarylbenzenes from aryl methyl ketones under solvent-free conditions



(4)

(**1**) (**2**)

R = (a) C_6H_5; (b) 4-MeC_6H_4; (c) 4-$MeOC_6H_4$; (d) 4-ClC_6H_4; (e) 4-BrC_6H_4; (f) –Me; (g) 4-$NO_2C_6H_4$

Entry	t (min)[a]	Power (W)	Yield of **2** (%)	m.p. (°C)
4a	3 × 2	400	91	172
4b	3 × 2	400	88	179-180
4c	3 × 2	400	90	143
4d	3 × 3	400	85	246
4e	3 × 3	400	85	263
4f	3 × 1.5	300	69	-
4g	3 × 3	400	60	153

Table IV — The analytical data for the compounds **2a-g**[b] and **4a-b**[c]

Compd	^1H NMR	MS	^{13}C NMR (100M)	m.p. (°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
4a	2.80(12H, m), 1.90(6H, m)		137.3, 27.2, 24.7	92
4b	2.57(12H, m), 1.77(12H, m)	240(M^+); 225; 212; 199; 183	132.6, 26.8, 23.1	236

[b] trimethylbenzene **2f** is easily detected by TLC.

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

condition instead of refluxing. The results are given in **Table II**.

The reactions were detected under the conditions of solid states. To an equimolar mixture of ketones, *p*-toluenesulfinic acid and catalytic amount of tin tetrachloride anhydrous(5%) placed in an open glass container, montmorillonite K 10 Clay is added and the reaction mixture is irradiated in a microwave oven. The results are given in **Table III**.

Clearly, the use of a microwave oven in solid state is convenient when compared to other experimental conditions and proceeds efficiently in a shorter period of time and higher yields. In conclusion, the $SnCl_4$/*p*-TsOH/pentanol condition we found is effective enough to catalyze the triple condensation of not only aryl methyl ketones but also cyclohexeanone. Microwave-induced version of the condensation reaction is more convenient due to 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.

All the analytical data for the compound **2a-g** and compound **4a-b** are given in **Table IV.**

Experimental Section

Melting points were measured on a Kofler apparatus and were uncorrected. MS were performed on ZAB-HS spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AM-600 and AM-400 instruments. Chemical shifts are referred to TMS on the 'δ' scale.

The *p*-toluenesulfinic acid (1.72 g, 10 mmoles) was added to a stirred solution of **1c** (1.50 g, 10 mmoles) in dry 1-pentanol (10 mL). Then the catalytic amount of tin tetrachloride anhydrous (5%) was added slowly by a syringe to the above mixture. The mixture was stirred for 5.5 hr at 110°C, then the solution was poured into ethanol (20 mL), stirred, filtered. Crystallization from EtOH and CH_2Cl_2 (1:1) gave **2c** (1.15 g), m.p. 143 °C, yield 72%.

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