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p-Toluene Sulfonic Acid-Promoted Rapid and Facile Baeyer Condensation with Microwave Irradiation under Solvent-Free Conditions

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A fast and efficient method has been developed for the synthesis of triarylmethanes catalyzed by *p*-TsOH under microwave irradiation. The reactions of different aryl aldehydes carrying activated and deactivated groups with N,N-dimethylaniline in the presence of a catalytic amount of *p*-TsOH produced the corresponding triarylmethanes in good to excellent yields.

Keywords: Aldehydes, Baeyer condensation, N,N-Dimethylaniline, Microwave, Catalyst, *p*-Toluene sulfonic acid

INTRODUCTION

Triarylmethanes (Leuco bases) constitute an important group of intermediates in the synthesis of compounds that industrial chemists are profoundly interested in. These compounds are particularly useful precursors for the preparation of printing inks, coloration of ceramics, drugs and leather, and dyeing of polyacrylonitrile fibers [1,2]. Thus, the development of facile and environmentally friendly methods to synthesize triarylmethanes constitutes an active area of investigation.

The most well-known route to synthesize triarylmethanes is the Baeyer condensation, which involves the direct reaction of arylaldehydes with N,N-dimethylaniline. Various reagents like HCl [3], $ZnCl_2$ [4], H_2SO_4 [5], montmorrilonite K-10 [6] and 1-*n*-butylpyridinium chloroaluminate [7] have been reported to improve this transformation.

However, in spite of their potential utility, many of these methods involve extended reaction times, drastic reaction conditions, unsatisfactory yields or the use of toxic solvents, which are serious disadvantages. Therefore, a need still exists for versatile, simple and environmentally friendly processes whereby triarylmethanes may be obtained under milder conditions.

Since its first application in 1986 [8], microwave irradiation has found increasing use in organic synthesis [9]. On the other hand, solvent-free organic synthesis has received considerable attention due to growing worldwide concerns over chemical waste and future resources [10]. From these points of view and in the course of our attempts to extend the application range of microwave-assisted methods to more sensitive substrates [11], we now to report the synthesis of triarylmethanes through the reaction of aryl aldehydes and N,N-dimethylaniline in the presence of *p*-toluene sulfonic acid (*p*-TsOH) under solvent-free conditions using microwave irradiation.

EXPERIMENTAL

Chemicals and Apparatus

All chemicals were purchased from Fluka, Merck, and Aldrich chemicals companies. All of the products refer to the

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pure triarylmethanes. The apparatus used for these reactions was a Samsung domestic microwave oven (900 W) without any modification.

Typical Procedure

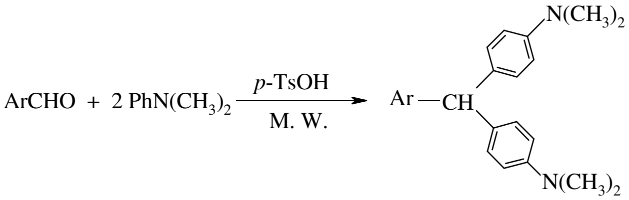
A mixture of benzaldehyde (0.106 g, 1 mmol), N,N-dimethylaniline (0.363 g, 3 mmol) and *p*-TsOH (0.017, g, 0.1 mmol) were added successively and mixed in a dry flask and then irradiated at 900 W for 15 min. After completion of the reaction (monitored by TLC), the mixture was transferred to a stirred solution of 0.5 N NaOH (25 ml). The precipitated product was filtered, washed with water and dried *in vacuo*. The product was purified by recrystallization from ethanol.

RESULTS AND DISCUSSION

In this work, different triarylmethane derivatives were obtained from the reaction as shown in Scheme 1.

To investigate the effect of different Lewis acids on the progress of this reaction under microwave condition, we first began our study by comparing the catalytic activity of *p*-TsOH and metallic derivatives or Lewis acids towards the reaction between benzaldehyde and N,N-dimethylaniline under microwave irradiation (Table 1). Among all the catalysts tested, *p*-TsOH had the highest yield (Table 1, Entry 7).

The reactions of different aryl aldehydes carrying activated and deactivated groups with N,N-dimethylaniline in the presence of a catalytic amount of *p*-TsOH produced the corresponding triarylmethanes in good to excellent yields. The results are shown in Table 2. Under these conditions, several functional groups like chloro, methoxy, amino, methyl or nitro on the benzaldehyde ring do survive during the course of the reaction and their corresponding triarylmethanes were achieved in good to high yields without any by-products (Table 2, entries 1-8). All of the products were characterized by spectroscopic comparison with previously published reports or the authentic samples.



Scheme 1

Table 1. Screening of Various Catalysts for the Reaction of Benzaldehye with N,N-Dimethylaniline under Microwave Irradiation

Entry	Catalyst	Yield (%)	Time (min)
1	none	0	60
2	$KHSO_4$	55[a]	10
3	NH_2SO_3H	70[a]	10
4	CAN	10[b]	10
5	$SnCl_2$	50[b]	15
6	$ZrCl_4$	58[b]	10
7	*p*-TsOH	80[b]	15

[a]100 mol% of catalyst. [b]10 mol% of catalyst.

In conclusion, the present microwave-assisted procedure provides an efficient, “green” and simple methodology for the preparation of triarylmethanes under solvent-free conditions using *p*-TsOH as a low cost, oxygen and moisture tolerant catalyst with very short reaction times. The present methodology offers advantages over traditional ones performed in organic solvents.

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Table 2. Formation of Triarylmethanes Catalyzed by *p*-TsOH under Microwave Irradiation

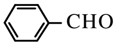
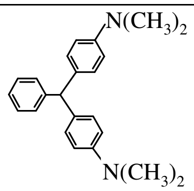
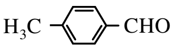
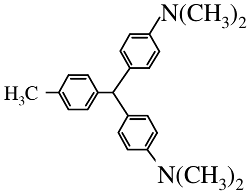
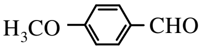
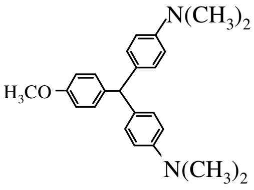
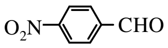
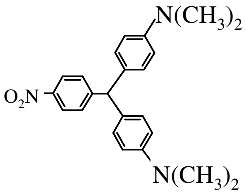
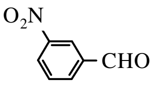
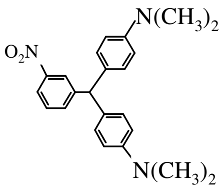
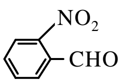
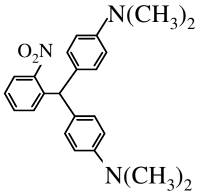
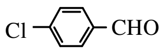
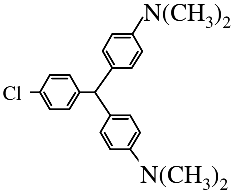
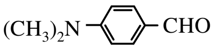
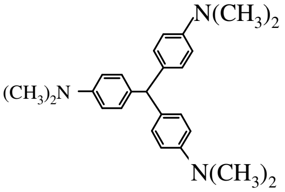
Entry	Aldehyde	Product[a]	Time (min)	Yield (%)[b]	M.p. (ºC)	
					Found	Reported[5-7]
1			15	80	96-97	97-98
2			15	75	98-100	99-100
3			15	70	101-102	102-103
4			10	98	182-184	184-185
5			10	92	152-154	152-153
6			15	88	161-162	159-160

Table 2. Continued

7			15	79	142-143	142-144
8			10	83	172-174	173-175

[a]All the products are known compounds and were characterized by comparison of their physical and spectral data with those reported in the literature. [b]Isolated yields.

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