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$ZrOCl_2$ catalyzed Baeyer condensation: A facile and efficient synthesis of triarylmethanes under solvent-free conditions

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A facile and efficient synthesis of an array of triarylmethanes by the Baeyer condensation of different arylaldehydes carrying activated and deactivated groups and N,N-dimethylaniline using a catalytic amount of $ZrOCl_2$ under solvent-free microwave irradiation conditions is described. Further, the catalytic activity of $ZrOCl_2$ is compared with traditional Lewis acid catalysts and found that this synthetic method has the advantages of excellent yields (70-96%), shorter reaction time (few minutes) and solvent-free conditions.

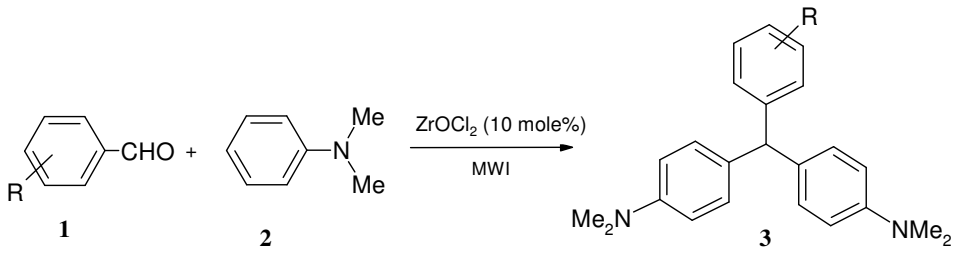
Keywords: $ZrOCl_2$, Baeyer condensation, triarylmethanes, solvent-free, microwave irradiation

Triarylmethane and its derivatives 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 dying of polyacrylonitrile fibres[1]. In view of the importance of triarylmethanes, many classical methods for the synthesis of triarylmethane derivatives were reported in the literature. The well known route to synthesize triarylmethanes is the Baeyer condensation, which involves the direct reaction of arylaldehydes with N,N-dimethylaniline. Various reagents such as H_2SO_4 (Ref. 2), HCl (Ref. 3), $ZnCl_2$ (Ref. 4), montmorillonite K-10 (Ref. 5), 1-*n*-butylpyridinium chloroaluminate[6], *p*-TsOH (Ref. 7), *etc*., have been reported to improve this transformation. However, in spite of their potential utility, some of the reported methods suffer from serious drawbacks like longer reaction times, drastic reaction conditions, unsatisfactory yields and the use of toxic solvents. Therefore, there is scope for alternative protocols which address the shortcomings of currently available methods and environment friendly processes whereby triarylmethanes may be obtained under mild conditions.

Of late, $ZrOCl_2$ has been shown to be a Lewis acid that is different from traditional Lewis acids such as $AlCl_3$, $SnCl_2$, $BF_3.OEt_2$, *etc*., and is also quite stable to water and reusable, non-toxic as well as highly effective in the case of many nitrogen containing compounds such as nitriles, amines, *etc*[8]. Additionally, Zr^{4+} with a high charge-to-size ratio (22.22 e^2 m^{-10}, Ref. 9) enables reactions with high to excellent yields due to strong coordination of Zr^{4+}. Therefore, it has emerged as a powerful Lewis acid catalyst imparting high regio- and chemoselctivity in various organic reactions such as Michael addition[10], crossed-Aldol condensation[11], Pechmann condensation[12], Knoevenagel condensation[13], Mannich reaction[14] and Biginelli reaction[15], as well as some other reactions[16,17]. In continuation of the interest in zirconium catalyzed organic transformations[15,18], herein is described a novel, efficient and high yielding protocol for the synthesis of triarylmethanes through the Baeyer condensation of aromatic aldehydes and N,N-dimethylaniline employing $ZrOCl_2$ as an efficient and mild Lewis acid catalyst under solvent-free microwave irradiation conditions.

Results and Discussion

In the course of the investigation to develop new synthetic methods, was studied the use of $ZrOCl_2$ and other Lewis acids as catalysts for the synthesis of triarylmethanes by the Baeyer condensation of arylaldehyde **1** and N,N-dimethylaniline **2** without using any organic solvent under microwave irradiation (**Scheme I**). The reaction led to formation of the corresponding triarylmethane **3**, especially the $ZrOCl_2$ catalyzed reaction proceeded rapidly to give the product in excellent yield with high purity when



1 **2** **3**

Scheme I

Table I — Reaction of benzaldehyde **1** and N,N-dimethyl-aniline **2** catalyzed by various Lewis acids under microwave irradiation

Entry	Catalyst	Catalyst amount (mole%)	Time (min)	Yield of **3a** (%)
1	none	—	60	05
2	$SnCl_2$	10	20	39
3	CAN	10	10	15
4	$Sm(OTf)_3$	10	10	47
5	$KHSO_4$	15	20	56
6	$Yb(OTf)_3$	10	10	70
7	NH_2SO_3H	15	15	63
8	$TiCl_4$	10	10	68
9	$ZrCl_4$	10	15	69
10	*p*-TsOH	10	10	78
11	$ZrOCl_2$	10	10	83
12	$ZrOCl_2$	7.5	10	80
13	$ZrOCl_2$	5.0	10	79
14	$ZrOCl_2$	2.5	10	62

compared to other Lewis acid catalyzed reactions (**Table I**). *p*-Toluenesulfonic acid (*p*-TsOH), a strong protonic acid, also acted as a catalyst for the reaction. However, the product yield was low and many bi-products were formed.

Under microwave irradiation, the reaction rate and therefore, the product yield increased dramatically and reaction time was shortened from several hours to a few minutes. It is noteworthy that the amount of $ZrOCl_2$ catalyst affects the product yield, and in the presence of $ZrOCl_2$ (>7.5 mole%), the reaction afforded the triarylmethane **3** in highest yield (83%, **Table I**).

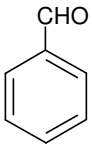
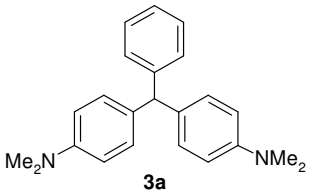
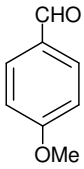
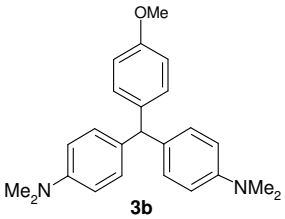
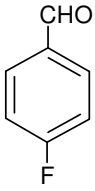
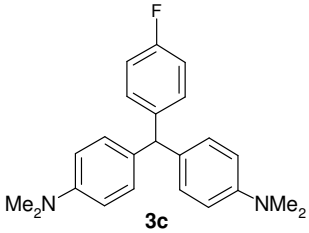
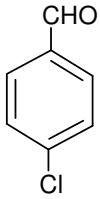
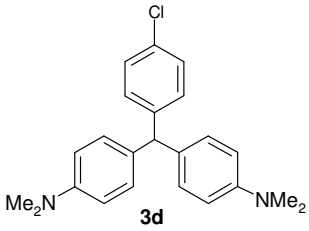
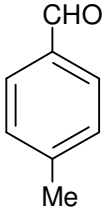
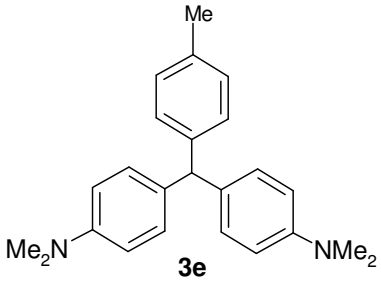
A wide range of structurally varied aldehydes **1**, including aromatic, heteroaromatic aldehydes, and N,N-dimethylaniline **2** were examined in the presence of a catalytic amount of $ZrOCl_2$ (10 mole%) under solvent-free microwave irradiation conditions (**Scheme I**) and the results are summarized in **Table II**. In all cases, the reaction proceeded rapidly to afford the corresponding triarylmethanes **3** in excellent yields. In general, electron-withdrawing groups on the aldehyde system (such as chloro and nitro) are beneficial for the reaction, possibly due to the decreased electron density of aromatic system and the carbonyl carbon (entries **3**, **10**, **11** and **12**, **Table II**), whereas electron-releasing groups (such as methoxy and methyl) are unfavorable for this condensation. Further the product yield of *ortho* and *meta* electron-withdrawing substituted aldehydes was lower than that of *para* electron-withdrawing substituted aldehydes (entries **10** and **11**, **Table II**). In the case of 2,4-dimethoxybenzaldehyde (entry **7**, **Table II**) and 3,4-methylenedioxybenzaldehyde (entry **8**, **Table II**) the product yield decreased and the reaction time was prolonged as compared to monosubstituted methoxybenzaldehyde (entry **2**, **Table II**).

This protocol has been further explored for the synthesis of methylene-bis-triarylmethane **5** by the reaction of 5-(3-formyl-4-methoxybenzyl)-2-methoxy-benzaldehyde **4** and N,N-dimethylaniline **2** in the presence of $ZrOCl_2$ (10 mole%) under solvent-free microwave irradiation resulted in 61% yield (**Scheme II**).

Experimental Section

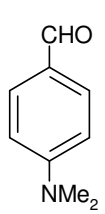
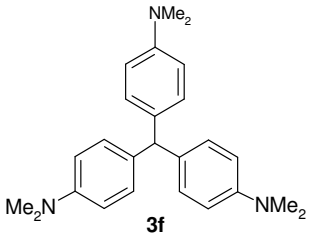
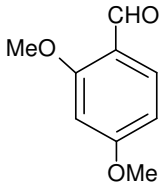
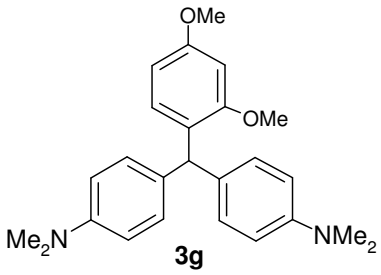
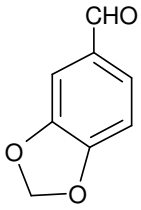
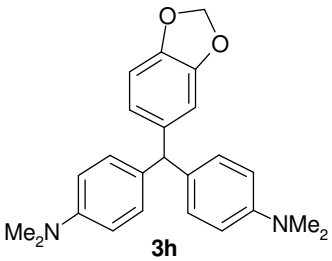
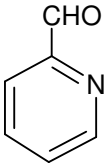
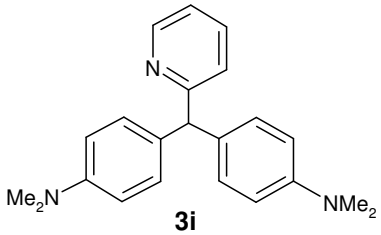
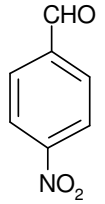
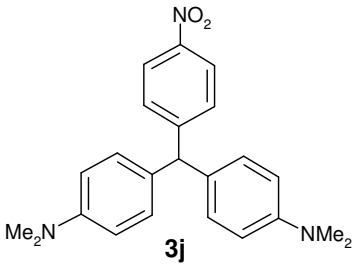
All the reagents were purchased from commercial sources and used as received. The compound **4** was prepared by the reported method[19]. TLC analysis was performed with glass backed plates precoated with silica gel and examined under UV (254 nm). Melting points were determined on a Fisher-Johns melting point instrument and are uncorrected. NMR spectra were recorded in DMSO-d_6 with TMS as the internal standard on a Varian Gemini spectrometer. Mass spectra were obtained on a VG Micromass 7070H spectrometer. Elemental analyses were performed on a Perkin-Elmer 240 CHN elemental analyzer. For the microwave irradiation, a conventional house-hold

Table II — $ZrOCl_2$ Catalyzed synthesis of triarylmethanes under solvent-free microwave irradiation

Entry	Aldehyde	Product[a]	Time (min)	Yield (%)[b]	m.p. (°C)	
					Found	Reported (Ref. 2,5,6)
1		 **3a**	10	83	97-99	97-98
2		 **3b**	12	72	100-02	102-04
3		 **3c**	10	79	139-41	–
4		 **3d**	12	77	143-44	142-44
5		 **3e**	11	76	97-99	99-100

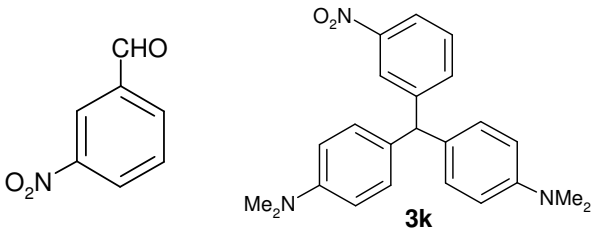
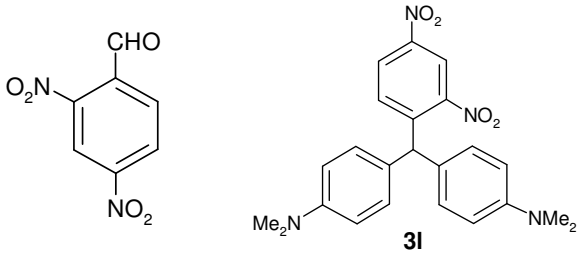
—Contd.

Table II — $ZrOCl_2$ Catalyzed synthesis of triarylmethanes under solvent-free microwave irradiation (*Contd.*)

6		 **3f**	12	75	172-74	173-75
7		 **3g**	15	70	147-49	–
8		 **3h**	15	81	162-64	–
9		 **3i**	8	95	170-72	–
10		 **3j**	6	96	182-84	184-86

—Contd.

Table II — $ZrOCl_2$ Catalyzed synthesis of triarylmethanes under solvent-free microwave irradiation (*Contd.*)

11	 **3k**	10	90	152-55	152-54
12	 **3l**	6	92	183-84	–

[a]The products were characterized by their NMR, Mass and elemental analysis. Spectral data of the known products were compared with the reported data.
[b]Isolated yields.

microwave oven (LG Electronics, India, Ltd.) was used.

General procedure for the synthesis of triarylmethanes, 3

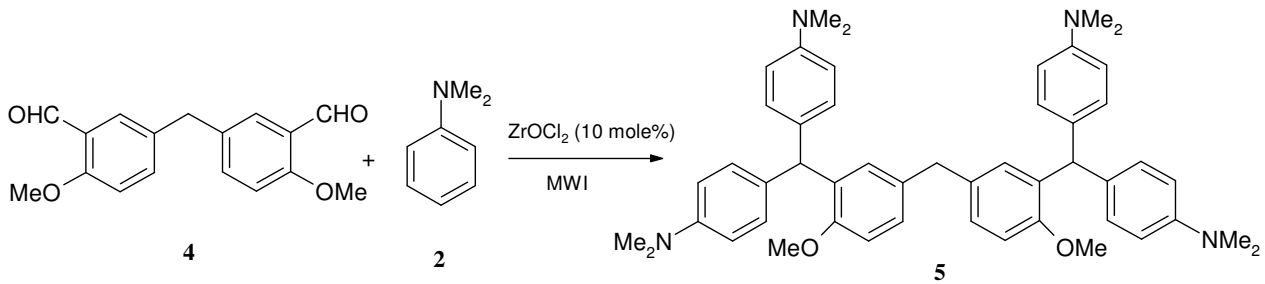
Aromatic aldehyde **1** (1 mmole), N,N-dimethylaniline **2** (3 mmole) and $ZrOCl_2.8H_2O$ (32 mg, 0.1 mmole) were mixed thoroughly in a dry flask, and then microwave irradiated at 900 W for an appropriate time (**Table II**). After completion of the reaction (monitored by TLC), the reaction-mixture was cooled to RT and transferred to 0.5 *N* NaOH solution (20 mL) while stirring. The precipitated product was filtered, washed with water, dried *in vacuo* and purified by recrystallization from ethanol.

Synthesis of methylene-bis-triarylmethane, 5

Compound **4** (1 mmole), N,N-dimethylaniline **2** (6 mmole) and $ZrOCl_2.8H_2O$ (32 mg, 0.1 mmole) were added successively and mixed thoroughly in a dry flask, and then microwave irradiated at 900 W for 12 min. After completion of the reaction (monitored by TLC), the reaction-mixture was cooled to RT and transferred to 0.5 *N* NaOH solution (20 mL) while stirring. The separated product was filtered, washed with water, dried *in vacuo* and purified by recrystallization from ethanol.

Spectral data for new compounds

Dimethyl-4-[[4-(dimethylamino)phenyl](4-fluoro phenyl)methyl]aniline, 3c. ^{1}H NMR (300 MHz,



4 **2** **5**

Scheme II

DMSO-d_6): δ 7.12 (d, 2H, *J* = 8.7 Hz), 6.98 (d, 4H, *J* = 8.9 Hz), 6.67 (d, 2H, *J* = 8.7 Hz), 6.52 (d, 4H, 8.9 Hz), 5.27 (s, 1H), 2.47 (s, 12H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 168.2, 150.3, 148.9, 145.4, 134.7, 132.4, 116.2, 114.8, 54.9, 42.5; MS: *m/z* 349 (M^+). Anal. Calcd. for $C_{23}H_{25}FN_2$: C, 79.28; H, 7.23; N, 8.04. Found: C, 79.29; H, 7.20; N, 8.01%.

Dimethyl-4-{(2,4-(dimethoxyphenyl)[4-(di-methyl amino)phenyl)methyl}aniline, 3g. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.10 (d, 1H, *J* = 8.8 Hz), 6.98 (d, 4H, *J* = 8.9 Hz), 6.50 (d, 4H, *J* = 8.9 Hz), 6.33-6.30 (m, 2H), 5.82 (s, 1H), 3.83 (s, 6H), 2.48 (s, 12H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 162.3, 159.7, 151.2, 134.7, 133.6, 127.0, 124.0, 114.6, 111.1, 102.0, 57.1, 55.5, 50.8, 41.9; MS: *m/z* 390 (M^+). Anal. Calcd. for $C_{25}H_{30}N_2O_2$: C, 76.89; H, 7.74; N, 7.17. Found: C, 76.85; H, 7.72; N, 7.14%.

Dimethyl-4-{1,3-benzodioxo-5-yl[4-(dimethyl amino)-phenyl)methyl}aniline, 3h. ^{1}H NMR (300 MHz, DMSO-d_6): δ 6.91 (m, 6H), 6.60 (s, 1H), 6.46 (d, 4H, *J* = 8.9 Hz), 5.47 (s, 1H), 5.21 (s, 1H), 2.48 (s, 12H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 150.1, 148.6, 148.4, 143.6, 137.2, 131.3, 123.2, 114.7, 111.4, 110.7, 102.3, 59.6, 42.1; MS: *m/z* 374 (M^+). Anal. Calcd. for $C_{24}H_{26}N_2O_2$: C, 76.98; H, 7.00; N, 7.48. Found: C, 76.93; H, 6.99; N, 7.50%.

Dimethyl-4-[[4-(dimethylamino)phenyl](2-pyridyl)-methylaniline, 3i. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 8.57-7.00 (m, 4H), 6.92 (d, *J* = 8.9 Hz, 4H), 6.44 (d, *J* = 8.9 Hz, 4H), 5.32 (s, 1H), 2.47 (s, 12H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 164.1, 151.0, 148.6, 141.4, 138.0, 130.9, 124.3, 121.3, 113.6, 58.0, 42.3; MS: *m/z* 331 (M^+). Anal. Calcd. for $C_{22}H_{25}N_3$: C, 79.72; H, 7.60; N, 12.68. Found: C, 79.70; H, 7.55; N, 12.66%.

Dimethyl-4-[[4-(dimethylamino)phenyl](2,4-dinitrophenyl)methyl]aniline, 3l. ^{1}H NMR (300 MHz, DMSO-d_6): δ 8.72 (s, 1H), 8.41 (d, 1H, *J* = 8.6 Hz), 7.67 (d, 1H, *J* = 8.6 Hz), 7.00 (d, 4H, *J* = 8.9 Hz), 6.49 (d, 4H, *J* = 8.9 Hz), 5.71 (s, 1H), 2.49 (s, 12H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 152.1, 150.6, 146.3,145.4, 139.1, 133.2, 131.5, 128.7, 120.9, 111.2, 56.1, 42.0; MS: *m/z* 420 (M^+). Anal. Calcd. for $C_{23}H_{24}N_4O_4$: C, 65.70; H, 5.75; N, 13.32. Found: C, 65.68; H, 5.76; N, 13.30%.

Dimethyl-4-[5-(3-di[4-(dimethylamino)phenyl] methyl-4-methoxybenzyl)-2-methoxyphenyl][4-(dimethylamino)-phenyl]methylaniline, 5. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.00-6.92 (m, 12H), 6.70 (d, 2H, *J* = 9.2 Hz), 6.42 (d, 8H, *J* = 8.8 Hz), 5.63 (s, 2H), 3.72 (s, 2H), 3.66 (s, 6H), 2.48 (s, 24H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 159.2, 149.5, 136.2, 134.7, 134.1, 132.6, 130.4, 123.8, 114.1, 113.0, 56.3, 54.9, 42.4, 41.0; MS: *m/z* 732 (M^+). Anal. Calcd. for $C_{49}H_{56}N_4O_2$: C, 80.29; H, 7.70; N, 7.64. Found: C, 80.24; H, 7.69; N, 7.65%.

The known compounds **3a**, **3b**, **3d**, **3e**, **3f**, **3j** and **3k** (**Table II**) have been identified by comparison of spectral data with those reported[2,5,6].

Conclusions

In summary, it can be concluded that $ZrOCl_2$ is an efficient and excellent catalyst for the Baeyer condensation of aromatic aldehydes and N,N-dimethylaniline to afford triarylmethanes in high yields under solvent-free microwave irradiation conditions in shorter reaction time. The notable factors of this condensation are: (a) good yields; (b) fast reaction; (c) mild reaction conditions; and (d) green synthesis avoiding use of solvents. Thus, it is believed that the procedure described here will find important applications in the synthesis of triarylmethanes to cater to the needs of academia as well as industries.

Acknowledgement

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