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Ultrasound-Assisted Eco-Friendly Synthesis of Triarylmethanes Catalyzed by Silica Sulfuric Acid

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An efficient and eco-friendly synthesis of triarylmethanes by the reaction of arenes with aldehydes in the presence of silica sulfuric acid as a heterogeneous and reusable catalyst under ultrasonic irradiation is reported. The advantages of this protocol are the use of green solvents, inexpensive catalyst, commercially available precursors, reusability of SSA, simple work-up, high yields and short reaction times.

Keywords: Triarylmethanes, Ultrasonic irradiation, Silica sulfuric acid, Reusable catalyst, Eco-friendly

INTRODUCTION

Many synthetic chemists have made a great deal of effort to design sustainable and clean procedures to replace the classical synthetic methods [1]. Application of sonochemistry to enhance the efficiency and/or selectivity of organic reactions is one of the most well-known challenges [2]. Ultrasound-assisted organic synthesis (UAOS) exploits a variety of factors such as milder and more efficient conditions, high yields and shorter reaction times, energy conservation, formation of purer products, waste minimization and easier manipulation. To date, many valuable organic compounds have been synthesized under ultrasound irradiation without need to potent conditions like the traditional methods [3].

Today, there is a great demand for solid acids instead of conventional mineral acids such as HF, H_2SO_4 and BF_3 in chemical processes. Mineral acids are corrosive and non-recoverable catalysts [4]. Preparation of silica sulfuric acid (SSA) as a stable solid acid has been reported and its catalytic activity in a wide range of organic reactions has been verified. Easy handling, separation and work-up processes, non-hazardous nature, recyclability and easier waste disposal are among the most common characteristics that make it a green catalyst [5].

Triarylmethane (TRAM) scaffold constitutes the fundamental member of several natural products, biologically active compounds, dyes and polymers. Typically, the application of triarylmethanes as promising candidates in textile industry, phenolic triarylmethanes as antioxidant and antitumor reagents and diheteroarylmethanes as natural components of certain foods and beverages has been reported. Triarylmethanes are also used as protecting groups in synthesis, bioconjugation, cross-linking, mass-spectroscopy, fluorescence and optics [6]. Several methods such as Suzuki-Miyaura coupling reaction of diarylmethyl carbonates with arylbronic acid in the presence of $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$-DPPPent

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(1,5-bis(diphenylphosphino)pentane) [7], direct alkylation of aryl(azaaryl)methanes with aryl halides catalyzed by palladium [8], Friedel-Crafts reaction of arenes with aldehydes catalyzed by $InCl_3$/chlorodimethylsilan [9], $[Ir(COD)Cl]_2$-$SnCl_4$ [10], $AuCl_3$ or $AuCl_3$/AgOTf [11], $Yb(OTf)_3$ [12], $Cu(OTf)_2$ [13], $FeCl_3$ [14], sulfuric acid [15], AcBr/$ZnCl_2$/SiO_2 [16], and trifluromethansulfonic acid or trifluroacetic acid [17] have been reported for the synthesis of TRAMs.

Although, the available methods are put to good use in certain synthetic conditions, many of them have drawbacks such as multistep processes [13], formation of by-products [17], low yields and selectivity, and tedious work-up process [10,12,14-17]. On the other hands, some of these methods require inert atmosphere [11], long reaction times [7,8,11,12,14] and high temperatures [7,8,11,13,14]. The use of corrosive reagents [14-16], toxic solvents [7,8,11,13-17], large amounts of catalyst [15,17] and non-reusable catalysts [7-17] are other problems with some of the reported methods. Therefore, the development of an efficient and eco-friendly method for the synthesis of TRAMs is clearly justified.

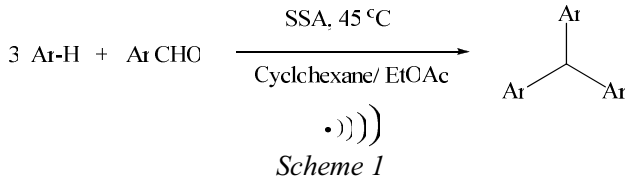
In continuation of our previous works on developing new and environmentally benign methods for the preparation of fine chemicals [18], here, we report a novel, efficient and eco-friendly method for the synthesis of triarylmethanes by the reaction of arenes with aldehydes catalyzed by silica sulfuric acid (SSA) under ultrasound irradiation (Scheme 1).

EXPERIMENTAL

Commercial solvents were used in the reactions after drying and distillation. SSA was prepared according to the literature [5a]. All other chemicals were obtained from Merck chemical company and used without further purification. Melting point was determined using Stuart Scientific SMP2 apparatus. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker-AC 500 MHz spectrometer in $CDCl_3$. FT-IR spectra were obtained as KBr pellets using a Nicolet-Impact 400D instrument in the range of 400-4000 cm^{-1}. Mass spectra were recorded on a Micromass Platform II spectrometer. A UP 400S ultrasonic processor equipped with a 3 mm wide and 100 mm long probe (made of titanium, Sonotrode H3), which was immersed directly into the reaction mixture, was used for sonication. The operating frequency was 24 KHz and the output power was 0-400 W through manual adjustment. During the sonication, the reaction temperature was maintained at 45 °C by the addition or removal of circulating water (Fig. 1).

General Procedure for Ultrasound-Promoted Synthesis of TRAMs

To a mixture of veratrole **1** (828 mg, 6 mmol) and aldehyde (2 mmol) in cyclohexene/ethyl acetate (6 ml/2 ml) was added SSA (600 mg) and exposed to US irradiation at 45 °C for the appropriate time according to Tables 2 and 3. The progress of the reaction was monitored by TLC (eluent:*n*-hexane/ethyl acetate, 10:4). After completion of the reaction, the solvent was evaporated. Then, absolute ethanol (2 × 10 ml)



Scheme 1

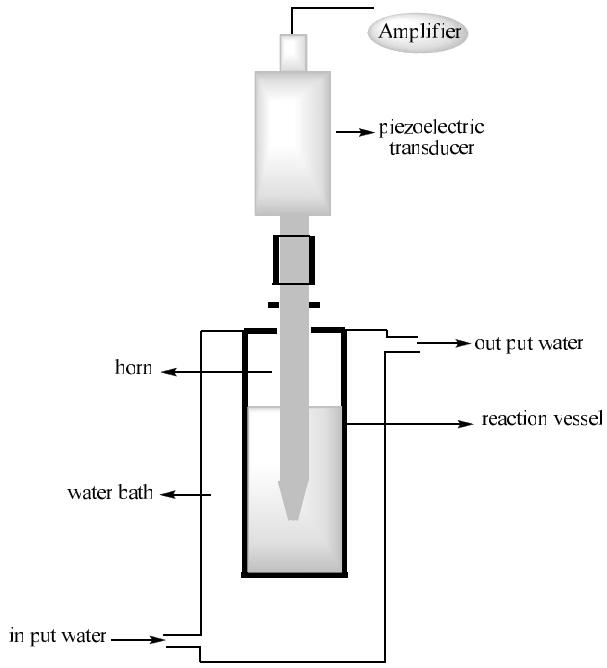


Fig. 1. Ultrasonic experimental set-up.

was added and the catalyst was filtered. The product was obtained by recrystallization from EtOH or EtOH/H_2O (10:2).

Spectral Data

1-(Bis(3,4-dimethoxyphenyl)methyl)-3-nitrobenzene (Table 2, entry 2). M.p.: 154-155.5 ºC. FT-IR (KBr)ν_{max} 3084, 3003, 2947, 1589, 1516, 1463, 1342, 1028, 916, 869, 736 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.05-8.08 (m, 1H), 8.00 (s, 1H), 7.44-7.46 (m, 2H), 6.81 (d, *J* = 8.25 Hz, 2H), 6.65 (d, *J* = 1.95 Hz, 2H), 6.57 (dd, *J* = 8.25 Hz, *J* = 1.95 Hz, 2H), 5.53 (s, 1H), 3.86 (s, 6H), 3.77 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.16, 148.44, 148.04, 146.68, 135.35, 135.17, 129.12, 124.05, 121.51, 121.39, 112.72, 111.26, 55.91, 55.59. MS (EI) m/z: 410.12 ($[M+1]^+$, 25.86), 409.11 (M^+, 100), 378.06 (46.26), 287.18 (40.23), 226.13 (9.99), 152.10 (7.33), 139.08 (6.90), 76.93 (21.83). Anal. Calcd. for $C_{23}H_{23}NO_6$: C, 67.47; H, 5.66; N, 3.42. Found: C, 67.34; H, 5.64; N, 3.42.

1-(Bis(3,4-dimethoxyphenyl)methyl)-4-nitrobenzene (Table 2, entry 3). M.p.: 116-118 °C. FT-IR (KBr)ν_{max} 3074, 2956, 2835, 1587, 1514, 1463, 1346, 1265, 1138, 1024, 806, 742, 700 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.75 Hz, 2H), 7.27 (d, *J* = 8.7 Hz, 2H), 6.79 (d, *J* = 8.3 Hz, 2H), 6.63 (d, *J* = 2 Hz, 2H), 6.56 (dd, *J* = 8.25 Hz, *J* = 2 Hz, 2H), 5.51 (s, 1H), 3.84 (s, 6H), 3.75 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.12, 149.14, 148.04, 146.51, 135.09, 130.09, 123.47, 121.41, 112.73, 111.25, 55.89, 55.76. MS (EI) m/z: 410.07 ($[M+1]^+$, 46.48), 409.07 ($[M]^+$, 100), 378.05 (89.44), 287.05 (78.87), 151.98 (35.39), 138.94 (36.97), 78.90 (29.05). Anal. Calcd. for $C_{23}H_{23}O_6N$: C, 67.47; H, 5.66; N, 3.42. Found: C, 67.39; H, 5.66; N, 3.40.

4-((2,4-Dichlorophenyl)(3,4-dimethoxyphenyl)methyl)-1,2-dimethoxybenzene (Table 2, entry 5). Mp 151-152 °C. IR (KBr)ν_{max} 3072, 2999, 2933, 1587, 1516, 1463, 1328, 1250, 1138, 1028, 960, 866, 815, 754, 638 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.39 (d, *J* = 2.15 Hz, 1H), 7.15 (dd, *J* = 8.5 Hz, *J* = 2.15 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.78 (d, *J* = 8.3 Hz, 2H), 6.61 (d, *J* = 2 Hz, 2H), 6.51 (dd, *J* = 8.25 Hz, *J* = 1.95 Hz, 2H), 5.76 (s, 1H), 3.86 (s, 6H), 3.77 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.03, 147.85, 140.76, 135.15, 134.82, 132.77, 131.74, 129.41, 126.83, 121.41, 112.89, 111.03, 55.89, 55.86, 52.16. MS (EI) m/z: 436.09 ($[M+4]^+$, 2.40), 434.06 ($[M+2]^+$, 10.16), 432.08 ($[M]^+$, 18.97), 365.07 (7.59), 287.12 (9.77), 139.05 (30.80), 94.00 (37.72), 78.99 (100), 77.00 (50.89). Anal. Calcd. for $C_{23}H_{22}Cl_2O_4$: C, 63.75; H, 5.12. Found: C, 63.49; H, 5.09.

1,2-Dimethoxy-4-((3,4-dimethoxyphenyl)(3-methoxyphenyl)methyl)benzene (Table 2, entry 8). M.p.: 120-122 °C. IR (KBr)ν_{max} 3010, 2935, 1602, 1581, 1463, 1317, 1246, 1139, 1091, 1026, 958, 860, 767 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.95 Hz, 1H), 6.78 (d, 8.25 Hz, 2H), 6.76 (dd, *J* = 8.2 Hz, *J* = 2.2 Hz, 1H), 6.72 (d, *J* = 7.65 Hz, 1H), 6.68-6.69 (m, 3H), 6.62 (dd, *J* = 8.25 Hz, *J* = 1.9 Hz, 2H), 5.41 (s, 1H), 3.86 (s, 6H), 3.77 (s, 6H), 3.74 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.63, 148.83, 147.57, 146.01, 136.62, 129.16, 121.85, 121.44, 115.46, 112.89, 111.32, 111.00, 55.96, 55.88, 55.86, 55.13. MS (EI) m/z: 395.10 ($[M+1]^+$, 73.79), 394.10 ($[M]^+$, 100), 364.07 (71.56), 363.07 (98.93), 287.05 (93.51), 257.06 (81.08), 241.05 (57.30), 225.05 (57.30), 181.07 (68.11), 152.01 (69.73), 138.97 (64.86), 114.99 (51.35), 94.87 (39.46), 76.98 (55.68). Anal. Calcd. for $C_{24}H_{26}O_5$: C, 73.08; H, 6.64. Found: C, 72.89; H, 6.65.

2-(Bis(3,4-dimeyhoxyphenyl)methyl)naphthalene (Table 2, entry 9). Mp 133-135 °C. FT-IR (KBr)ν_{max} 3005, 2954, 1629, 1587, 1462, 1365, 1261, 1184, 1028, 964, 862, 761 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.81-7.83 (m, 1H), 7.79 (d, *J* = 8.5 Hz, 1H), 7.73-7.75 (m, 1H), 7.52 (s, 1H), 7.46 (d, *J* = 3.5 Hz, 1H), 7.44 (d, *J* = 3.35 Hz, 1H), 7.36 (dd, *J* = 8.52 Hz, *J* = 1.6 Hz, 1H), 6.81 (d, *J* = 8.3 Hz, 2H), 6.79 (d, *J* = 1.85 Hz, 2H), 6.69 (dd, *J* = 8.25, 1.85, 2H), 5.65 (s, 1H), 3.88 (s, 6H), 3.79 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.97, 147.70, 142.07, 136.60, 133.49, 132.25, 128.09, 127.93, 127.84, 127.63, 127.60, 126.04, 125.66, 121.68, 113.05, 111.12, 56.13, 55.91, 55.90. MS (EI) m/z: 415.11 ($[M+1]^+$, 69.51), 414.09 ($[M]^+$, 100), 383.07 (91.97), 287.05 (80.00), 277.07 (65.88), 245.07 (57.06), 215.06 (52.94), 127.96 (61.18), 119.46 (68.24), 77.00 (25.29). Anal. Calcd. for $C_{27}H_{26}O_4$: C, 78.24; H, 6.32. Found: C, 77.95; H, 6.34. 52.94), 127.96 (61.18), 119.46 (68.24), 77.00 (25.29).

1,1-Bis(3,4-dimethoxyphenyl)butane (Table 2, entry 12). Oil. IR (neat)ν_{max} 2995, 2931, 1589, 1463, 1425, 1259, 1141, 1028, 952, 856, 808, 754 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 6.79 (s, 4H), 6.74 (s, 2H), 3.88 (s, 6H), 3.87 (s, 6H), 3.81 (t, *J* = 6.83 Hz, 1H), 1.97 (q, *J* = 7.65 Hz, 2H), 1.29 (sext, *J* = 7.55 Hz, 2H), 0.93 (t, *J* = 7.32 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.87, 147.36, 138.28, 119.58, 111.50,

111.24, 55.89, 50.17, 38.34, 21.19, 14.07. MS (EI) m/z: 331.15 ([M+1]$^+$, 29.55), 330.14 (M$^+$, 64.09), 288.13 (62.27), 287.13 (84.55), 166.94 (90.91), 148.90 (100), 127.95 (61.82), 114.81 (66.36), 112.98 (85.91), 103.89 (65.91), 82.92 (80.45), 76.89 (49.09).

1,2-Dimethoxy-4-(1-(3,4-dimethoxyphenyl)-2-phenylpropyl)benzene (Table 2, entry 13). Oil. IR (neat)ν_{max} 3057, 2931, 1589, 1463, 1334, 1263, 1184, 1028, 856, 810, 761, 700 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.15-7.2 (m, 4H), 7.08 (t, *J* = 6.9 Hz, 1H), 6.96 (dd, *J* = 8.22 Hz, *J* = 1.8 Hz, 1H), 6.88 (d, *J* = 1.7 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 6.68 (dd, *J* = 8.22 Hz, *J* = 1.85 Hz, 1H), 6.61 (d, *J* = 8.3 Hz, 1H), 6.55 (d, *J* = 1.75 Hz, 1H), 3.97 (d, *J* = 11.1 Hz, 1H), 3.89 (s, 3H), 3.86 (s, 3H), 3.67 (s, 3H), 3.66 (s, 3H), 3.45-3.49 (m, 1H), 1.24 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.99, 148.26, 147.58, 146.94, 146.06, 136.97, 136.78, 128.12, 127.69, 125.82, 120.25, 120.16, 111.95, 111.45, 110.92, 58.39, 55.97, 55.91, 55.74, 55.69, 44.89, 21.93. MS (EI) m/z: 393.06 ([M+1]$^+$, 2.04), 392.05 ([M]$^+$, 7.72), 287.09 (100), 257.03 (75.72), 197.04 (62.17), 167.01 (64.78), 152.03 (71.30), 128.04 (72.17), 115.00 (80.43), 105.02 (90.87), 77.00 (85.65).

1,4-Bis(bis(4-methoxyphenyl)methyl)benzene (Table 3, entry 1). M.p.: 114-116 °C. FT-IR (KBr)ν_{max} 3001, 2951, 1608, 1581, 1462, 1301, 1246, 1111, 1033, 813, 759 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04-7.08 (m, 12H), 6.85 (d, *J* = 16.7 Hz, 8H), 5.46 (s, 2H), 3.81 (s, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.39, 142.76, 137.02, 130.70, 129.56, 114.06, 113.94, 55.67, 55.30. MS (EI) m/z: 532.29 ([M+2]$^+$, 7.58), 531.26 ([M+1]$^+$, 28.79), 530.26 ([M]$^+$, 100), 423.20 (16.48), 303.14 (66.67), 227.19 (60.98), 152.10 (37.12), 121.18 (51.14), 77.17 (19.03). Anal. Calcd. for $C_{36}H_{34}O_4$: C, 81.48; H, 6.46. Found: C, 81.36; H, 6.45.

2-(Bis(2-methoxy-5-methylphenyl)methyl)naphthalene (Table 3, entry 3). M.p.: 137.5-139 °C. FT-IR (KBr)ν_{max} 3049, 2935, 1608, 1492, 1436, 1363, 1234, 1105, 1035, 804, 742 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84-7.86 (m, 1H), 7.78 (d, *J* = 8.78 Hz, 1H), 7.74-7.77 (m, 1H), 7.47 (d, *J* = 3.24 Hz, 1H), 7.45 (d, *J* = 3.26 Hz, 1H), 7.44 (s, 1H), 7.34 (dd, *J* = 7.4 Hz, *J* = 1.71 Hz, 1H), 7.07 (dd, *J* = 8.22 Hz, *J* = 1.96 Hz, 2H), 6.85 (d, *J* = 8.24 Hz, 2H), 6.71 (d, *J* = 2.08 Hz, 2H), 6.38 (s, 1H), 3.71 (s, 6H), 2.24 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.79, 142.41, 133.90, 132.66, 132.53, 131.40, 129.68, 129.14, 128.33, 128.08, 127.94, 127.79, 127.64, 125.94, 125.51, 111.39, 56.44, 43.61, 21.24. MS (EI) m/z: 384.15 ([M+2]$^+$, 9.55), 383.14 ([M+1]$^+$, 56.50), 382.04 ([M]$^+$, 97.56), 367.07 (47.97), 351.02 (81.30), 260.14 (33.33), 140.96 (100), 135.08 (60.98), 104.96 (73.98), 77.05 (17.99). Anal. Calcd. for $C_{27}H_{26}O_2$: C, 84.78; H, 6.85. Found: C, 84.31; H, 6.86.

4-Chloro-2-((5-chloro-2-methoxyphenyl)(phenyl) methyl)-1-methoxybenzene (Table 3, entry 4). M.p.: 138-140 °C. FT-IR (KBr)ν_{max} 3007, 2935, 1593, 1485, 1240, 1176, 1026, 887, 702, 644 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.31 (m, 2H), 7.23-7.27 (m, 1H), 7.21 (dd, *J* = 8.7 Hz, *J* = 2.61 Hz, 2H), 7.07 (d, *J* = 7.21 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 6.77 (d, *J* = 2.56 Hz, 2H), 6.10 (s, 1H), 3.71 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.21, 142.43, 134.29, 130.10, 129.62, 128.70, 127.77, 126.79, 125.73, 112.43, 56.39, 43.83. MS (EI) m/z: 375.94 ([M+4]$^+$, 4.76), 373.95 ([M+2]$^+$, 26.15), 371.95 ([M]$^+$, 38.30), 337.00 (33.03), 195.06 (15.83), 165.05 (16.51), 121.12 (23.85), 91.02 (100), 77.03 (12.44). Anal. Calcd. for $C_{21}H_{18}O_2Cl_2$: C, 67.57; H, 4.86. Found: C, 67.48; H, 4.85.

4-Chloro-2-((5-chloro-2-methoxyphenyl)(4-nitrophenyl) methyl)-1-methoxybenzene (Table 3, entry 5). M.p.: 168-170 °C. FT-IR (KBr)ν_{max} 3007, 2935, 1593, 1485, 1435, 1402, 1290, 1240, 1120, 1068, 1026, 887, 835, 794, 702, 644 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.56 Hz, 2H), 7.26 (dd, *J* = 8.68 Hz, *J* = 2.34 Hz, 2H), 7.23 (d, *J* = 8.57 Hz, 2H), 6.86 (d, *J* = 8.71 Hz, 2H), 6.72 (d, *J* = 2.28 Hz, 2H), 6.15 (s, 1H), 3.72 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.06, 150.83, 147.04, 132.34, 130.25, 129.99, 128.53, 125.96, 123.96, 112.51, 56.29, 44.03. MS (EI) m/z: 420.95 ([M+4]$^+$, 12.25), 418.96 ([M+2]$^+$, 68.42), 417.98 ([M+1]$^+$, 23.48), 416.95 ([M]$^+$, 100), 381.98 (90.28), 155.10 (93.93), 121.14 (78.95). Anal. Calcd. for $C_{21}H_{17}Cl_2NO_4$: C, 60.30; H, 4.10; N, 3.35. Found: C, 60.17; H, 4.12; N, 3.34.

RESULTS AND DISCUSSION

We initially optimized the reaction conditions in the reaction of veratrole **1** with 3-nitrobenzaldehyde **2b** as a model. As shown in Table 1, the reaction parameters such as the kind of solvent, reaction temperature, amount of catalyst, molar ratio of reagents and the power of ultrasonic irradiation were optimized. Previously, toxic solvents such as chloroform, dichloromethane and benzene have been used in the synthesis

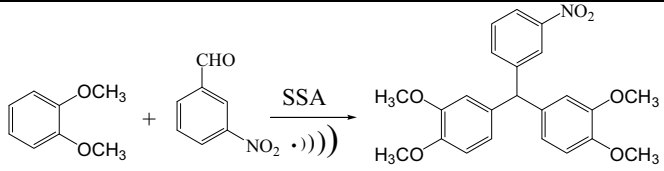
of TRAMs. To find a green and suitable solvent, the model reaction was triggered in several solvents and the best results were obtained in 3:1 mixture of *n*-hexane/ethyl acetate or cyclohexane/ethyl acetate (Table 1, entries 1-8).

Since, cyclohexane is greener than *n*-hexane [19], all reactions were allowed to take place in cyclohexane/ethyl acetate (3:1) mixture. To find the molar ratio of reactants, the model reaction was investigated with different molar ratios of veratrole and aldehyde (Table 1, entries 8-10). The reaction was completed with 3:1 molar ratio of veratrole to aldehyde. As illustrated in Table 1, the use of a lower amount of veratrole led to lower yields (Table 1, entry 10), while higher amount did not have considerable effect on the yield and reaction time (Table 1, entry 9).

The model reaction was explored with different amounts of SSA and the best results were obtained with 300 mg of SSA (Table 1, entries 8, 11 and 12). To confirm the catalytic role of SSA, the model reaction was repeated in the absence of the catalyst and no considerable improvement was observed (Table 1, entries 17). Further, the model reaction was studied in varied intensities of the ultrasound processor. The results showed that the reaction was completed at 80% of full power of US processor (Table 1, entries 8, 15 and 16).

The effect of the reaction temperature was also studied. As can be seen (Table 1, entries 8, 13 and 14), the 45 °C was chosen as the optimal reaction temperature. In order to show

Table 1. Optimization Conditions in the Synthesis of TRAMs under Ultrasound Irradiation



1 **2b** **3b**

Entry	SSA (mg)	Veratrole (mmol)	Aldehyde (mmol)	Solvent	Intensity (%)	T (°C)	Yield (%)[a]	Time (min)
1	300	3	1	$CHCl_3$	80	45	93	20
2	300	3	1	EtOH	80	45	20	30
3	300	3	1	EtOAc (EA)	80	45	20	30
4	300	3	1	CH_3CN	80	45	40	30
5	300	3	1	*n*-Hexane	80	45	88	25
6	300	3	1	Cyclohexane	80	45	88	25
7	300	3	1	*n*-Hexane/EA	80	45	95	20
8	300	3	1	Cyclohexane/EA	80	45	95	20
9	300	3.5	1	Cyclohexane/EA	80	45	95	20
10	300	2.5	1	Cyclohexane/EA	80	45	74	25
11	350	3	1	Cyclohexane/EA	80	45	95	20
12	250	3	1	Cyclohexane/EA	80	45	88	30
13	300	3	1	Cyclohexane/EA	80	60	95	20
14	300	3	1	Cyclohexane/EA	80	RT	66	30
15	300	3	1	Cyclohexane/EA	100	45	95	20
16	300	3	1	Cyclohexane/EA	60	45	83	30
17	-	3	1	Cyclohexane/EA	80	45	trace	60

[a]Isolated yield.

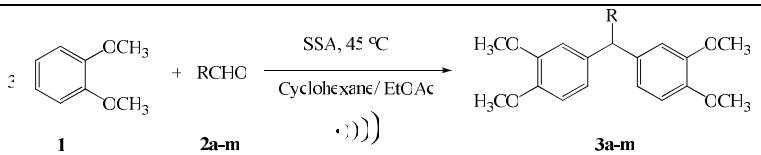
the efficiency of SSA, the model reaction was allowed to occur in the presence of sulfuric acid under similar experimental conditions (molar ratio and temperature); the corresponding triarylmethane **3b** was obtained in only 27% yield. In addition, SSA as a solid acid, in comparison with sulfuric acid, affords the advantages of easy separation, non-corrosiveness and low pollution effects.

To check the generality of this method, a wide range of aldehydes were treated with veratrole **1** and the corresponding TRAMs were synthesized in good to excellent yields in short reaction times.

As shown in Table 2, the nature of the substitutes on the aromatic aldehydes has a significant effect on the yields. Electron-withdrawing groups such as nitro, chloro, cyano and formyl increased the yields and diminished the reaction times (Table 2, entries 2-8), while electron-donating substituents such as hydroxy and methoxy groups behaved differently in the synthesis of TRAMs (Table 2, entries 10 and 11). In the reaction of 2-naphthaldehyde with veratrole, the corresponding TRAM was obtained in high yield (Table 2, entry 9). Aliphatic aldehydes such as butanal and 2-phenyl propionaldehyde were also converted to their corresponding diveratylmethanes in high yields under the same reaction conditions (Table 2, entries 12 and 13). However, when terephthalaldehyde **2g** was used under these conditions, only one aldehyde moiety reacted with veratrole. Therefore, this method can be used for the selective synthesis of mono-TRAM **3g** without the formation of *tetrakis*(veratryl) adduct **4** (Scheme 2).

In general, US has chemical and mechanical effects. The chemical effects of ultrasound do not derive from a direct coupling of the acoustic field with the chemical species on a molecular level. Rather, sonochemistry and sonoluminescence derive principally from acoustic cavitation: the formation, growth and implosive collapse of bubbles in liquids irradiated with high-intensity ultrasound. Bubble collapse during

Table 2. Ultrasound-Assisted Synthesis of Diveratrylmethanes in the Presence of SSA[a]

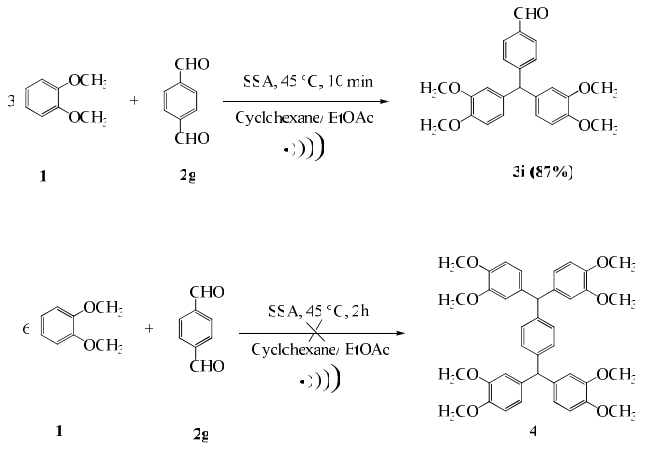


1 **2a-m** **3a-m**

R= Aryl or Alkyl

Entry	RCHO	Time (min)	Yield (%)[b]	product	M.p. (°C) [Ref.]
1	PhCHO (**2a**)	30	75 (23)[c]	**3a**	122-124 [16]
2	3-$NO_2C_6H_4CHO$ (**2b**)	20	95 (48)[c]	**3b**	154-155.5
3	4-$NO_2C_6H_4CHO$ (**2c**)	20	93	**3c**	116-118
4	4-ClC_6H_4CHO (**2d**)	25	90	**3d**	155-157 [16]
5	2,4-$Cl_2C_6H_3CHO$ (**2e**)	20	89	**3e**	151-152
6	4-NCC_6H_4CHO (**2f**)	30	88 (36)[c]	**3f**	115-116 [15]
7	4-$OHCC_6H_4CHO$ (**2g**)	9	87	**3g**	128-129 [15]
8	3-$CH_3OC_6H_4$ CHO (**2h**)	30	78	**3h**	120-122
9	2-Naphthaldehyde (**2i**)	30	93 (29)[c]	**3i**	133-135
10	4-HOC_6H_4CHO (**2j**)	60	Trace	**3j**	-
11	4-$CH_3OC_6H_4CHO$ (**2k**)	60	Trace	**3k**	-
12	*n*-PrCHO (**2l**)	20	89	**3l**	Oil
13	2-Phenylpropionaldehyde (**2m**)	20	90	**3m**	Oil

[a]Reaction conditions: veratrole (6 mmol), aldehyde (2 mmol), SSA (600 mg), cyclohexane/ethylacetate (3:1), T = 45 °C, intensity (80%). [b]Isolated yield. [c]Reaction was performed under thermal conditions and vigorous stirring.



Scheme 2

cavitation serves as an effective means of concentrating the diffuse energy of sound: compression of a gas generates heat. When the compression of bubbles occurs during cavitation, heating is more rapid than thermal transport, creating a short-lived localized hot spot. There is a nearly universal consensus that this hot spot is the source of homogeneous sonochemistry [20].

The mechanical effects of ultrasound offer an opportunity to overcome the following types of problems associated with the conventional solid/metal reactions: break-up of the surface structure allows penetration of reactants and/or release of materials from the surface, degradation of large solid particles due to shear forces induced by shock waves and microstreaming leads to the reduction of particle size and increase of surface area and accelerated motion of suspended particles leads to better mass transfer [21].

To verify the effect of ultrasound, some of these reactions were allowed to occur under thermal conditions and vigorous stirring. As can be seen in Table 2 (entries 1, 2, 6 and 9), the lower yields were obtained under the same reaction conditions. These results clearly indicate that the energy provided by ultrasound accelerates the reactions. Increasing the yields and reducing the reaction times may be a consequence of the specific effects of ultrasound. The observed effect on the reaction is due to cavitation, a physical process that creates, enlarges, and implodes gaseous and vaporous cavities in an irradiated liquid, thus enhancing the mass transfer [21,22] and allowing chemical reactions to occur.

The creation of the so-called hot spots in the reaction mixture produces intense local temperatures and high pressures generated inside the cavitation bubble and its interfaces when it collapses (the rise in the reaction temperature is an evidence of this). Since this system is a heterogeneous catalytic one, it seems that another part of US is due to its mechanical effect. On the other hand, US waves can break up the surface structure and facilitate the penetration of reactants and/or release of materials from the surface. The accelerated motion of the suspended particles enhances the mass transfer [21]. Another effect of ultrasonic irradiation on the catalytic activity enhancement may be due to the break-up of the agglomerates during the sonication process. To explore this point, the catalytic activity of a sonicated sample of SSA was studied in the reaction of veratrole **1** with 3-nitrobenzaldehyde **2b** under thermal conditions. It was found that the reaction yield increased from 48% to 67%. These results show that the break-up of the agglomerates and thorough mixing of the reactants are important factors in the acceleration of the reactions.

The effect of US intensity was also investigated in the reaction of veratrole with 3-nitrobenzaldehyde. The results showed that the highest yield was obtained at 80% intensity (Fig. 2).

In order to show the generality of the presented method,

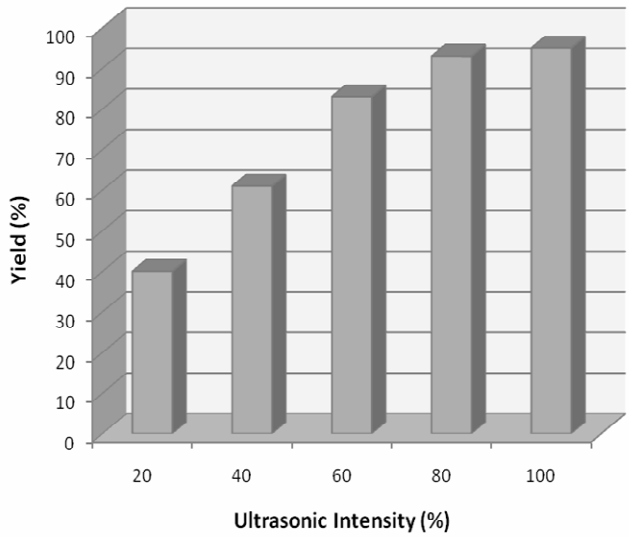


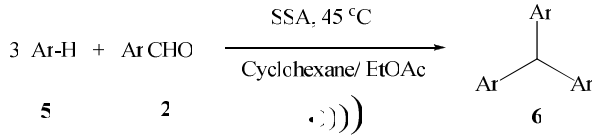
Fig. 2. The effect of US intensity on the synthesis of TRAMs.

different arenes such as anisole and its derivatives were allowed to react with different aldehydes under US irradiation. As shown in Table 3, the corresponding TRAMs were obtained in high yields and short reaction times.

CATALYST RECOVERY AND REUSE

In recent years, employing environmentally-friendly processes has attracted considerable attention in laboratories

Table 3. Ultrasound-Assisted Synthesis of TRAMs in Presence of SSA[a]



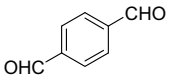
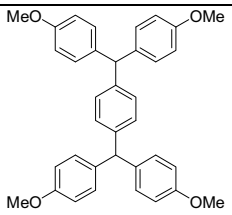
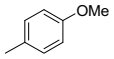
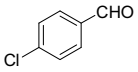
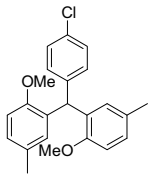
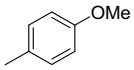
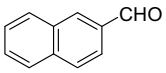
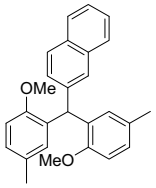
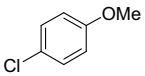
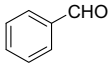
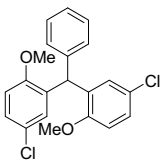
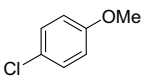
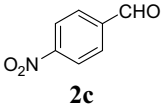
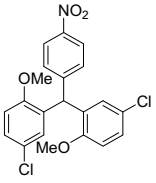
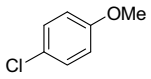
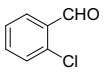
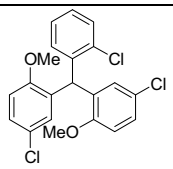
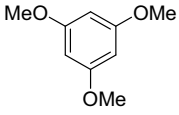
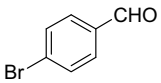
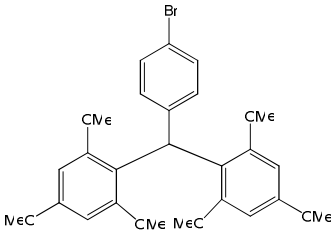
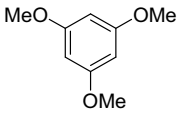
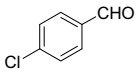
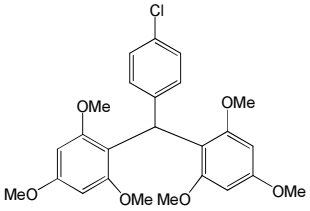
Entry	Ar-H	Ar'CHO	Product	Time (min)	Yield (%)[b]
1	 **5a**	 **2g**	 **6a**	120[c]	94
2	 **5b**	 **2d**	 **6b**	35	94
3	 **5b**	 **2i**	 **6c**	40	92
4	 **5c**	 **2a**	 **6d**	40	71
5	 **5c**	 **2c**	 **6e**	35	90

Table 3. Continued

6	 **5c**	 **2n**	 **6f**	40	88
7	 **5d**	 **2o**	 **6g**	15	94
8	 **5d**	 **2d**	 **6h**	15	93

[a]Rection conditions: arene (6 mmol), aldehyde (2 mmol), SSA (600 mg), cyclohexane/ethyl acetate (3:1), T = 45 °C, intensity (80%). [b]Isolated yield. [c]The reaction was carried out by 8 mmol anisol and 1 mmol terephthalaldehyde in the presence of 600 mg of SSA.

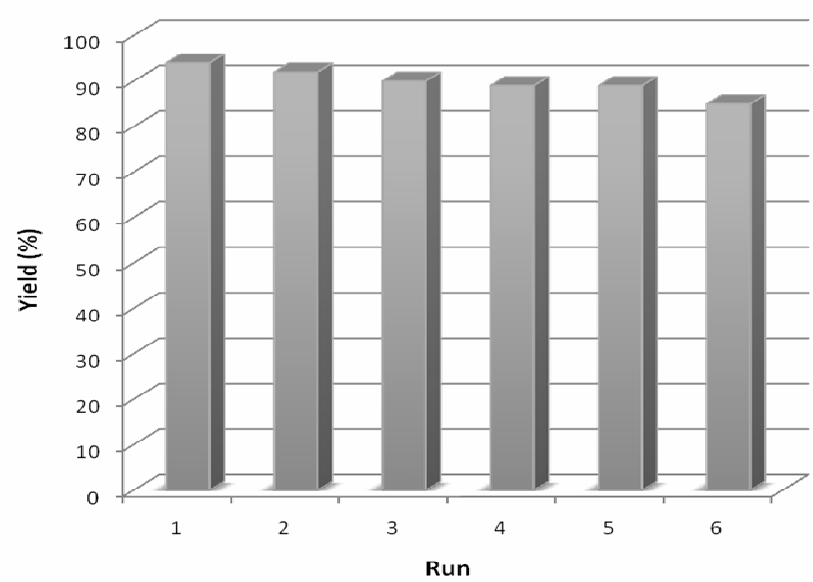


Fig. 3. Investigation of catalyst reusability in the synthesis of TRAMs.

and industrial chemistry. In fact, the reusability of a catalyst is one of the most important factors which determine its potential in commercial applications. So, we examined the reusability of SSA by the sequential reaction of veratrole **1** with 3-nitrobenzaldehyde **2b** (Table 2, entry 2). After completion of the reaction, the solvent was evaporated and absolute EtOH was added. The SSA catalyst was easily separated by simple filtration, washed with absolute EOH and dried at 70 °C and reused at least five successive times successfully (Fig. 3).

CONCLUSIONS

In conclusion, a novel, efficient and convenient method for the synthesis of triarylmethanes catalyzed by SSA under US irradiation is reported. It is noteworthy that the toxic solvents which were used in the previous methods have been successfully replaced with cyclohexane/ethyl acetate as green solvents. In addition, the use of a cheap and reusable catalyst, commercially available precursors, easy work-up, high yields and short reaction times are other advantages of this procedure which make it readily applicable for the preparation of triarylmethanes.

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