



Full paper/Mémoire

Facile and green synthesis of triarylmethanes using silica sulfuric acid as a reusable catalyst under solvent-free conditions

I. Mohammadpoor-Baltork^{a,*}, M. Moghadam^a, S. Tangestaninejad^a, V. Mirkhani^a,
K. Mohammadiannejad-Abbasabadi^a, M.A. Zolfigol^b

^a Catalysis Division, Department of Chemistry, University of Isfahan, Isfahan 81746-73441, Iran

^b Department of Chemistry, Bu-Ali Sina University, Hamadan 65175, Iran

ARTICLE INFO

Article history:

Received 2 November 2010

Accepted after revision 17 February 2011

Available online 8 September 2011

Keywords:

Triarylmethanes
Silica sulfuric acid
Reusable catalyst
Solvent-free
Veratrole

ABSTRACT

A facile and environmentally-benign protocol has been developed for the synthesis of triarylmethanes (TAMs) from the reaction of different arenes and aldehydes in the presence of silica sulfuric acid (SSA) as a heterogeneous and reusable catalyst under solvent-free conditions. Easy work-up, short reaction times, high yields, high selectivity, mild and green conditions are other salient features of this method.

© 2011 Académie des sciences. Published by Elsevier Masson SAS. All rights reserved.

1. Introduction

Triarylmethyl derivatives are an important class of organic compounds which have received considerable attention in recent years due to their wide range of activities and interesting properties [1–3]. Some TAM derivatives have been known to exhibit antioxidant properties, antitumor activity and inhibitory activity toward the histidine protein kinase [4]. These compounds have also been used as dyes [5,6] and as protecting groups for nucleosides and carbohydrates [3,7]. Due to their importance, considerable attention has been paid to develop efficient methods for the synthesis of TAMs.

Several synthetic methods such as Suzuki-Miyaura coupling of diarylmethyl carbonates with arylboronic acids in the presence of $[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_2\text{-DPPPEnt}$ (1,5-bis(diphenylphosphino) pentane) catalyst [8] and alkylation of arenes with aromatic aldehydes catalyzed by trifluoromethanesulfonic acid (TFSA) or TFSA-trifluoroac-

etic acid (TFA) [9], sulfuric acid [10], $[\text{Ir}(\text{COD})\text{Cl}]_2\text{-SnCl}_4$ [11], AuCl_3 or $\text{AuCl}_3/\text{AgOTf}$ [12], $\text{Cu}(\text{OTf})_2$ [13], FeCl_3 [14], $\text{Yb}(\text{OTf})_3$ [15] and $\text{AcBr}/\text{ZnBr}_2/\text{SiO}_2$ [16] have been developed for the preparation of TAMs. However, in spite of their potential utility, most of the reported methods require high reaction temperatures [8,11,14], long reaction times [8,9,12,14,15] and excess amounts of catalyst [9,10] for successful reactions. Further, the use of toxic organic solvents [9,10,12–14,16], a corrosive catalyst [10] and formation of a side product [9] limit the usefulness of some of these methods, especially in large scale operation and lead to serious environmental and safety problems. Another disadvantage of the existing methods is that the catalysts are destroyed during the work-up procedure and can not be recovered and reused [8–16]. Consequently, the design of simple, efficient and green approaches for the synthesis of TAMs is still in demand.

In recent years, the use of solid acid catalysts has gained considerable attention in a wide range of organic transformations [17–20]. The ease of separation, recovery and re-use render the processes employing solid acid catalysts as green and economically viable processes. Among several solid acid catalysts used in organic

* Corresponding author.

E-mail address: imbaltork@sci.ui.ac.ir (I. Mohammadpoor-Baltork).

reactions, silica sulfuric acid is one of the most attractive, because of its reusability, environmental compatibility, low cost, non-toxicity and operational simplicity. Due to these advantages, silica sulfuric acid has been used as an efficient catalyst in some important organic transformations [21–27]. This catalyst is prepared easily by the reaction of silica gel with chlorosulfonic acid [21].

In continuation of our interest towards development of useful synthetic methodologies [28–31], herein we wish to report a facile and environmentally-friendly method for the synthesis TAMs using silica sulfuric acid as a safe, inexpensive and reusable solid acid catalyst under solvent-free conditions (Scheme 1).

2. Experimental

Silica sulfuric acid (SSA) was prepared according to the literature [21]. The chemicals used in this work were purchased from Fluka and Merck chemical companies. The progress of reactions was monitored by TLC using 0.25 μm pre-coated silica gel plates. Melting points were determined using Stuart Scientific SMP2 apparatus and are uncorrected. ^1H and ^{13}C NMR (500 and 125 MHz) spectra were recorded on a Bruker-AC 500 spectrometer in CDCl_3 using TMS as internal standard. FT-IR spectra were obtained as KBr pellets using a Nicolet-Impact 400D instrument in the range of 400–4000 cm^{-1} . Elemental analysis was done on LECO, CHNS-932. Mass spectra were recorded on a Platform II spectrometer from Micromass; EI mode at 70 eV.

2.1. General procedure for the synthesis of diveratrylmethanes (DVMS) under solvent-free conditions

A mixture of veratrole **1** (402 mg, 3 mmol), aldehyde (1 mmol) and SSA (150 mg, 0.39 mmol) was heated at 65 °C for the appropriate time according to Table 2. The progress of the reaction was checked by TLC (n-hexane/ethyl acetate 10:4). After completion of the reaction, the mixture was cooled to room temperature and absolute EtOH (2 \times 5 mL) was added. The catalyst was filtered by simple filtration and the pure product was obtained by recrystallization from EtOH (In the case of liquid products, the crude material was purified by column chromatography on silica gel).

2.2. General procedure for the synthesis of TAMs under solvent-free conditions

A mixture of arene (3 mmol), aldehyde (1 mmol) and SSA (200 mg, 0.52 mmol) was heated at 65 °C for the time

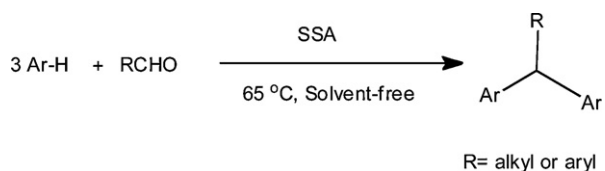
given in Table 3. After completion of the reaction as indicated by TLC (n-hexane/ethyl acetate 10:4), the reaction mixture was cooled to room temperature and absolute EtOH (2 \times 5 mL) was added. The catalyst was filtered by simple filtration and the crude product was purified by recrystallization from EtOH or EtOH/H₂O.

2.3. Physical and spectroscopic data

1,2-Dimethoxy-4-((3,4-dimethoxyphenyl)(phenyl)-methyl)benzene (Table 2, compound 3a). Mp 122–124 °C; IR (KBr): ν (cm^{-1}) 2999, 2960, 1589, 1512, 1463, 1448, 1340, 1265, 1224, 1138, 1074, 1026, 958, 871, 817, 744, 704. ^1H -NMR (500 MHz, CDCl_3): δ (ppm) 7.32 (2H, t, J = 7.6 Hz, 3,5-H phenyl), 7.22 (1H, t, J = 7.5 Hz, 4-H phenyl), 7.13 (2H, d, J = 7.4 Hz, 2,6-H phenyl), 6.79 (2H, d, J = 8.3 Hz, 5-H veratryl), 6.68 (2H, d, J = 1.7 Hz, 2-H veratryl), 6.51 (2H, dd, J = 8.2 Hz, J = 1.9 Hz, 6-H veratryl), 5.45 (1H, s, Ar_3CH), 3.86 (6H, s, OCH_3), 3.77 (6H, s, OCH_3). ^{13}C -NMR (125 MHz, CDCl_3): δ 148.85, 147.56, 144.36, 136.79, 129.30, 128.26, 126.27, 121.47, 112.94, 111.01, 55.96, 55.89, 55.85. MS (EI, 70 eV) (m/z , %): 365.16 ($[\text{M} + 1]^+$, 21.07), 364.16 (M^+ , 85.95), 333.14 (100), 287.16 (46.9), 227.15 (22.93), 165.08 (35.33), 143.18 (34.50), 115.02 (29.75), 77.00 (24.59). Anal. Calcd for $\text{C}_{23}\text{H}_{24}\text{O}_4$: C, 75.80; H, 6.64. Found: C, 75.37; H, 6.67.

1-(Bis(3,4-dimethoxyphenyl)methyl)-3-nitrobenzene (Table 2, compound 3b). Mp 154–155.5 °C; IR (KBr): ν (cm^{-1}) 3084, 3003, 2947, 1589, 1516, 1463, 1342, 1028, 916, 869, 736. ^1H -NMR (500 MHz, CDCl_3): δ (ppm) 8.05–8.08 (1H, m, 4-H 3-nitrophenyl), 8.00 (1H, s, 2-H 3-nitrophenyl), 7.44–7.46 (2H, m, 5,6-H 3-nitrophenyl), 6.81 (2H, d, J = 8.3 Hz, 5-H veratryl), 6.65 (2H, d, J = 2.0 Hz, 2-H veratryl), 6.57 (2H, dd, J = 8.3 Hz, J = 2.0 Hz, 6-H veratryl), 5.53 (1H, s, Ar_3CH), 3.86 (6H, s, OCH_3), 3.77 (6H, s, OCH_3). ^{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, 70 eV) (m/z , %): 410.12 ($[\text{M} + 1]^+$, 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 $\text{C}_{23}\text{H}_{23}\text{NO}_6$: C, 67.47; H, 5.66; N, 3.42. Found: C, 67.34; H, 5.64; N, 3.42.

4-((2-Chlorophenyl)(3,4-dimethoxyphenyl)methyl)-1,2-dimethoxybenzene (Table 2, compound 3c). Mp 136–137 °C; IR (KBr): ν (cm^{-1}) 3078, 2997, 2933, 1589, 1514, 1465, 1413, 1332, 1263, 1139, 1026, 960, 869, 763, 704, 642. ^1H -NMR (500 MHz, CDCl_3): δ (ppm) 7.38 (1H, dd, J = 5.3 Hz, J = 3.7 Hz, 3-H 2-chlorophenyl), 7.17 (1H, t, J = 3.5 Hz, 4-H 2-chlorophenyl), 7.16 (1H, t, J = 3.6 Hz, 5-H 2-chlorophenyl), 6.96 (1H, dd, J = 5.5 Hz, J = 3.1 Hz, 6-H 2-chlorophenyl), 6.78 (2H, d, J = 8.3 Hz, 5-H veratryl), 6.64 (2H, d, J = 1.9 Hz, 2-H veratryl), 6.54 (2H, dd, J = 8.3 Hz, J = 1.9 Hz, 6-H veratryl), 5.84 (1H, s, Ar_3CH), 3.86 (6H, s, OCH_3), 3.77 (6H, s, OCH_3). ^{13}C -NMR (125 MHz, CDCl_3): δ 148.93, 147.69, 142.01, 135.39, 134.54, 130.91, 129.65, 127.71, 126.55, 121.51, 113.03, 110.97, 55.86, 52.55. MS (EI, 70 eV) (m/z , %): 400.07 ($[\text{M} + 2]^+$, 44.57), 398.07 (M^+ , 76.71), 367.05 (77.12), 287.09 (59.72), 143.05 (100), 127.53 (54.09), 100.91 (32.58), 76.90 (12.69). Anal. Calcd for $\text{C}_{23}\text{H}_{23}\text{ClO}_4$: C, 69.26; H, 5.81. Found: C, 69.17; H, 5.78.



Scheme 1.

Download English Version:

<https://daneshyari.com/en/article/171241>

Download Persian Version:

<https://daneshyari.com/article/171241>

[Daneshyari.com](https://daneshyari.com)