Research Article

Rapid and Efficient Synthesis of Hydroxytriarylmethanes under Ultra Sonic Irradiation Using Keggin Heteropolyacids and Preyssler Catalysts in Green Conditions

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A new synthesis of hydroxytriarylmethane derived from the reaction of 2-sulfobenzoic anhydride and phenols in the presence of heteropolyacids as green, reusable, and efficient catalyst (using catalytic amount) under ultrasonic irradiation is reported in this paper.

1. Introduction

Triarylmethanes (TAMs) are highly colored materials and have been used as dyes and pigments for a very long time [1]. They have received much attention and have been widely used for many purposes such as for photochromic agents [2], protective groups [3], building blocks for dendrimers and NLOs [4, 5]. Some triarylmethanes have shown a wide range of pharmaceutical properties such as antioxidant, antiviral, and antitumor activities [6, 7].

Two basic methods to synthesize triarylmethanes (TAMs) are the Grignard reaction of various carbonyl compounds like benzophenone and methyl benzoate, and the aromatic electrophilic substitution reaction in acidic media [8, 9]. Symmetric triarylmethanes (TAMs) were prepared by the treatment of electrophilic reagents such as triethyl orthoformate or chloroform with arene nucleophiles [10, 11].

Recently, an efficient synthesis of unsymmetrical triarylmethanes has been reported by Friedel-Crafts reaction of aromatic nucleophiles with heteroarylcarbinols [12]. Werbel et al. have reported a facile method for the synthesizing of triarylmethane by the catalytic hydrogenation of the diaryl ketone and the subsequent treatment of the carbinol with aryl amines and HCl [13].

The selective condensation of oxophilic metal phenolates with an aromatic aldehyde at the ortho position of the starting phenol has been utilized in the synthesizing of a 2,2'-dihydroxy triphenylmethane, another TAM derivative [7].

Development of methods using heteropolyacids (HPAs) as catalysts for fine organic synthetic processes related to fine chemicals, such as flavors, pharmaceuticals, and food industries have been under attention in the last decade. The catalysts based on HPAs have many advantages over liquid acid catalysts. They are not corrosive and environmentally benign, presenting fewer disposal problems. Solid HPAs have attracted much attention in organic synthesizing owing to easy workup procedures, easy filtration, and minimization of cost and waste generation because of reusing and recycling of the catalysts [14, 15].

Newly some books and papers have been published which show that the synthesizing of compounds has been accelerated by ultrasound irradiation. In comparison with the traditional methods, this method is more convenient and easier to work up [16, 17].

Herein, we report a simple method for synthesizing of hydroxytriarylmethane derivatives from reaction of 2-sulfobenzoic anhydride with phenols in the presence of catalytic amounts of $H_{14}[NaP_5W_{30}O_{110}]$, $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$, under ultrasonic irradiation (Scheme 1).

SCHEME 1: Synthesis of hydroxytriarylmethane derivatives.

2. Experimental

2.1. Chemicals and Apparatus. All the chemicals were obtained from Merck, Fluka, and Aldrich Companies and were used without further purification. Melting points were measured using Thermo-Fisher Scientific. IR spectra were recorded by Bruker tensor 27, FT-IR Spectrophotometer. All ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400 MHz Spectrophotometer. Chemical shifts are reported in parts per million (ppm), using tetra methyl silane (TMS) as an internal standard. The microanalyses for C and H were performed on Perkin-Elmer elemental analyzer. The ultrasonic apparatus was the cleaning bath Wiseclear 770 W (Seoul, Korea). The operating frequency was 40 kHz and the output power was 200 W, estimated calorimetrically. The reaction flasks were located in the maximum energy area in the water bath, where the surface of reactants (reaction vessel) was slightly lower than the surface level of the water, and the addition or removal of water which controlled the temperature of the water bath. The temperature of the water bath was controlled at 55–65°C. Silica-supported Preyssler nanoparticles were prepared according to [18].

2.2. General Procedure. A mixture of 2-sulfobenzoyl anhydride (20 mmol), phenol derivatives (60 mmol), and catalytic amount of heteropolyacid (0.03 mmol) in 10 mL CH₃CN was irradiated under ultrasound at 55–65°C for required reaction time. The progress of the reaction was monitored by TLC. When the reaction was completed, the catalyst was

filtered off, the solvent was evaporated under vacuum, and the product was poured into 100 mL NaOH 10%. Then, the solution was acidified by HCl. The precipitate was collected under filtration. All products were identified by their physical and spectroscopic data (Tables 1 and 2).

2.3. Recycling of the Catalyst. After filtration of the catalyst, it could be recycled, washing it with diethylether in each case. The recovered catalyst could be dried and reused for the next reaction with only a modest loss in activity. The catalyst has been recovered and reused for six times in reactions. The obtained results are summarized in Table 3.

3. Results and Discussions

The progress of reaction 2-sulfobenzoyl anhydride with phenols was monitored by TLC and reported yields were based on isolated products. The results showed that the highest yield of the products was achieved when H₁₄[NaP₅W₃₀O₁₁₀] was used as the catalyst.

Comparison of the catalysts in Tables 4 and 5 showed that H₁₄[NaP₅W₃₀O₁₁₀] is the catalyst of choice. Comparison of supported and nonsupported Preyssler catalyst showed that, in all cases, the supported Preyssler catalyst was less active than the nonsupported one. One plausible interpretation of this observation is that, in supported type, there are polyanion-support interactions of an acid-base nature. Some protons of the polyacid and some basic sites of the support (e.g., hydroxyl groups) can interact. This would lead to diminished availability of hydrogens because of this extra ionic

TABLE 1: Physical and spectral data of the compounds (a–f).

Entry	Product	Structure	^1H NMR (DMSO, ppm)	IR (ν , cm^{-1})	% Analysis Calc (Found)	m.p. ($^{\circ}\text{C}$)
1	a		6.33–8.06 (m, 14H, OH, SO ₃ H, Ar–H)	3441, 1662, 1676	C: 64.40 (64.22), H: 3.95 (4.09)	296–297
2	b		2.09 (s, 3H, CH ₃), 2.48 (s, 3H, CH ₃), 6.07–8.10 (m, 12H, OH, SO ₃ H, Ar–H)	3433, 1667, 1671	C: 65.97 (66.28), H: 4.71 (5.01)	—
3	c		1.90 (s, 3H, CH ₃), 2.34 (s, 3H, CH ₃), 5.92–8.13 (m, 12H, OH, SO ₃ H, Ar–H)	3438, 1666, 1678	C: 65.97 (65.75), H: 4.71 (4.96)	247–248
4	d		6.25–7.98 (m, 12H, OH, SO ₃ H, Ar–H)	3427, 1665, 1677	C: 44.53 (44.78), H: 2.34 (2.59)	225–227
5	e		6.29–8.11 (m, 12H, OH, SO ₃ H, Ar–H)	3421, 1668, 1680	C: 53.90 (54.22), H: 2.84 (3.09)	256–258
6	f		6.37–8.01 (m, 10H, OH, SO ₃ H, Ar–H)	3425, 1664, 1678	C: 34.03 (33.81), H: 1.49 (1.29)	266–269 (decom)

interaction [19]. Interestingly, this behavior is similar to that of Keggin heteropolyacids. However, when $\text{H}_3[\text{PW}_{12}\text{O}_{40}]$ or $\text{H}_4[\text{SiW}_{12}\text{O}_{40}]$ were used instead of $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ the yield of product was slightly decreased.

The results point out that the catalytic effectiveness may be enhanced as the number of tungsten atoms (or the number of protons) is increased. Both possibilities stand to reason. In addition, the large anion also provides many “sites” on

TABLE 2: ^{13}C NMR data of the compounds (a–f).

Entry	Product	^{13}C NMR (ppm)
1	a	100.2, 117.4, 120.7, 123.9, 125.7, 126.1, 126.8, 131.5, 135.1, 136.6, 145.8, 148.2, 155.9, 158.1, 183.4
2	b	20.4, 21.6, 98.61, 99.5, 120.2, 120.4, 124.6, 126.0, 127.1, 127.4, 127.8, 129.6, 130.7, 133.8, 134.9, 137.4, 146.1, 152.0, 154.3, 155.2, 181.9
3	c	14.2, 17.5, 93.2, 100.2, 118.9, 120.6, 121.1, 124.7, 126.7, 127.5, 127.7, 127.9, 128.7, 129.9, 134.2, 136.1, 145.3, 147.1, 156.8, 157.3, 179.5
4	d	80.1, 96.3, 110.0, 115.9, 124.3, 124.6, 125.9, 126.9, 127.5, 127.6, 127.9, 131.0, 134.5, 137.7, 144.5, 150.0, 150.7, 161.1, 173.9
5	e	83.2, 98.8, 119.4, 122.2, 123.1, 124.8, 126.1, 126.9, 127.4, 127.5, 127.8, 130.5, 132.0, 134.1, 145.9, 150.0, 154.3, 155.6, 175.3
6	f	78.9, 115.9, 120.0, 123.9, 127.4, 127.6, 128.4, 129.0, 135.6, 141.1, 147.7, 148.2, 156.0, 170.1, 173.3

TABLE 3: Recyclability of $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$.

Entry	Phenol	Yield (%) ^a /Run					
		1	2	3	4	5	6
1	phenol	95	93	90	88	86	84
2	<i>m</i> -cresol	96	93	91	88	86	85
3	<i>o</i> -cresol	95	92	91	89	87	84
4	2-bromophenol	93	90	87	86	84	82
5	2-Chlorophenol	94	91	90	88	85	83
6	2,6-dibromophenol	94	92	89	87	86	85

^a Isolated yields.TABLE 4: The reaction of *o*-cresol and 2-sulfobenzoeic anhydride in the presence of different catalyst at 140 °C (time of reaction 60 min).

Entry	Catalyst	Yield ^a (%)
1	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	65
2	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	68
3	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	72
4	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]/\text{SiO}_2$	35
5	H_2SO_4	58
6	ZnCl_2	44

^a Isolated yield.TABLE 5: The reaction of *o*-cresol and 2-sulfobenzoeic anhydride in the presence of different catalysts at 55–65 °C under ultrasonic irradiation (time of reaction 15 min).

Entry	Catalyst	Yield ^a (%)
1	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	87
2	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	90
3	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	95
4	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]/\text{SiO}_2$	26
5	H_2SO_4	31
6	ZnCl_2	12

^a Isolated yield.

the oval-shaped molecule that are likely to render the catalyst effectiveness. Interestingly, the comparison of Preyssler heteropolyacid, with its exclusive properties, with Keggin heteropolyacids, ZnCl_2 , and H_2SO_4 showed that the activity

TABLE 6: Comparison of efficiency of $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{H}_3\text{PW}_{12}\text{O}_{40}$, and $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ in synthesis of hydroxytriarylmethane derivatives under ultrasonic irradiation.

Entry	Phenol	Catalyst	Yield (%) ^a
1	phenol	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	86
2	phenol	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	90
3	phenol	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	91
4	<i>m</i> -cresol	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	88
5	<i>m</i> -cresol	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	90
6	<i>m</i> -cresol	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	94
7	<i>o</i> -cresol	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	87
8	<i>o</i> -cresol	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	90
9	<i>o</i> -cresol	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	95
10	2-bromophenol	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	85
11	2-bromophenol	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	91
12	2-bromophenol	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	94
13	2-chlorophenol	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	83
14	2-chlorophenol	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	88
15	2-chlorophenol	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	92
16	2,6-dibromophenol	$\text{H}_4\text{SiW}_{12}\text{O}_{40}$	84
17	2,6-dibromophenol	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	86
18	2,6-dibromophenol	$\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$	90

^a Isolated yield.TABLE 7: Synthesis of hydroxytriarylmethane derivatives using $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ under ultra sonic irradiation.

Entry	Phenol	Time (min)	Yield (%) ^a
1	phenol	20	91
2	<i>m</i> -cresol	20	94
3	<i>o</i> -cresol	15	95
4	2-bromophenol	25	94
5	2-chlorophenol	30	92
6	2,6-dibromophenol	40	90

^a Isolated yield.

for $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ is the most. The comparison of efficiency of heteropolyacids has been carried out. The results are shown in Table 6. It is clear that $\text{H}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ gave the better yields than others. The catalytic activity is increased

TABLE 8: Synthesis of hydroxytriarylmethane derivatives using $H_{14}[NaP_5W_{30}O_{110}]$ under heating condition.

Entry	Phenol	Time (min)	Yield (%) ^a
1	phenol	90	69
2	<i>m</i> -cresol	75	61
3	<i>o</i> -cresol	60	72
4	2-bromophenol	120	63
5	2-chlorophenol	120	58
6	2,6-dibromophenol	150	54

^a Isolated yield.

in the following order: $H_{14}[NaP_5W_{30}O_{110}] > H_3[PW_{12}O_{40}] > H_4[SiW_{12}O_{40}]$.

Phenols with electron withdrawing groups gave hydroxytriarylmethane derivative in low yields. To show the merit of this method, reaction has been performed using the same catalyst repeatedly under classical heating condition. As it is shown under heating condition the higher reaction time is required. The results are shown in Tables 7 and 8.

As ultrasound generated intense turbulence and microscale liquid circulation currents, uniform mixing at microlevel has occurred and the mass transfer resistances have been eliminated [20]. This explanation can justify the shorter reaction time observed for reactions under ultrasonic condition.

This catalyst retained its activity over six consecutive runs (Table 3).

4. Conclusion

We developed a new method using heteropolyacids under ultrasonic irradiation for synthesis of hydroxytriarylmethanes. The short reaction times, high yields, reusability of catalyst, and easy work up procedure are some advantages of this method.

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