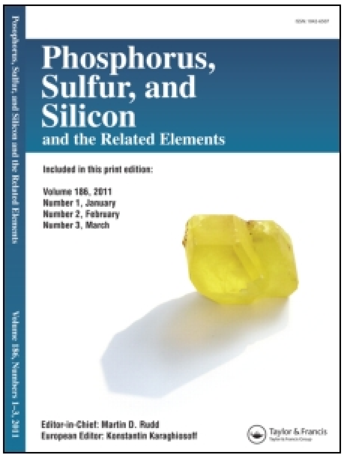

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Magnesium Hydrogensulfate [$Mg(HSO_4)_2$] as an Efficient Catalyst for the Preparation of Silyl Ethers, Dibenzo[a,j]xanthenes, and Octahydroxanthene Derivatives

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MAGNESIUM HYDROGENSULFATE [$Mg(HSO_4)_2$] AS AN EFFICIENT CATALYST FOR THE PREPARATION OF SILYL ETHERS, DIBENZO[a,j]XANTHENES, AND OCTAHYDROXANTHENE DERIVATIVES

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Magnesium hydrogensulfate [$Mg(HSO_4)_2$], as a heterogeneous solid acid catalyst, has been used for the mild formation of trimethylsilyl (TMS) ethers from various primary, secondary, and tertiary aliphatic alcohols; aromatic alcohols; and oximes using hexamethyldisilazane (HMDS) under ambient conditions. In addition, 14-aryl-14*H*-dibenzo[a,j]xanthenes and 1,8-dioxo-octahydroxanthene derivatives were synthesized in the presence of $Mg(HSO_4)_2$ with short reaction times in high to excellent yield under solvent-free conditions.

Keywords Dibenzo[a,j]xanthene; 1,8-dioxo-octahydroxanthene; heterogeneous catalyst; hexamethyldisilazane; $Mg(HSO_4)_2$; trimethylsilyl ether

INTRODUCTION

One of the most important objectives in chemistry now is to adapt classical processes so that pollution effects are kept to a minimum, with both a reduction in energy and consumption of raw materials.[1] In this respect, heterogeneous systems are promising, and a new approach has been undertaken using solid acid chemistry. Heterogeneous systems have many advantages, such as simple experimental procedures, mild reaction conditions, and minimal chemical waste, when compared to analogous liquid-phase reactions.[2] Solid acid catalysts are easier to handle because they hold the acidity internally and are easily separated from products by simple filtration. Moreover, constraining a reaction to the surface of a solid habitually allows one to apply milder conditions. So far, a number of solid acid–catalyzed reactions have been reported.[1–3]

Inorganic solid acidic salts, such as metal hydrogensulfates or solid acids, play a prominent role in organic synthesis under heterogeneous conditions. In order to promote environmental safety and due to their safe and ecofriendly nature, the importance of these

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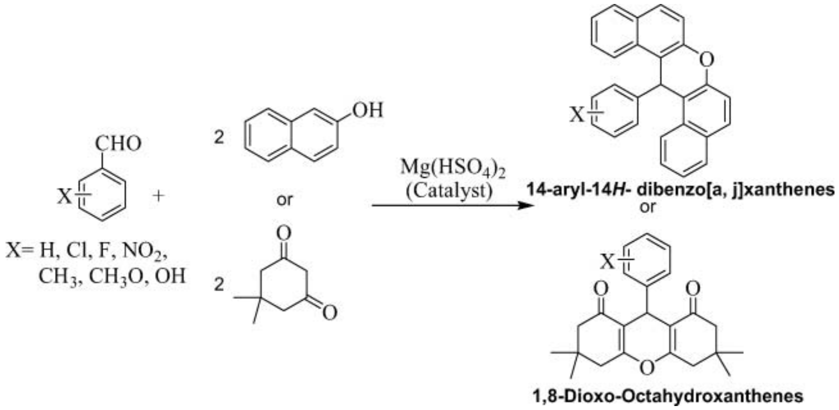
solid acid catalysts is growing as attention is directed toward the development of clean and green technologies for important organic molecules.[3]

In this article, we show that magnesium hydrogensulfate, as a solid heterogeneous acid catalyst, can be used for the efficient synthesis of silyl ethers under ambient conditions (Scheme 1).

$$ROH + (CH_3)_3SiNHSi(CH_3)_3 \xrightarrow[CH_3CN,\ r.t.]{\substack{Mg(HSO_4)_2\\(Catalyst)}} ROSi(CH_3)_3 + NH_3$$

Scheme 1 Preparation of silyl ethers.

In addition, 14-aryl-14*H*-dibenzo[a,j]xanthenes and 1,8-dioxo-octahydroxanthene derivatives were synthesized in the presence of the mentioned catalyst (Scheme 2) with short reaction times in high to excellent yield. This catalyst is safe, easy to handle, environmentally benign, presents fewer disposal problems, and is stable in reaction media.[4]



Scheme 2 Preparation of 14-aryl-14*H*-dibenzo[a,j]xanthene and 1,8-dioxo-octahydroxanthene derivatives.

RESULTS AND DISCUSSION

Preparation of Silyl Ethers

Silyl ethers are a group of chemical compounds that contain a silicon atom covalently bonded to an alkoxy group and are usually used as protecting groups for alcohols in organic synthesis. One of the silyl ethers is trimethylsilyl (TMS) ether. This group of chemical compounds provides a wide spectrum of selectivity for protecting group chemistry. This group is particularly useful because it can be introduced and removed very selectively under mild conditions.[5]

Although many methods are available for forming trimethylsilyl ethers, there are two common strategies: reaction of the alcohol with a silyl chloride and an amine base and reaction of the alcohol with a 1,1,1,3,3,3-hexamethyldisilazane (HMDS) with a Lewis

Table I Preparation of benzyl trimethylsilyl ether using $Mg(HSO_4)_2$ (0.05 g) as catalyst under solvent and solvent-free conditions at room temperature

Entry	Solvent	Time (min)	GC yield (%)	Yield (%)[a]
1	Dichloromethane	91	100	83
2	Chloroform	120	100	85
3	Ethyl acetate	200	100	81
4	n-Hexane	105	100	89
5	Solvent-free	115	100	87
6	Diethyl ether	191	100	83
7	Acetonitrile	3	100	93

[a] Isolated yield, and the product gave satisfactory IR and NMR spectra.

or Brønsted acid catalyst. HMDS is a stable, commercially available, cheap reagent and gives ammonia as the only byproduct. In addition, silylation with HMDS is nearly neutral and does not need special precautions. The low silylation power of HMDS is the main drawback to its application. Therefore, there are varieties of catalysts for activating this reagent.[5] Now we show that magnesium hydrogensulfate can be added to this library collection. This catalyst can be used for the efficient synthesis of silyl ethers under ambient conditions.

To optimize the reaction conditions, initially we converted benzyl alcohol (1mmol) to its corresponding benzylsilylether with a predetermined amount of $Mg(HSO_4)_2$ (0.05 g, 0.23 mmol) as catalyst and HMDS (0.75 mmol) in the presence of various solvents and also solvent-free conditions at room temperature (Table I). The results in Table I show that among these solvents, acetonitrile was the solvent of choice in terms of reaction time.

To find out the optimum quantity of the catalyst, the reaction of benzyl alcohol (1 mmol) with HMDS (0.75 mmol) was carried out using different quantities of $Mg(HSO_4)_2$ under ambient conditions in acetonitrile as solvent (Table II). As can be seen from Table II, the best results were obtained by using 0.05 g of the catalyst.

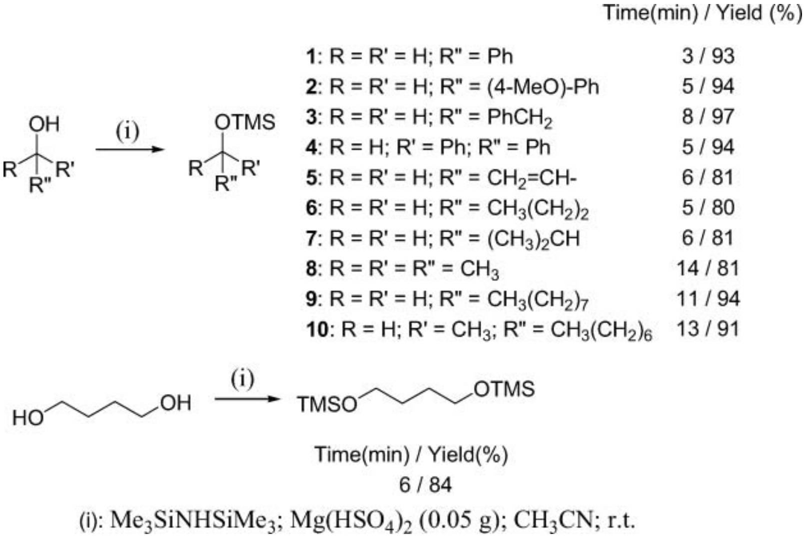
Thus, we prepared a range of silyl ethers under the optimized reaction conditions: hydroxyl compound (1 equiv), HMDS (0.75 equiv), $Mg(HSO_4)_2$ (0.05 g, 0.23 mmol), and acetonitrile (2 mL) (Schemes 3–8).

A wide range of structurally diverse and functionalized phenols, alcohols, and oximes underwent silylation by this procedure to provide the corresponding TMS ethers in high to excellent isolated yields (Schemes 3–8). Primary alcohols mostly reacted faster than secondary and tertiary alcohols. Generally, in the all cases of benzyl and primary, secondary, and tertiary alcohols, the reactions were completed in less than 20 min at ambient conditions accompanied by evolution of NH_3 gas from the reaction mixture (Schemes 3–6).

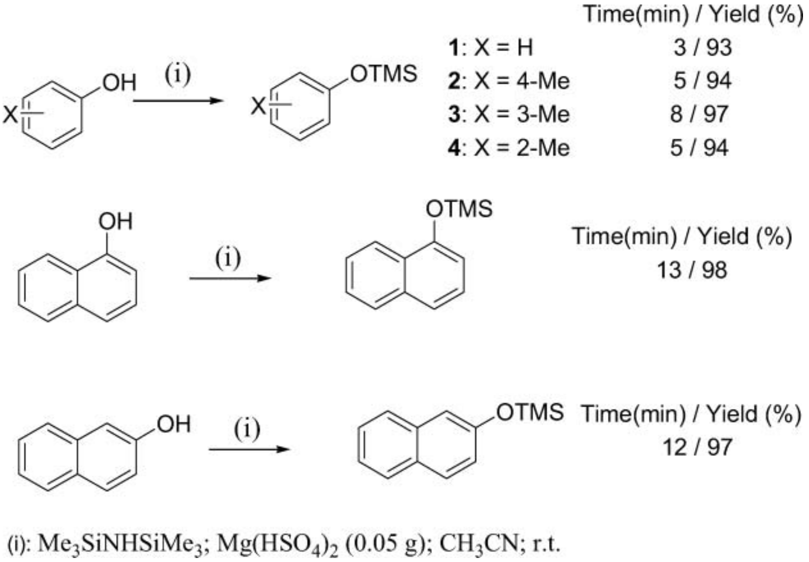
Amines remained unaffected under the reaction conditions (Scheme 7).

Table II Optimization of catalyst in the synthesis of benzyl trimethylsilyl ether in acetonitrile as solvent

Entry	Catalyst (g)	Time (min)	Isolated yield (%)
1	0.05	3	93
2	0.025	18	91
3	0.0125	25	89



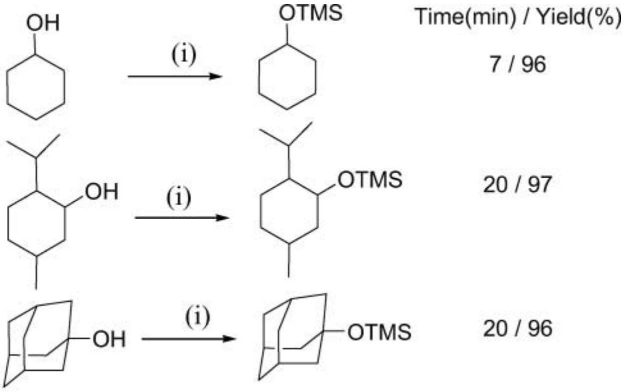
Scheme 3



Scheme 4

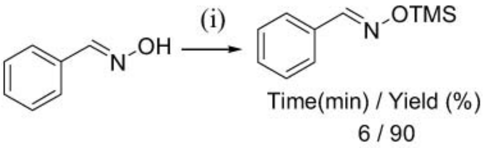
In order to examine the functional group compatibility, we tested some more alcohols having other functional groups such as carbonyl group, amino group, alkene, and ethers. Alcohols were successfully converted to the corresponding silyl ethers, whereas other functional groups were intact (Scheme 3, entry 5; Schemes 7 and 8).

We also investigated selective silylation of different binary mixtures of alcohols (Table III). This method was shown to be highly selective for primary alcohols such as benzyl alcohols compare to secondary and tertiary alcohols (Table III, entries 1–3). The



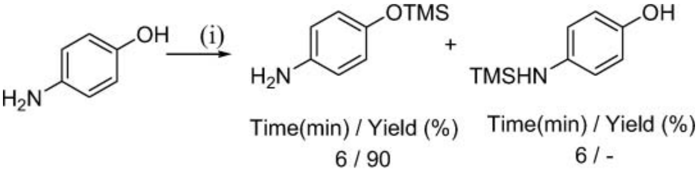
(i): $Me_3SiNHSiMe_3$; $Mg(HSO_4)_2$ (0.05 g); CH_3CN; r.t.

Scheme 5



(i): $Me_3SiNHSiMe_3$; $Mg(HSO_4)_2$ (0.05 g); CH_3CN; r.t.

Scheme 6



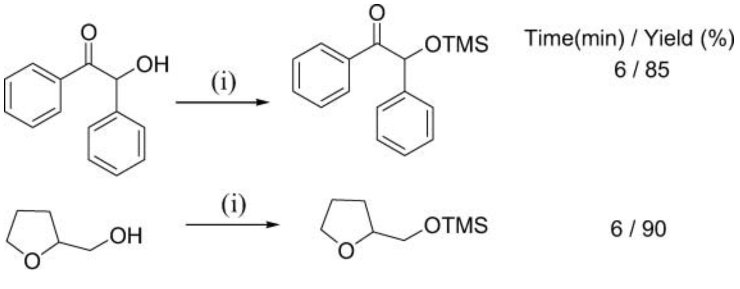
(i): $Me_3SiNHSiMe_3$; $Mg(HSO_4)_2$ (0.05 g); CH_3CN; r.t.

Scheme 7

primary alcohols were completely converted to the corresponding silyl ethers, while the secondary and tertiary alcohols were converted to the corresponding silylated product with 0–15% yield. It is noteworthy that this method can be used for chemoselective silylation of primary alcohols in the presence of secondary and tertiary alcohols.

Preparation of 14-Aryl-14*H*-dibenzo[a,j]xanthene and 1,8-Dioxo-octahydroxanthene Derivatives

Derivatives of xanthene are commonly referred to collectively as xanthenes, and among these are benzoxanthenes[6] and octahydroxanthene[7] derivatives. This group of chemical compounds provides a wide spectrum of selectivity for the basis of a class of dyes and biological and therapeutic properties.[6a–e] Many methods are available for forming



(i): $Me_3SiNHSiMe_3$; $Mg(HSO_4)_2$ (0.05 g); CH_3CN; r.t.

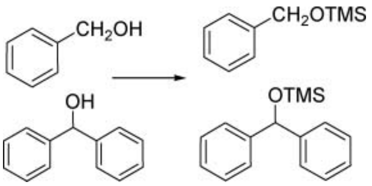
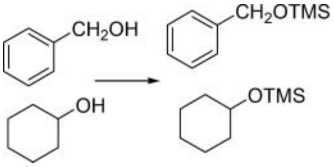
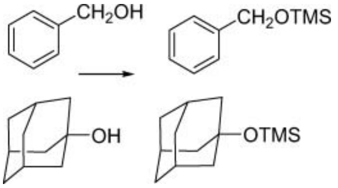
Scheme 8

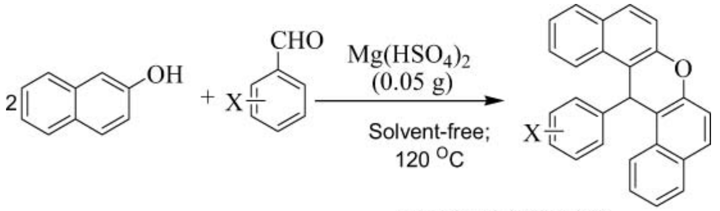
benzoxanthenes, and there are two common strategies: i) dehydration of bis(2-hydroxy-1-naphthyl) methane using $POCl_3$ or by boiling acetic acid diester of bis(2-hydroxy-1-naphthyl) methane[6f–g] and ii) condensation of β-naphthol with aliphatic and aromatic aldehydes in the presence Lewis or Brønsted acid catalyst.[6h–o]

In our research, we tried to prepare a range of 14-aryl-14*H*-dibenzo[a,j]xanthene (Scheme 9) and 1,8-dioxo-octahydroxanthene derivatives (Scheme 10) using $Mg(HSO_4)_2$ as a Brønsted acid catalyst.

In order to carry out the condensation in a more efficient way by minimizing the time, temperature, and amount of catalyst, the reaction of benzaldehyde and 2-naphthol

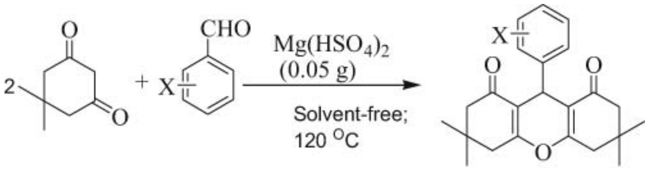
Table III Selective silylation of different binary mixture of alcohols

Entry	Substrate / Product Binary mixture	Molar Ratio Substrate 1/Substrate 2/HMDS/Catalyst (g)	Time (min)	GC yield (%)
1		1/1/0.75/0.05	5	100 4
2		1/1/0.75/0.05	5	100 15
3		1/1/0.75/0.05	5	100 0



	Time (min) / Yield (%)
1: X = H	4 / 95
2: X = 3-NO_2	2 / 96
3: X = 4-NO_2	3 / 94
4: X = 2,4-Dichloro	3 / 90
5: X = 4-Cl	2 / 91
6: X = 4-OMe	60 / 85
7: X = 4-F	4 / 87
8: X = 2-Me	4 / 81
9: X = 2-Cl	3 / 85
10: X = 4-OH	4 / 80
11: X = 4-Me	3 / 89

Scheme 9



	Time (min) / Yield (%)
1: X = H	1 / 90
2: X = 3-NO_2	2 / 93
3: X = 4-NO_2	0.5 / 89
4: X = 2,4-Dichloro	1 / 93
5: X = 4-Cl	2 / 92
6: X = 4-OMe	0.5 / 88
7: X = 4-F	0.5 / 85
8: X = 2-Me	2 / 87
9: X = 2-Cl	2 / 81
10: X = 4-OH	1 / 83
11: X = 4-Me	4 / 85

Scheme 10

(1:2 molar ratio) was selected as model to investigate the effects of the catalyst at different reaction temperatures (50, 100, 120, and 150°C) and different amounts of catalyst (0.1, 0.05, 0.025, and 0.01 g), The best result was obtained by carrying out the reaction using 0.05 g of $Mg(HSO_4)_2$ (0.23 mmol) at 120°C under thermal solvent-free conditions.

Using these optimized reaction conditions, the scope and efficiency of these procedures were explored for the synthesis of a wide variety of substituted 14-aryl-14*H*-dibenzo[a,j]xanthene and 1,8-dioxo-octahydroxanthene derivatives. The results are summarized in Schemes 9 and 10.

The process tolerates aromatic aldehydes containing both electron-donating and electron-withdrawing substituents. It can be observed that all the aldehydes have reacted in short reaction times under thermal solvent-free conditions to afford the desired xanthenes in high isolated yields (Scheme 9 and 10).

CONCLUSION

In conclusion, $Mg(HSO_4)_2$ showed an efficient catalytic activity for the preparation of silyl ethers, 14-aryl-14*H*-dibenzo[a,j]xanthenes, and 1,8-dioxo-octahydroxanthene derivatives. Simple procedures, easy workup, low cost, ease of preparation, high efficiency, and eco-friendliness of the catalyst are some advantages of this method.

EXPERIMENTAL

All reagents were purchased from Merck and Aldrich and were used without further purification. $Mg(HSO_4)_2$ was prepared according to the reported procedure.[4] All yields refer to isolated products after purification. Products were characterized by comparison with authentic samples and by spectroscopy data (IR, ^1H NMR spectra). The NMR spectra were recorded on a Bruker Avance DPX 300 and 500 MHz instrument. The spectra were measured in $CDCl_3$ relative to TMS (0.00 ppm). GC analysis was run with Shimadzu GC-14A. IR spectra were recorded on a Jasco FT-IR 460plus spectrophotometer. TLC was performed on silica-gel polygram SIL G/UV 254 plates.

General Procedure for the Trimethylsilylation of Hydroxyl Compounds

To a stirred solution of alcohols or oximes (1 mmol), HMDS (0.75 mmol) and acetonitrile as solvent (2 mL), $Mg(HSO_4)_2$ (0.05 g, 0.23 mmol) was added at room temperature, and the mixture was stirred for the appropriate time (Schemes 3–8). The reaction was followed by TLC (*n*-hexane:EtOAc, 9:1). After completion of the reaction, the solvent was evaporated. Then *n*-hexane was added, and the catalyst was easily isolated by simple filtration. The resulting mixture was adsorbed on silica gel, passed through a short pad column of silica gel, and washed with *n*-hexane (2 × 10 mL). Evaporation of the solvent under reduced pressure gave pure product(s) (Schemes 3–8). The desired pure product(s) was characterized by comparison of its physical data with those of known compounds.[5] The isolated catalyst was washed several times with *n*-hexane, dried, and reused. The recovered catalyst was reused three times subsequently for the same reaction without any loss in activity (Scheme 3, entry 1).

General Procedure for Preparation of 14*H*-Dibenzo[a,j]xanthene Derivatives

To a mixture of aldehyde (1 mmol) and β-naphthol (2 mmol), magnesium hydrogensulfate (0.05 g, 0.23 mmol) was added, and the mixture was inserted in an oil bath and heated for 120°C for the appropriate time (Scheme 9). Completion of the reaction was indicated by TLC. After the reaction was completed, ethyl acetate was added and the reaction mixture was stirred until solid crude product was dissolved. Then, the heterogeneous catalyst was isolated from the mixture of the reaction by simple filtration. In continuation of workup, the filtrate organic solution was evaporated. The crude product was recrystallized using aqueous ethanol 15% twice. The desired pure product(s) were characterized by comparison of their physical data with those of known benzoxanthenes.[6]

General Procedure for Preparation of 1,8-Dioxo-octahydroxanthene Derivatives

To a mixture of aryl aldehyde (1 mmol) and dimedone (2 mmol), $Mg(HSO_4)_2$ (0.05 g, 0.23 mmol) was added, and the mixture was heated at 125°C for the appropriate time (Scheme 10). Completion of the reaction was indicated by TLC. After completion, the reaction mass was cooled to 25°C, then ethyl acetate was added until the solid crude product was dissolved. Then, the heterogeneous catalyst was isolated from the mixture of the reaction by simple filtration. In continuation of workup, the filtrate organic solution was evaporated. The crude product was recrystallized using aqueous ethanol 15% twice. The desired pure product(s) was characterized by comparison of its physical data with those of known 1,8-dioxo-octahydroxanthenes.[7]

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