

## Research Article

# Mg(HSO<sub>4</sub>)<sub>2</sub>/SiO<sub>2</sub> as a Highly Efficient Catalyst for the Green Preparation of 2-Aryl-1,3-Dioxalanes/Dioxanes and Linear Acetals

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Silica-supported magnesium hydrogen sulfate has been used as a recyclable catalyst for the synthesis of some linear and cyclic aromatic acetals under solvent-free conditions. This environmentally friendly method has advantages, such as high yield of products, simple work-up procedure, and avoidance of the organic solvents, which will contribute in serving as a green process greatly.

## 1. Introduction

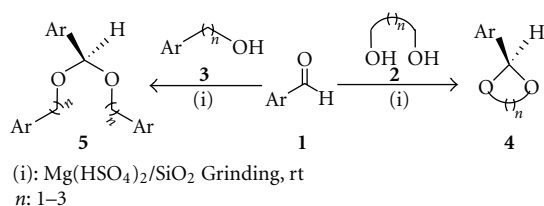
Recently, silica supported catalysts have attracted the special attention of chemists [1–3] due to their eco-friendly nature, simple handling, recyclability, and high reactivity [4–6]. Similarly, protection of carbonyl functionalities from nucleophilic attack is one of the major problems faced during multistep syntheses. These problems remain a crucial challenge to organic chemists. A suitable method for solving this problem is the acetalization of carbonyl functions since acetals and 1,3-dioxanes are stable under neutral and basic conditions [7, 8]. Besides the interest in acetals as protecting groups, many of them can serve for fragrances in cosmetics, pharmaceuticals, detergents, lacquer industries, and applications as food and beverage additives [9–11].

Until now, several methods for the acetalization of the carbonyl function have been reported using ionic liquids [12–15], protonic acids such as HCl and H<sub>2</sub>SO<sub>4</sub> and Lewis acids [16–19], and transitional metal complexes including Rh, Pd, and Pt [20, 21]. Some of these strategies suffer from the drawback of green chemistry, and have been associated with several shortcomings such as use of corrosive protic acids and unrecyclable catalyst, long-reaction times and low product yields, difficult work-up procedure, and the

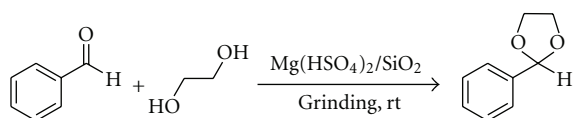
use of organic solvents. Therefore, presentation of a new, inexpensive and eco-friendly method for the protection of carbonyl functionality is an important topic, and one which is an active ongoing research area. There is a scope for the further improvement towards green reaction conditions and improved yields. We wish to report here a green and simple method for the protection of aromatic aldehydes **1** by diols **2** or aromatic alcohols **3** as 1,3-dioxanes, 1,3-dioxalanes **4**, and linear acetals **5** using a catalytic quantity of silica supported magnesium hydrogen sulfate under solvent-free conditions in excellent yields (Scheme 1).

## 2. Results and Discussion

A solvent-free reaction reduces pollution and cost due to simplification of experimental procedure, work-up technique, and saving of labour. To exploit simple and suitable conditions for the synthesis of **4** and **5** using Mg(HSO<sub>4</sub>)<sub>2</sub>/SiO<sub>2</sub> as an efficient solid acid catalyst, the treatment of benzaldehyde and ethanediol was chosen as a model reaction (Scheme 2). Firstly, we found that in the absence of catalyst, the reaction did not proceed even at a high temperature (25–90°C). After examining the various amounts of Mg(HSO<sub>4</sub>)<sub>2</sub>/SiO<sub>2</sub>, we found that the



SCHEME 1: Acetalization of aromatic aldehydes using  $\text{Mg}(\text{HSO}_4)_2/\text{SiO}_2$ .



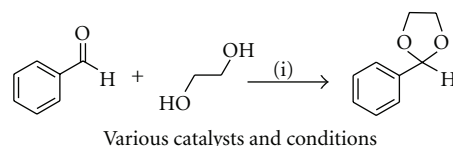
SCHEME 2: The reaction of benzaldehyde and ethanediol under solvent-free conditions.

condensation reaction can be efficiently carried out by adding 0.2 g of the catalyst under grinding conditions at room temperature in a short time span of 10 min. The use of excessive amounts of the catalyst does not increase the yield or reaction rate (Table 1).

After optimization, the scope of this reaction was examined using a variety of aromatic aldehydes and aromatic alcohols and diols. It was found that both electron rich and electron poor aldehydes reacted well in this process to afford the corresponding products **4** and **5** in excellent yields. The obtained results are summarized in Table 2.

The main advantages of the presented protocol over existing methods can be seen by comparing our results with those of some previous reported procedures, as shown in Table 3 (Scheme 3).

As can be concluded from Table 3, the present method is more appropriate than the others due to its excellent product yield in shorter reaction time without using organic solvents. In many cases, in order to achieve fast synthesis in an organic process, a catalyst must be used. The need to implement green chemistry principles (e.g., safer solvents, less hazardous chemical synthesis, atom economy, and catalysis) is a driving force towards the development of safe and reusable catalysts and avoidance of the use of organic solvents [22–25]. In this protocol,  $\text{Mg}(\text{HSO}_4)_2/\text{SiO}_2$  acts as a safe, highly efficient, and recyclable catalyst under solvent-free conditions. It should be also mentioned that our efforts on the acetalization of aliphatic aldehydes and ketalization of aromatic ketones using silica supported magnesium hydrogen sulfate under similar conditions were unsuccessful. The problem with alkyl aldehydes is likely to be a result of their being enolizable. To conclude, we present a new and green method for the synthesis of 1,3-dioxanes, 1,3-dioxalanes, and linear acetals by employing silica supported magnesium hydrogen sulfate as a safe, inexpensive, and reusable solid acid catalyst under solvent-free conditions. Higher yields and shorter reaction times than the classical methods, and simple work-up procedure are the appealing attributes of this work.



SCHEME 3: The reaction of benzaldehyde and ethanediol under various conditions.

TABLE 1: Optimization of the amounts of  $\text{Mg}(\text{HSO}_4)_2/\text{SiO}_2$  under solvent-free conditions for the reaction of benzaldehyde with ethanediol.

Entry	catalyst amount (g)	Time (min)	Yield (%) <sup>a</sup>	Temp. (°C)
1	0.03	120	60	rt
2	0.05	120	75	rt
3	0.1	25	80	rt
4	0.2	5	98	rt
5	0.5	15	95	rt

<sup>a</sup> Isolated yields.

### 3. Experimental Section

**3.1. General.** Chemicals were purchased from Fluka, Merck, and Aldrich chemical companies. Yields refer to isolated pure products. The products were characterized by comparison of their spectral (IR and <sup>1</sup>H-NMR) and physical data with authentic samples which were produced by other reported procedures.

**3.2. Preparation of Silica Supported Magnesium Hydrogen sulfate.** A 50 mL suction flask was equipped with a constant-pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution (water) and an alkali trap. Anhydrous magnesium chloride (4.0 g, 40 mmol) was charged in the flask and concentrated sulfuric acid (98%, 7.35 g, 40 mmol) was added dropwise over a period of 30 min at room temperature. HCl evolved immediately. After completion of the addition, the mixture was shaken for 30 min, while the residual HCl was eliminated by suction. The  $\text{Mg}(\text{HSO}_4)_2$  (6.46 g) was obtained as white gel. The obtained solid acid was mixed by silica gel 40 (6.43 g).

**3.3. General Procedure for the Synthesis of **4** and **5**.** A mixture of 1 mmol of aldehyde, 1.5 mmol of diol or 2 mmol of aromatic alcohol, and  $\text{Mg}(\text{HSO}_4)_2/\text{SiO}_2$  (0.2 g) was added to a mortar. The mixture was thoroughly ground with a pestle at room temperature. The progress of the reaction was monitored by TLC (EtOAc/hexane, 1 : 3). After completion of the reaction, the mixture was dissolved in  $\text{CHCl}_3$  ( $2 \times 10$  mL) and the catalyst was filtered. After evaporation of the solvent under reduced pressure and addition of ethanol and water, almost pure **4** and **5** were obtained in 90–98%. Further purification was achieved by recrystallization from the appropriate solvent. The catalyst was washed with diethyl ether, dried at 70 °C for 45 min and reused in another reaction.

TABLE 2: Synthesis of **4** and **5** using  $\text{Mg}(\text{HSO}_4)_2/\text{SiO}_2$  under solvent-free conditions.

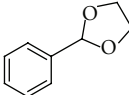
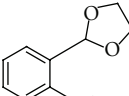
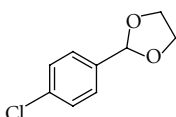
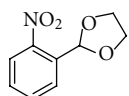
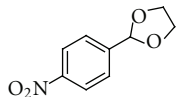
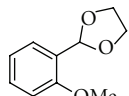
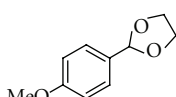
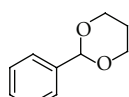
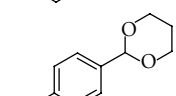
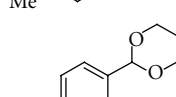
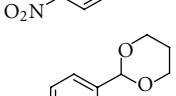
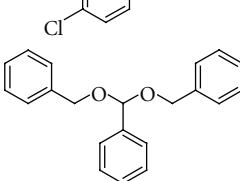
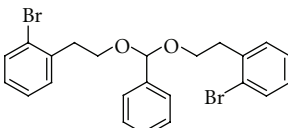
Entry	Product	Time (min)	Yield (%) <sup>a</sup>	[References]
4a		10	98	[14]
4b		10	95	[13]
4c		10	92	[26]
4d		18	90	[26]
4e		15	90	[13]
4f		12	87	[26]
4g		10	90	[13]
4h		12	90	[14]
4i		8	92	[27]
4j		16	95	[27]
4k		15	90	[14]
5a		5	95	[19]
5b		5	97	[27]

TABLE 2: Continued.

Entry	Product	Time (min)	Yield (%) <sup>a</sup>	[References]
5c		10	95	[27]
5d		7	97	[27]

<sup>a</sup> Isolated yields.

TABLE 3: Comparison of our method with previous reported method in the synthesis of 4a.

Entry	Conditions (catalyst/temperature (°C)/solvent)	Time (min)	Yield (%) <sup>a</sup>	[References]
1	Ionic liquid [SOCIMIm]Cl/40/-	1200	80	[15]
2	In(OTf) <sub>3</sub> /80 (reflux)/Benzene	180	92	[18]
3	Multi-SO <sub>3</sub> H functionalized ionic liquids/25/-	180	96.5	[13]
4	SG-[(CH <sub>2</sub> ) <sub>3</sub> SO <sub>3</sub> H-HIM]HSO <sub>4</sub>	90	95	[12]
5	Ionic liquid [TMPSA]HSO <sub>4</sub> /25/-	30	77	[14]
6	SiO <sub>2</sub> -SO <sub>3</sub> H/68 (reflux)/ <i>n</i> -hexane	60	58	[28]
7	Mg(HSO <sub>4</sub> ) <sub>2</sub> /SiO <sub>2</sub>	10	98	This work

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## References

- [1] M. A. Zolfigol, G. Chehardoli, and S. E. Mallakpour, "Silica sulfuric acid/NaNO<sub>2</sub> as a novel heterogeneous system for the oxidation of urazoles under mild conditions," *Synthetic Communications*, vol. 33, no. 5, pp. 833–841, 2003.
- [2] G. Szöllösi, Z. Makra, F. Fülöp, and M. Bartók, "The first case of competitive heterogeneously catalyzed hydrogenation using continuous-flow fixed-bed reactor system: Hydrogenation of binary mixtures of activated ketones on Pt-alumina and on Pt-alumina-cinchonidine catalysts," *Catalysis Letters*, vol. 141, no. 11, pp. 1616–1620, 2011.
- [3] W. Gil, K. Boczoń, A. M. Trzeciak et al., "Supported *N*-heterocyclic carbene rhodium complexes as highly selective hydroformylation catalysts," *Journal of Molecular Catalysis A: Chemical*, vol. 309, no. 1-2, pp. 131–136, 2009.
- [4] B. Karami, V. Ghashghae, and S. Khodabakhshi, "Novel silica tungstic acid (STA): preparation, characterization and its first catalytic application in synthesis of new benzimidazoles," *Catalysis Communications*, vol. 20, pp. 71–75, 2012.
- [5] B. Karimi and M. Khalkhali, "Silica functionalized sulfonic acid as a recyclable interphase catalyst for chemoselective thioacetalization of carbonyl compounds in water," *Journal of Molecular Catalysis A*, vol. 271, no. 1-2, pp. 75–79, 2007.
- [6] N. Fukaya, M. Ueda, S. Y. Onozawa et al., "Palladium complex catalysts immobilized on silica via a tripodal linker unit with amino groups: preparation, characterization, and application to the Suzuki-Miyaura coupling," *Journal of Molecular Catalysis A*, vol. 342-343, pp. 58–66, 2011.
- [7] M. Rahimizadeh, T. Bazazan, A. Shiri, M. Bakavoli, and H. Hassani, "Preyssler-type heteropoly acid: a new, mild and efficient catalyst for protection of carbonyl compounds," *Chinese Chemical Letters*, vol. 22, no. 4, pp. 435–438, 2011.
- [8] T. Kawabata, T. Mizugaki, K. Ebitani, and K. Kaneda, "Highly efficient heterogeneous acetalization of carbonyl compounds catalyzed by a titanium cation-exchanged montmorillonite," *Tetrahedron Letters*, vol. 42, no. 47, pp. 8329–8332, 2001.
- [9] J. H. Clark, "Solid acids for green chemistry," *Accounts of Chemical Research*, vol. 35, no. 9, pp. 791–797, 2002.
- [10] P. T. Anastas and J. B. Zimmerman, "Design through the 12 principles of green engineering," *Environmental Science and Technology*, vol. 37, no. 5, pp. 94A–101A, 2003.
- [11] A. W. Faull, A. G. Brewster, G. R. Brown, M. J. Smithers, and R. Jackson, "Dual-acting thromboxane receptor antagonist/synthase inhibitors: Synthesis and biological properties of [2-substituted-4-(3-pyridyl)-1,3-dioxan-5-yl]alkenoic acids," *Journal of Medicinal Chemistry*, vol. 38, no. 4, pp. 686–694, 1995.
- [12] J. Miao, H. Wan, Y. Shao, G. Guan, and B. Xu, "Acetalization of carbonyl compounds catalyzed by acidic ionic liquid immobilized on silica gel," *Journal of Molecular Catalysis A*, vol. 348, no. 1-2, pp. 77–82, 2011.
- [13] J. Zhang, S. Bao, and J. G. Yang, "Synthesis of a novel multi-SO<sub>3</sub>H functionalized strong Brønsted acidic ionic liquid and its catalytic activities for acetalization," *Chinese Science Bulletin*, vol. 54, no. 21, pp. 3958–3964, 2009.
- [14] D. Fang, K. Gong, Q. Shi, and Z. Liu, "A green procedure for the protection of carbonyls catalyzed by novel task-specific room-temperature ionic liquid," *Catalysis Communications*, vol. 8, no. 10, pp. 1463–1466, 2007.
- [15] D. Li, F. Shi, J. Peng, S. Guo, and Y. Deng, "Application of functional ionic liquids possessing two adjacent acid sites for acetalization of aldehydes," *Journal of Organic Chemistry*, vol. 69, no. 10, pp. 3582–3585, 2004.

- [16] T. W. Greene, *Protective Groups in Organic Synthesis*, Wiley Interscience, New York, NY, USA, 1981.
- [17] J. Bornstein, S. F. Bedell, P. E. Drummond, and C. L. Kosloski, "The synthesis of  $\alpha$ -amino-o-tolualdehyde diethylacetal and its attempted conversion to pseudoisindole," *Journal of the American Chemical Society*, vol. 78, no. 1, pp. 83–86, 1956.
- [18] B. T. Gregg, K. C. Golden, and J. F. Quinn, "Indium(III)trifluoromethanesulfonate as a mild, efficient catalyst for the formation of acetals and ketals in the presence of acid sensitive functional groups," *Tetrahedron*, vol. 64, no. 15, pp. 3287–3295, 2008.
- [19] S. Madabhushi, K. K. R. Mallu, N. Chinthala, C. R. Beeram, and V. S. Vangipuram, "Efficient and chemoselective acetalization and thioacetalization of carbonyls and subsequent deprotection using  $\text{InF}_3$  as a reusable catalyst," *Tetrahedron Letters*, vol. 53, no. 6, pp. 697–701, 2012.
- [20] M. Cataldo, E. Nieddu, R. Gavagnin, F. Pinna, and G. Strukul, "Hydroxy complexes of palladium(II) and platinum(II) as catalysts for the acetalization of aldehydes and ketones," *Journal of Molecular Catalysis A*, vol. 142, no. 3, pp. 305–316, 1999.
- [21] E. Nieddu, M. Cataldo, F. Pinna, and G. Strukul, "Acetalization of  $\alpha,\beta$ -unsaturated carbonyl compounds catalyzed by complexes of Pt(II)," *Tetrahedron Letters*, vol. 40, no. 38, pp. 6987–6990, 1999.
- [22] G. R. Najafi, "A green and efficient oxidation of benzylic alcohols using  $\text{H}_2\text{O}_2$  catalyzed by Montmorillonite-K10 supported  $\text{MnCl}_2$ ," *Chinese Chemical Letters*, vol. 21, no. 10, pp. 1162–1164, 2010.
- [23] B. Karami, S. J. Hoseini, S. Nikoseresht, and S. Khodabakhshi, " $\text{Fe}_3\text{O}_4$  nanoparticles: a powerful and magnetically recoverable catalyst for the synthesis of novel calix[4]resorcinarenes," *Chinese Chemical Letters*, vol. 23, no. 2, pp. 173–176, 2012.
- [24] I. Mohammadpoor-Baltork, M. Moghadam, V. Mirkhani, S. Tangestaninejad, and H. Reza Tavakoli, "Highly efficient and green synthesis of 14-aryl(alkyl)-14H-dibenzo[a,j]xanthene and 1,8-dioxooctahydroxanthene derivatives catalyzed by reusable zirconyl triflate [ $\text{ZrO}(\text{OTf})_2$ ] under solvent-free conditions," *Chinese Chemical Letters*, vol. 22, no. 1, pp. 9–12, 2011.
- [25] H. Eshghi, M. Rahimizadeh, and S. Saberi, " $\text{Fe}(\text{HSO}_4)_3$  as an inexpensive, eco-friendly, heterogeneous and reusable catalyst for acetal/ketal formation and their facile regeneration," *Catalysis Communications*, vol. 9, no. 14, pp. 2460–2466, 2008.
- [26] M. Moghadam, I. Mohammadpoor-Baltork, S. Tangestaninejad, V. Mirkhani, P. Yazdani, and S. Ghorjipoor, "Highly efficient and chemoselective acetalization of carbonyl compounds catalyzed by new and reusable zirconyl triflate,  $\text{ZrO}(\text{OTf})_2$ ," *Heteroatom Chemistry*, vol. 20, no. 3, pp. 131–135, 2009.
- [27] H. Firouzabadi, N. Iranpoor, and B. Karimi, "Zirconium tetrachloride ( $\text{ZrCl}_4$ ) catalyzed highly chemoselective and efficient acetalization of carbonyl compounds," *Synlett*, no. 3, pp. 321–323, 1999.
- [28] B. B. F. Mirjalili, M. A. Zolfigol, A. Bamoniri, and A. Hazar, "Acetalization of carbonyl compounds by using silica-bound sulfuric acid under green condition," *Bulletin of the Korean Chemical Society*, vol. 25, no. 6, pp. 865–868, 2004.



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