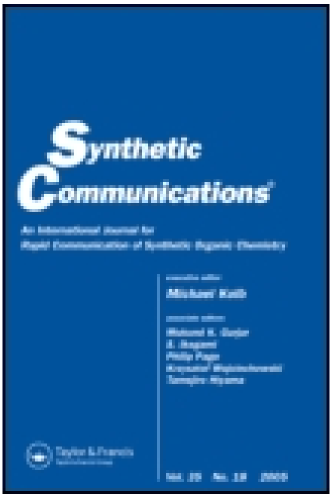
This article was downloaded by: [North Dakota State University]
On: 03 October 2014, At: 21:29
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Triacylperhydro-1,3,5-triazines over Phenylsulfonic Acid Functionalized Mesoporous Silica

Jianming Yang [a] , Qinwei Yu [a] , Fengwei Zhao [a] , Jian Lu [a] & Zhongxue Ge [a]

[a] Xi'an Modern Chemistry Research Institute , Xi'an Shaanxi , China

Published online: 04 Aug 2011.

To cite this article: Jianming Yang , Qinwei Yu , Fengwei Zhao , Jian Lu & Zhongxue Ge (2011) Triacylperhydro-1,3,5-triazines over Phenylsulfonic Acid Functionalized Mesoporous Silica, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:23, 3455-3461, DOI: 10.1080/00397911.2010.517887

To link to this article: http://dx.doi.org/10.1080/00397911.2010.517887

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

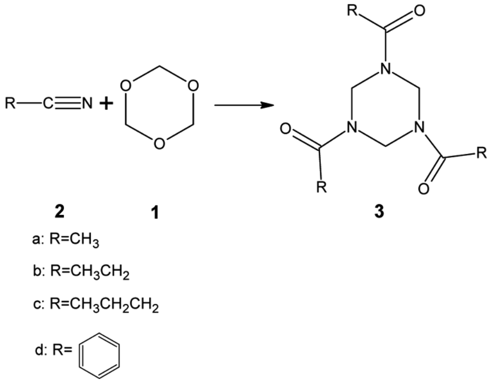
Synthetic Communications®, 41: 3455–3461, 2011

ISSN: 0039-7911 print/1532-2432 online
DOI: 10.1080/00397911.2010.517887

TRIACYLPERHYDRO-1,3,5-TRIAZINES OVER PHENYLSULFONIC ACID FUNCTIONALIZED MESOPOROUS SILICA

Jianming Yang, Qinwei Yu, Fengwei Zhao, Jian Lu, and Zhongxue Ge
Xi'an Modern Chemistry Research Institute, Xi'an Shaanxi, China

GRAPHICAL ABSTRACT



Abstract *An operationally simple, efficient, and environmentally benign synthesis of 1,3,5-triacylperhydro-1,3,5-triazines in good yields by reaction of different organic nitriles and trioxane in the presence of phenylsulfonic acid functionalized mesoporous silica under mild conditions was examined. The yields of the corresponding 1,3,5-trisubstituted perhydro-s-triazines synthesized from acetonitrile, propionitrile, butyronitrile, benzonitrile, and 1.3.5-trioxane were 95.7%, 96.1%, 84.2%, and 98.1%, respectively. The products were characterized by ^1H NMR, infrared, mass spectrometry, and elemental analysis. The mechanism of the formation of 1,3,5-triacylperhydro-1,3,5-triazines in acidic conditions was also described using a model reaction of butyronitrile with trioxane.*

Keywords Environmentally benign synthesis; nitrile; 1,3,5-triazines; solid acid

Received December 12, 2007.

Address correspondence to Jianming Yang, Xi'an Modern Chemistry Research Institute, 168 Zhangba Donglu, Xi'an Shaanxi, 710065, China. E-mail: yangjm204@163.com

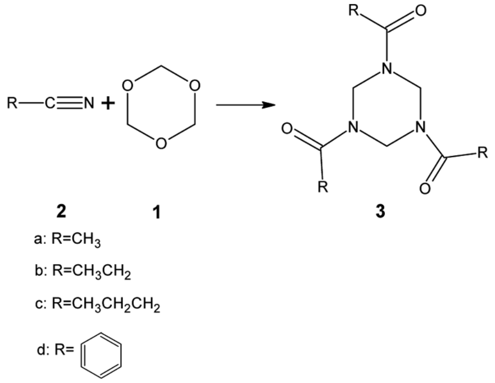
INTRODUCTION

Substituted 1,3,5-triazines are of considerable importance as reinforcement promoters in polymer chemical industry.[1,2] In addition, these compounds are used as a key precursor for the synthesis of RDX (hexogen, trimethylene trinitramine) by further nitration, so the syntheses of 1,3,5-triazines have been the subject of investigations. Generally, 1,3,5-triazine compounds have been prepared by reaction of organic nitriles with polymeric formaldehyde such as paraformaldehyde or trioxane and an aliphatic anhydride in the presence of sulfuric acid, p-toluenesulfonic acid, and ion-exchange resins as catalysts.[3] However, most of the procedures suffer from difficulties separating catalyst from the reaction mixture, environmental problems, or erosion problems. The acidic ion-exchange resins possess poor heat resistance and are easily swollen in organic solvents for a longer time. The method described has proven unsatisfactory for commercial usage because the reaction has been found to be uncontrollable and quite violent after an unpredictable and rather long induction period upon scale-up. Therefore, an operationally simple, efficient, and environmentally benign synthesis of these compounds that overcomes these deficiencies is in demand.

Recently, the use of sulfonic acid functionalized mesoporous silica has attracted great interests.[4–8] We found that phenylsulfonic acid functionalized mesoporous silica is a green, reusable, and versatile acidic catalyst in organic syntheses such as esterification, ethericication, and condensation.[9–11] With the aim of obtaining a more practical synthesis of this group of compounds, here we present a novel modification of the synthesis of 1,3,5-triacylperhydro-1,3,5-triazines from 1,3,5-trioxane (paraformaldehyde 1) and organic nitriles using a solid acid catalyst of phenylsulfonic acid functionalized mesoporous silica (Scheme 1).

RESULTS AND DISCUSSION

The phenylsulfonic acid functionalized mesoporous silica is as reported in the previous work.[10] It belongs to the mesoporous material, with surface area of 722 m^2g^{-1}, mean pore size of 14.3 nm, and pore volume of 0.59 mLg^{-1}. The introduced



Scheme 1. Syntheses of 1,3,5-triacylperhydro-1,3,5-triazines from 1,3,5-trioxane (paraformaldehyde 1) and nitriles.

Table 1. Condensation of model reaction in various solvents

Entry	Solvents	Time (h)	Yield (%)
1	1,1,1-Trichloroethane	8	71.0
2	1,1,2-Trichloroethane	8	55.6
3	1,2-Dichloroethane	8	96.1
4	Tetrachloromethane	8	74.5
5	DMF	18	<10
6	DMSO	18	<10
7	DMI	16	<10
8	H_2O	18	—
9	CS_2	18	Very low

sulfonic acid groups by sulfonation are highly dispersed in the precursor and bonded on the *meta*-position of the phenyl ring, which covalently is anchored onto the organic–inorganic hybrid material. So we use the prepared material as the catalyst in our experiments.

Searching for the appropriate solvent is of important for successful syntheses. First, a combination of propionitrile and trioxane is chosen a model for the reaction of organic nitriles with trioxane. The reactions were carried out with propionitrile and trioxane in a molar ratio of 4:1 in the presence of the catalyst at 80 °C in various solvents such as 1,1,1-trichloroethane, 1,2-dichloroethane, tetrachloromethane, dimethylformamide (DMF), dimethylsulfoxide (DMSO), and 1,3-dimethyl-imidazolinone (DMI). The results are summarized in Table 1. The results in Table 1 indicate that the crude products, 1,3,5-tripropionylperhydro-1,3,5-triazines, obtained with 1,2-dichloroethane have been in every case superior to those obtained under any other conditions, and therefore they are the better choice. However, strongly polar nonprotonic solvents as DMF, DMSO, and DMI afford relatively poor yields of 1,3,5-triacylperhydro-1,3,5-triazines (entries 5–9, Table 1), and a bulk of the staring material is recovered in the same conditions.

Having established the better reaction conditions, various 1,3,5-triacylperhydro-1,3,5-triazines are synthesized in good yields by reaction of different organic nitriles with trioxane. Several representative titled compounds are summarized in Table 2.

In all cases of the organic nitriles, either the aliphatic nitriles or the aromatic nitriles, as the starting materials, 1,3,5-triacylperhydro-1,3,5-triazines were the sole products in better and more reproducible yields in dichloroethane (entries 1–4, Table 2). The amides fail to give the corresponding 1,3,5-triazines when the reactions are performed at 80 °C within 18 h (entries 5–7), and the reason might be the poor nucleophilicity of the amides. Unexpectedly, it has been found that the formation of 1,3,5-triacylperhydro-1,3,5-triazines in condensation of organic nitriles with trioxane is relatively susceptible to moisture. To verify this finding, the experiment was carried out in the presence of a slight trace of water, affording the corresponding methyl-bisamides, as listed in Table 2 (entry 8). As far as cyanoacetamide is concerned, the reaction does not proceed well in the same condition; moreover, the product of the corresponding 1,3,5-triazine is unobtainable even if the reaction temperature is raised to 140 °C.

On the basis of the experimental results reported previously, a mechanism for the condensation of organic nitriles with trioxane is proposed, as shown in Scheme 2. First, trioxane **1** undergoes a tautermic process to form formaldehyde,

Table 2. Synthesis of the representative 1,3,5-triacylperhydro-1,3,5-triazines compounds

Entry	Nitrile R=	Molar ratio	Solvents	Products	Yield (%)[a]
1	CH_3	4:1	1,2-dichloroethane	**3a**	88.0
2	CH_3CH_2	4:1	1,2-dichloroethane	**3b**	95.7
3	$CH_3CH_2CH_2$	4:1	1,2-dichloroethane	**3c**	84.2
4	Phenyl	4:1	1,2-dichloroethane	**3d**	98.1
5	$CNCH_2CONH_2$	4:1	1,2-dichloroethane	—	—
6	CH_3CONH_2	4:1	1,2-dichloroethane	—	93.9[c]
7	$CH_3CH_2CONH_2$	4:1	1,2-dichloroethane	—	89.6[c]
8	Butyl	4:1	1,2-dichloroethane	—	85.6[b]

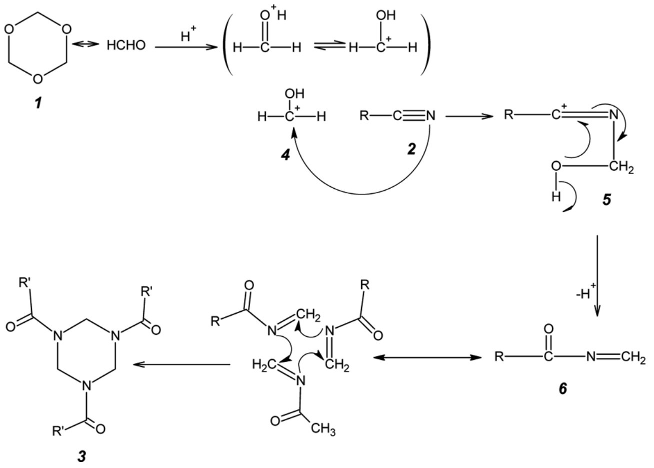
[a] Isolated yields from solution.

[b] The reaction is performed in the presence of a slight trace of water; the product is methyl bis-amides.

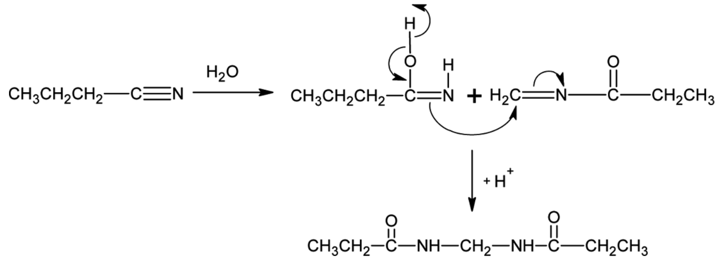
[c] The yields of the starting materials recovered.

with protonization occurring in the presence of the acid catalyst, thus generating an oxonium ion of formaldehyde and forming a carbonation ion **4** by a tautermic process. The carbonation ion **4** suffers from a nucleophilic attack by the organic nitrile **2** and gives rise to an adduct **5,** which then transforms an acyl imide **6** through an electron-transfer process and a deprotonation process. The intermidiate **6** are unstable in acidic surroundings and readily to proceed to a cyclization reaction to afford the products 1,3,5-triacylperhydro-1,3,5-triazines **3**. When the reaction is performed in a moist environment and the reactants are the butyronitrile and trioxane, the product methylene bis-butyric acid amides will be generated. A plausible elucidation is shown in Scheme 3.

In conclusion, a novel and highly efficient approach to the synthesis of 1,3,5-triacylperhydro-1,3,5-triazines by the condensation reaction of organic nitriles with trioxane catalyzed by phenylsulfonic acid functionalized mesoporous silica has been established. The method offers several significant advantages such as high conversions, easy handling, and a clean reaction profile, which make it a useful and attractive process for the rapid synthesis of 1,3,5-triacylperhydro-1,3,5-triazines.



Scheme 2. Proposed mechanism of the formation of the 1,3,5-triacylperhydro-1,3,5-triazines.



Scheme 3. Proposed mechanism of the formation of the methylene bis-butyric acid amide.

EXPERIMENTAL

Typical Procedure for Synthesis of 1,3,5-Tributyrylperhydro-1,3,5-triazines

To a solution of 11.0 g (0.16 mol) of freshly distilled butyronitrile in 70 mL of dry 1,2-dichloroethane, 2 g of phenylsulfonic acid functionalized mesoporous silica was added. Another solution of 11.0 g (0.16 mol) of butyronitrile and 7.2 g (0.08 mol) of trioxane in 50 mL of 1,2-dichloroethane was added dropwise to the solution with stirring under reflux. After completion of the reaction, the catalyst was filtered, and a white solid was precipitated, the filtrate being cooled to rt. The precipitated solid was collected and recrystallized with cyclohexane to afford the product with a purity of 99.51%.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruck Gemini 500-MHz spectrometer, and chemical shifts are reported in δ units (ppm) relative to tetramethylsilane (TMS) as an internal standard. Fourier transform infrared (FTIR) spectra of all the products were recorded on a Nicolet spectrometer with KBr pellet in the transmission. High-performance liquid chromatographic (HPLC) analyses were carried out on a Varian liquid chromatograph (250 × 4.6 mm C18 column, gradient elution 60% methanol and 40% H_2O, 1 mL/min, ultraviolet detection at 254 nm). All the regents used were of analytical reagent grade.

DATA

1,3,5-Triacetyclperhydro-1,3,5-triazines

Yield 88.0%, mp 70.3–71.8 °C; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 2.12 (s, 9H, CH_3), 5.22 (s, 6H, N-CH_2-N); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 20.88, 55.98, 169.32; IR (KBr) 2970, 1635 cm^{-1}; ES/MS m/z (%): 213 (M^+), 43 (100). Anal. calcd. for $C_9H_{15}O_3N_3$: C, 50.70; H, 7.042; N, 19.61. Found: C, 50.61; H,7.031; N, 19.72.

1,3,5-Tripropionylperhydro-1,3,5-triazines

Yield 95.7%, mp 173.1–173.8 °C; ^{1}H NMR (DMSO-d_6, 500 MHz), δ: 0.96–0.99 (t, 9H, CH_3), 2.45–2.51 (q, 6H, CH_2), 5.23 (s, 6H, N-CH_2-N); ^{13}C NMR (DMSO-d_6, 125 MHz) δ: 13.67, 34.66, 55.93, 172.25; IR (KBr) 2980, 2943, 2881, 1464, 1369, 1650 cm^{-1}; ES/MS *m/z* (%): 255(M$^+$), 57(100). Anal. calcd. for $C_{12}H_{21}O_3N_3$: C, 56.47; H, 8.235; N, 16.47. Found: C, 56.51; H, 8.231; N, 16.41.

1,3,5-Tributyrylperhydro-1,3,5-triazines

Yield 84.2%, mp: 69.2–79.2 °C; ^{1}H NMR (DMSO-d$_6$, 500 MHz), δ: 0.94–0.97 (t, 3H, CH_3), 1.61–1.69 (q, 2H, CH_2), 2.49–2.52 (t, 2H, CH_2), 5.28 (s, 6H, N-CH_2-N); ^{13}C NMR (DMSO-d$_6$, 125 MHz) δ: 13.67, 18.21, 34.66, 55.93, 172.25; IR (KBr) 2960, 2934, 2873, 1466, 1649 cm^{-1}; ES/MS *m/z* (%): 297 (M$^+$), 43 (100). Anal. calcd. for $C_{15}H_{27}O_3N_3$: C, 60.61; H, 9.091; N, 14.14. Found: C, 60.54; H, 9.085; N, 14.09.

1,3,5-Tribenzoylperhydro-1,3,5-triazines

Yield 98.1%, mp: 220.3–223.0 °C; ^{1}H NMR (DMSO-d$_6$, 500 MHz), δ: 5.33 (s, 6H, N-CH_2-N), 7.36–7.42 (m, 15H, aromatic); ^{13}C NMR (DMSO-d$_6$, 125 MHz) δ: 127.33, 128.34, 130.52, 133.67, 169.18; IR (KBr) 3034, 3058, 1670, 1649, 1601, 721, 697 cm^{-1}; ES/MS *m/z* (%): 398 (M$^+$ − 1), 105 (100). Anal. calcd. for $C_{25}H_{23}O_3N_3$: C, 72.62; H, 5.61; N, 10.16. Found: C, 71.60; H, 5.60; N, 10.15.

Methylene Bis-butyric Acid Amide

Yield 85.6%, mp: 181.3–182.5 °C; ^{1}H NMR (DMSO-d$_6$, 500 MHz), δ: 0.92–0.95 (t, 3H, CH_3), 1.61–1.69 (q, 2H, CH_2), 2.14–2.17 (t, 2H, CH_2), 4.57–4.60 (t, 1H, N-CH_2-N), 6.93 (s, 1H, CH_2-NH-CO);^{13}C NMR (DMSO-d$_6$, 125 MHz) δ: 13.79, 19.04, 38.35, 44.65, 174.39; IR (KBr) 2960, 2934, 2873, 1466, 1649 cm^{-1}; ES/MS *m/z* (%): 173.2(M$^+$ + 1), 43 (100). Anal. calcd. for $C_8H_{16}O_2N_2$: C, 55.79; H, 9.36; N, 14.27. Found: C, 55.83; H, 9.34; N, 14.23.

ACKNOWLEDGMENT

Financial support from the Major State Basic Research Foundation Department of Equipment, China, is grateful acknowledged.

REFERENCES

1. Louis, B. C.; Newark, J.; Walter, T.; Warren, R. Solution synthesis of 1,3,5-triacylylhexahydro-s-triazines. U.S. Patent 4413123, 1983.
2. Emmons, W. D.; Rolewicz, H. A.; Cannon, W. N.; Ross, R. M. Solvent effects in the conversion of nitriles to perhydro-*s*-triazines. *J. Am. Chem. Soc.* **1952**, *74* (21), 5524–5525.
3. Ladhar, E.; Gharbi, R. E.; Delmas, A. G. Synthesis of 1,3,5-triacylperhydro-1,3,5-tiazines catalyzed by ion-exchange resins. *Synthesis* **1986**, 643–644.
4. Mbaraka, I. K.; Daniela, R. R.; Lin, V. S. Organicsulfonic acid functionalized mesoporous silicas for the esterification of fatty acid. *J. Catal.* **2003**, *219*, 329–326.
5. Hamoudi, S.; Kaliaguine, S. Sulfonic acid functinalized periodic mesoporous organosilica. *Micropor. Mesopor. Mater.* **2003**, *59*, 195–204.

6. Christopher, W.; Katsuyuyki, T.; Davas, E. M. Organic functionalized molecular sieve as shape-selective catalyst. *Nature* **1998**, *393* (7), 52–54.
7. Minoo, D.; Peyman, S.; Mostafa, B.; Mohammand, A. Z.; Mahboobeh, B. Silica sulfuric acid: An efficient and versatile acidic catalyst for the rapid and ecofriendly synthesis of 1,3,4,-oxadiazoles at ambient temperature. *Synth. Commun.* **2007**, *37*, 1201–1209.
8. Meler, J. A.; Grieken, R. V.; Morales, G. Friedel–Crafts acylation of aromatic compounds over arenesulfonic containing mesostructured SBA-15 materials. *Catal. Commun.* **2004**, *5*(3), 131–137.
9. Yang, J. M.; Kou, L. G.; Lu, J. Preparation and catalytic performance of phenylsulfonic acid functionalized mesoporous silica. *Acta Chim. Sin.* **2005**, *63* (5), 396–401.
10. Yang, J. M.; Lu, J. Phenylsulfonic acid functionalized mesoporous silica catalyzed transetherification of alcohols with dimethoxymethane. *Chin. J. Chem.* **2005**, *23* (3), 349–352.
11. Yang, J. M.; Lu, J. Synthesis of coumarin derivatives over phenylsulfonic acid functionalized mesoporous molecular sieve. *Chin. J. Org. Chem.* **2004**, *24* (4), 450–453.