



Dimethyl sulfite a potential agent for methylation



Rim Mouselmani, Eric Da Silva, Marc Lemaire*

Laboratoire Catalyse, Synthèse et Environnement, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires (ICBMS), CNRS, UMR 5246, Université Claude Bernard Lyon 1, Bât. CPE, 43 Boulevard du 11 novembre 1918, 69622, Villeurbanne, France

ARTICLE INFO

Article history:

Received 19 June 2015

Received in revised form 28 September 2015

Accepted 29 September 2015

Available online 3 October 2015

ABSTRACT

The synthesis of methylated ether compounds is an important challenge. A pathway for the synthesis of methyl ethers was investigated using dimethyl sulfite (DMSi). Methylation of 1-octanol was carried out in liquid phase upon different heterogeneous organic and inorganic catalysts at 130 °C. Aluminium oxide gave the best result with high conversion and moderate selectivity for methyl 1-octyl ether. Reactions in gas phase at higher temperatures (200 °C) were also performed. Methyl 1-octyl ether was obtained in a very high level of selectivity up to 98%. Primary and secondary ethers from unsymmetrical alkyl methyl sulfite were also performed by SO₂ extrusion.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

Several methods were developed to form methyl ethers of aliphatic alcohols and research has focused on economical and environmentally friendly reagents that operate with less toxic by products.¹ Methyl ethers are considered as good oxygenated molecules due to their capacity to reduce CO emission, and to enhance gasoline combustion increasing octane numbers. They also exhibit excellent properties as solvents for extractions, and are used in several applications such as coatings, inks, paints, cleaning agents and pharmaceuticals.² The well known Williamson ether synthesis for linear alcohols employs toxic reagents such as alkyl halides, and during the reaction inorganic salt byproducts are formed.³ Diazomethane is widely used for the formation of methyl ether in mild and neutral reaction conditions but its toxicity and explosive nature limit its broad application.⁴ Dimethyl sulfate is also used as a methylating agent. Ogawa et al. performed the methylation of alcohols using alumina and excess of dimethyl sulfate with cyclohexane as a solvent.⁵ For example, 1-heptanol was successfully methylated in 99% yield. However in the case of secondary alcohols, diols, and phenols, a decrease in yields was observed. Concerning polyols, Chang et al. used a mixture of dimethyl sulfate/glycerol (3:2 molar ratio), in the presence of sodium hydroxide to methylate glycerol at 70 °C. Di- and tri-methoxyglycerol ethers were obtained

in 71% combined yield.⁶ Lemaire group has conducted the formation of ethers from glycerol by phase transfer catalysis, so that 1,2,3-trimethoxypropane was obtained in 95% yield and 96% selectivity in one step with dimethyl sulfate as the methylating agent, potassium hydroxide as the base, in the presence of tetrabutyl ammonium hydrogen sulfate at room temperature.⁷ Despite that dimethyl sulfate is available in industry, it is mutagenic showing very high toxicity.⁸ The use of methanol provides safer catalytic reactions, but these reactions require a large excess of MeOH as well as high temperatures which ensure the degradation of alcohol leading to the formation of alkene derivatives and dimethyl ether, finally giving moderate selectivities.⁹ More recently, the catalytic etherification of isosorbide to methyl ethers has been reported in the presence of 1,2-dimethoxyethane as alkylating agent and tungstic acid catalyst.¹⁰ Dimethyl carbonate (DMC) has shown to be a great interest as an alkylating agent due to its non-toxicity, biodegradability, and its tunable reactivity: methoxy carbonylating agent at 90 °C and methylating agent at higher reaction temperatures.¹¹ For example, Tundo et al. have reported the synthesis of methyl ethers from aliphatic alcohols in good yields at 200 °C with a 1:15 weight ratio of alcohol/dimethyl carbonate in the presence of basic alumina or hydrotalcite KW 2000 as catalyst.¹² It was found that the conversion was complete for the 1-octanol giving 100% selectivity for the corresponding ether, while secondary alcohols were methylated with lower selectivity reaching 87%. These catalysts also performed in gas phase using 1:3 weight ratio of 1-pentanol/dimethyl carbonate at 180 °C in the presence of basic alumina, giving 90% selectivity of methylpentyl ether. Poliakoff

* Corresponding author. Tel.: +33 (0) 4 72 43 14 07; fax: +33 (0) 4 72 43 14 08; e-mail address: marc.lemaire@univ-lyon1.fr (M. Lemaire).

et al. have showed that methyloctylether can be synthesized in 86% yield using a 1:2 molar ratio of 1-octanol/dimethyl carbonate in the presence of acidic alumina and supercritical carbon dioxide under 100 bars at 262 °C.¹³ The group has also reported the methylation of compounds containing multiple hydroxyl groups such as 1,3-propanediol with yield reaching 68%. Moreover, the etherification of glycerol formal or solketal was done by Selva,¹⁴ at $T \geq 200$ °C both were efficiently alkylated affording the corresponding methyl ethers with selectivity up to 99% and excellent yields (86–99%). The O-methylation of phenols with dimethyl carbonate was also reported in the literature using different catalysts, such as potassium

2. Results and discussion

2.1. Synthesis of methyl 1-octyl ether in liquid phase

Reactions with 1-octanol (**1**, as model substrate) and DMSi were carried out over several heterogeneous catalysts (Table 1). All experiments were performed under argon at 130 °C in a batch system using 1:5 molar ratio of 1/DMSi, 2 g of catalyst. In the absence of catalyst (entry 1), a low conversion of **1** was observed. Methyl 1-octyl ether **2** and methyl 1-octyl sulphite **4** were formed with a ratio of 13 and 87%, respectively.

Table 1

Comparison of the behaviour of different inorganic and organic catalysts for the methylation of 1-octanol with dimethyl sulfite in liquid phase^a

1-octanol (**1**) $\xrightarrow[\text{Argon flow 75 mL/min}]{\substack{1.5 \text{ of 1/DMSi} \\ 2\text{g catalyst} \\ T=130^\circ\text{C}}}$ **2**, **3**, **4**, **5**, **6**

Entry	Catalyst	Time [h]	Conv. [%] ^e	Ratio [%] ^e					Unknown
				2	3	4	5	6	
1	—	4.5	4	13	—	87	—	—	—
2	Al ₂ O ₃ acidic	24	100	62	—	37	1	—	—
3	Al ₂ O ₃ acidic ^b	7	23	9	—	78	—	—	13
4	Al ₂ O ₃ acidic ^c	22	100	62	—	37	1	—	—
5	Al ₂ O ₃ acidic ^d	23	87	—	7	—	31	—	62
6	Al ₂ O ₃ neutral	3.5	100	41	—	56	2	—	—
7	Al ₂ O ₃ basic	5.5	100	42	—	57	1	—	—
8	Amberlyst 15	5	97	44	35	—	—	21	—
9	Amberlyst 35	5	74	65	28	—	—	7	—
10	Amberlyst 36	5	81	68	30	—	—	2	—
11	Amberlyst 36 ^c	5	58	24	—	31	45	—	—
12	Amberlyst 36 ^d	5	5	—	40	—	—	—	60
13	KSF	5.5	100	—	—	70	30	—	—
14	K10	3	100	3	—	75	22	—	—
15	ZMS-5	3	100	3	—	85	12	—	—
16	Al/Si ₂ H ₂ O	1.5	68	7	—	86	7	—	—

^a Experimental conditions: **1** (1 equiv), DMSi (5 equiv), catalyst (2 g), $T=130$ °C, argon flow (75 mL/min), stirring speed 700 rpm.

^b Without argon flow.

^c Toluene (72 mmol, 1M).

^d N-Methyl-2-pyrrolidone (79 mmol, 1M).

^e Conversion and ratio % were determined by GC.

carbonate at 160 °C,¹⁵ ionic liquids such as 1-*n*-butyl-3-methylimidazolium chloride at 120 °C,¹⁶ and 1,8-diazabicyclo [5.4.0]undec-7-ene at 220 °C.¹⁷ All of these catalysts gave yield up to 90%. Therefore, the dimethyl carbonate appears, for the moment, the best alternative in many cases. Nevertheless, high temperature is required and alkylation of primary alcohol remains by far the best results. This is mainly due to the poor electrophilic properties of such reagent. Looking for new methylating agent, we investigated alternatives to classical alkylating agents with a lower toxicity, readily available and cheaper like dimethyl sulfite (DMSi). Such reagent may be expected more electrophilic than DMC (pK_a of $H_2SO_3=1.8$ and pK_a of $H_2CO_3=6.3$). However, there is only two examples showing the synthesis of methyl ethers using dimethyl sulfite. The approach was done in 1984 by Nelson,¹⁸ where he prepared alkylated phenolic ethers. For example, 3,4,5-trimethoxybenzaldehyde was obtained with 40% yield by the reaction of syringaldehyde with potassium carbonate at 100 °C. The second work showed the alkylation of enolate of ethylacetate by dimethyl sulfite in liquid SO_2 .¹⁹ In this article, we described the O-methylation reaction of linear alcohols with DMSi using various heterogeneous acid catalysts in both liquid and gas phases.

2.1.1. Aluminium oxides. As described in the literature, methylation reactions with dimethyl carbonate in the presence of aluminium oxides showed moderate results towards the formation of the methyl ether. With acidic aluminium oxide (entry 2), after 24 h the conversion of **1** was complete. Methyl 1-octyl ether was formed in 62%, 1-methyloctylsulfite in 37% and only 1% of the dioctyl sulfite **5**. When following the reaction, it was noticed that the amount of methyl 1-octyl sulfite **4** decreased while the amount of methyl 1-octyl ether increased (see [Supplementary data, SM3](#)). Thus there is competition between two reactions: the direct O-alkylation and the O-sulfoxymethylation. We suppose that compound **4** could be an intermediate of the reaction by SO_2 extrusion. The released sulfur dioxide has been highlighted using DABCO molecule as scavenger by forming bis(sulfur dioxide)-1,4-diazabicyclo[2.2.2]-octane (DABSO as white solid).^{20,21} Moreover, removing SO_2 gas could improve the conversion and the selectivity for the methyl 1-octyl ether. Indeed, the conversion of 1-octanol was low in the absence of argon flow (entry 3). 9% of **2** and 78% of **4** were observed, with 13% of unknown byproduct. This result could be explained by the inhibition of the catalyst by SO_2 gas, or by monomethyl sulfite species formed during the reaction.²² Experiments were performed

Download English Version:

<https://daneshyari.com/en/article/5214427>

Download Persian Version:

<https://daneshyari.com/article/5214427>

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