

무용매 조건하에서 황산/젖은 SiO₂와 마이크로웨이브를 이용한 아세탈의 새로운 탈보호기 방법

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Silica Sulfuric Acid/Wet SiO₂ as a Novel System for the Deprotection of Acetals by Using Microwave Irradiation under Solvent Free Conditions

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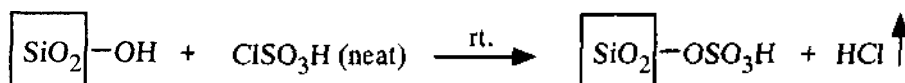
요 약. 클로로술폰산을 실리카겔과 반응시키면 실리카겔 표면에 황산이 공유결합으로 고정된 실리카 황산을 얻게 된다. 무용매 조건하에서 마이크로웨이브를 쬐여주면서 실리카 황산과 젖은 SiO₂를 함께 사용하게 되면 아세탈을 카보닐 화합물로 변화시키는 효과적인 탈아세탈 시약으로 사용할 수 있다.

ABSTRACT. Neat chlorosulfonic acid reacts with silica gel to give silica sulfuric acid in which sulfuric acid is immobilized on the surface of silica gel via covalent bond. A combination of silica sulfuric acid and wet SiO₂ was used as an effective deacetalizing agent for the conversion of acetals to their corresponding carbonyl derivatives by using microwave irradiation under solvent free conditions.

Protection¹ and deprotection² of functional groups are important processes in organic synthesis. Deprotection of acetals and ketals to the original aldehydes and ketones are performed under acidic aqueous media,³ with iodotrimethylsilane,⁴ by cobalt or manganese salt in the presence of air or O₂,⁵ and by photoinduced electron transfer with a pyrilium salt,⁶ etc.

On the other hand, any reduction in the amount

of sulfuric acid needed and/or any simplification in handling procedures is required for risk reduction, economic advantage and environmental protection.⁷ In addition, there is current research and general interest in heterogeneous systems because of the importance such systems have in industry and in developing technologies.⁸ In continuation of our studies on the application of inorganic acidic salts⁹ we found that silica gel reacts with chlorosulfonic



I

Scheme 1.

acid to give silica sulfuric acid (I). It is interesting to note that the reaction is easy and clean without any work-up procedure because HCl gas is evolved from the reaction vessel immediately (Scheme 1).

We hoped that the silica sulfuric acid (I) would be a superior proton source to all of the reported acidic solid supports or acidic resins such as polystyrene sulfonic acid and Nafion-H¹⁰ for running reactions under heterogeneous conditions.

Here we wish to report a convenient method for the deacetalization of acetals by using silica sulfuric acid (I), wet SiO₂ (II) and microwave irradiation under solvent free conditions.

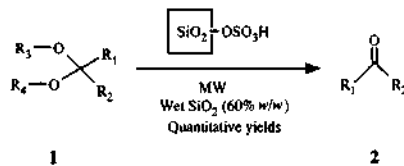
Different types of acetals (1) were subjected to the deacetalization reaction in the presence of silica sulfuric acid (I), wet SiO₂ (60% w/w) and microwave irradiation under solvent free conditions with quantitative yields (Scheme 2).

Although the deacetalization reaction was occurred in the presence of silica sulfuric acid and a few drops of water but the wet SiO₂ causes the reaction to perform under mild conditions and prevents the materials scattering in the vessel of reaction in microwave oven. The presence of wet SiO₂ thus provides an effective surface area for *in situ* generation of H₂SO₄. It also eases the reaction work-up.

In conclusion silica sulfuric acid is an excellent proton source in terms of convenience, cheapness, easy production and insolubility to all of organic solvents. The cheapness and availability of the reagents, easy procedure and work-up make this method attractive for the large scale operation.

EXPERIMENTAL SECTION

General. Chemicals such as carbonyl compounds, ethylene glycol, chlorosulfonic acid and silica gel were purchased from Fluka, Merck and Aldrich chemicals companies. Acetals and 5-norbornene-2,2-dimethylol were synthesized according to the our previously reported procedure.¹ The deacetalization products were characterized by comparison of their spectral (IR, ¹H-NMR), TLC and physical data with the authentic samples. The microwave oven Sanyo (EM-374T, 1300 W, 2450 MHz) was



1	Structure of substrates	2	Structure of products
a		a	
b		b	
c		c	
d		d	
e		e	
f		f	
g		g	
h		h	
i		i	
j		j	
k		k	
l		l	
m		m	

Scheme 2.

used for running the described reactions.

Preparation of silica sulfuric acid. A 500 mL suction flask was used. It was equipped with a constant-pressure dropping funnel containing chlorosulfonic acid (23.3 g, 0.2 mol) and gas inlet tube for conducting HCl gas over an adsorbing solution, i.e., water. Into it were charged 60.0 g of silica gel. Chlorosulfonic acid was added dropwise over a period of 30 min at room temperature. HCl gas evolved from the reaction vessel immediately (Scheme 1). After the addition was completed the mixture was shaken for 30 min. A white solid (silica sulfuric acid) 76.0 g was obtained.

Deacetalization of 1 g to the corresponding aldehyde 2 g. A typical procedure. A mixture of 1 g (0.07 g, 0.25 mmol), silica sulfuric acid (I) (0.3 g) and wet SiO₂ (60% w/w, 0.3 g) were irradiated in domestic microwave oven for 1 min. Then dichloromethane was added to the resulting reaction mixture and triturated and also then filtered. By evaporation of solvent and then addition of ethanol-water, the 4-nitobenzaldehyde (2g) was obtained in quantitative yield.

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