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## A NEW METHOD FOR THE ESTERIFICATION OF SULFONIC ACIDS

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#### ABSTRACT

Sulfonic acids can be smoothly converted to their methyl and ethyl esters by reaction with trimethyl and triethyl orthoformate, respectively.

In connection with our continuing studies directed towards the elucidation of lignin sulfonate structures<sup>1,2</sup>, we wish to report new methodology for the facile methylation (and ethylation) of sulfonic acids with trimethyl (and triethyl) orthoformate respectively.

Currently, the only means of converting sulfonated lignin fragments into stable, organic soluble derivatives, under relatively mild conditions, is to prepare their **a**) S-benzylthiourea salts<sup>3</sup> or **b**) acetyl lignin sulfonate methyl esters<sup>4</sup>. This latter method, requiring initial acetylation of a suspension of lignin sulfonates in acetic anhydride/pyridine, and subsequent methylation of the silver salt of the sulfonic acid with methyl iodide, is somewhat tedious.

Methyl sulfonates<sup>5</sup> and methyl sulfinates<sup>6</sup> can be readily prepared by the treatment of the corresponding acid with diazomethane. However, with sulfonated lignin model compounds e.g. **5** (**Table 1**) alkylation of both phenolic and sulfonic acid functionalities occur<sup>2</sup>. Since we were interested in the selective alkylation of the sulfonic acid group, we turned our attention to other methods.

Previously, it had been reported<sup>7</sup> that carboxylic acids can be efficiently converted to their esters by the simple treatment of an alcoholic solution of the with 2.5 equivalents acid of trimethylsilylchloride (TMSCI). Unfortunately, even in the simplest case (p-toluenesulfonic acid), esterification with methanol and TMSCI gave only unreacted starting material, as evidenced by <sup>1</sup>H-NMR and infrared spectroscopy.

We therefore addressed the action of trimethyl orthoformate on

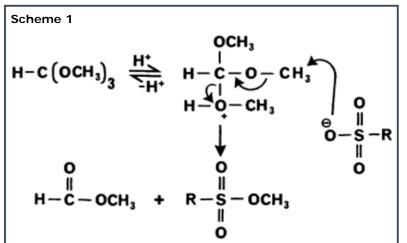
Table 1

Alkylation of Sulfonic Acids with Trialkyl Orthoformates

Sulfonic Acid		Reagent	Product	Yield
1	Me-SO <sub>2</sub> -OH	HC(OMe) <sub>3</sub>	Me-SO <sub>2</sub> -OMe	43%*
	Me-SO <sub>2</sub> -OH	HC(OEt)3	Me-SO <sub>2</sub> -OEt	80%*
2	Et-SO <sub>2</sub> -OH	HC(OMe) <sub>3</sub>	Et-SO <sub>2</sub> -OMe	83%*
	Et-SO <sub>2</sub> -OH	HC(OEt) <sub>3</sub>	Et-SO <sub>2</sub> -OEt	73% <sup>*</sup>
3	p-Me-Ph-SO <sub>2</sub> -OH	HC(OMe) <sub>3</sub>	p-Me-Ph-SO <sub>2</sub> -OMe	99%
	p-Me-Ph-SO <sub>2</sub> -OH	HC(OEt) <sub>3</sub>	p-Me-Ph-SO2-OEt	98%
4	4-OH-3-MeO- PhCH <sub>2</sub> -SO <sub>2</sub> -OH	HC(OMe) <sub>3</sub>	4-OH-3-MeO- PhCH <sub>2</sub> -SO <sub>2</sub> -OMe	85%
5	4-OH-3-MeO- PhCHCHCH2-SO2-OH	HC(OMe) <sub>3</sub>	4-OH-3-MeO- PhCHCHCH2-SO2-OMe	82%

\* Yield low due to volatility of product

p-toluenesulfonic acid, since the former has been used successfully for both acid-catalysed ketalisations<sup>8,9</sup> and esterification of carboxylic acids<sup>10,11</sup>. Thus, when acid **3** (see **Table 1**) was allowed to stand in excess trimethyl orthoformate (17 equivalents) for 14 h. at room temperature, a quantitative yield of methyl p-toluenesulfonate was obtained. In a similar fashion, triethyl orthoformate gave the corresponding ethyl ester. The general applicability of this method can be seen from **Table 1**. Each of the reactions gave a single product in high yield, unless it was very volatile and then recovery was lower. Note also that in the case of sulfonic acids **4** and **5**, containing free phenolic groups, only the acid functionality was alkylated.



**Scheme 1** represents a possible pathway for the formation of these products.

For non-volatile products, the alkylation could also be carried out by heating to reflux, e.g., the acid **3** with trimethyl orthoformate for 30 min.

Further, since paucidisperse lignosulfonic acids can be dissolved in methanolic solution<sup>2</sup>, we have investigated the use of the alkylating agent in methanol. Thus, **3** was smoothly converted to methyl p-toluenesulfonate using a 1:1 solution of methanol: trimethyl orthoformate, and slowly distilling off the methanol over a period of 1 h.

### EXPERIMENTAL

#### **General Procedure**

A solution of the sulfonic acid (200 mg) in trimethyl (or triethyl) orthoformate (2 mL) was either allowed to stir at room temperature for 14 h., or heated to ref lux for 30 min., under an atmosphere of nitrogen. The excess orthoformate was then removed under vacuum (0.5 mmHg) to give the corresponding methyl (or ethyl) ester. Where the solubility of the substrate was poor, the reagent was mixed with an equal volume

of methanol, following which slow distillation over 1 h. gave the required ester in high yield.

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