

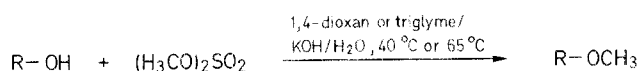
### Reactions in Slightly Hydrated Solid/Liquid Heterogeneous Media: The Methylation Reaction with Dimethyl Sulfoxide

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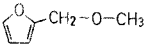
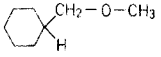
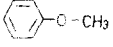
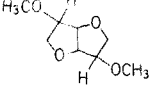
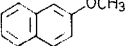
The *O*-methylation of alcohols and phenols with stoichiometric amounts of dimethyl sulfate in 1,4-dioxan or triglyme in the presence of solid potassium hydroxide and small amounts of water represents a useful method for the synthesis of methyl ethers in high yields and with high selectivity. The complete consumption of dimethyl sulfate in this reaction avoids the problems connected with the work-up of reaction mixtures still containing excess amounts of this toxic reagent.

We have recently shown that ylide generation under solid/liquid phase-transfer conditions in the presence of small amounts of water and condensation of the ylide with carbonyl compounds leads to alkenes<sup>1,2,3</sup> or epoxides<sup>4</sup> in high yields and with high selectivity. We report now a new modification of the synthesis of methyl ethers by *O*-methylation with stoichiometric amounts of dimethyl sulfate in the solid/liquid two-phase system 1,4-dioxan or triglyme/potassium hydroxide using small amounts of water as phase-transfer catalyst.



In contrast to some other modifications of the *O*-methylation reaction with dimethyl sulfate<sup>5,6,7</sup>, dimethyl sulfoxide is not required as solvent. The use of solid potassium hydroxide avoids the hydrolysis of dimethyl sulfate and it avoids possible difficulties arising at various stages of this reaction from the presence of an aqueous phase<sup>8,9</sup>. Work-up of the

**Table.** Methyl Ethers Prepared

Product	Yield <sup>a</sup> [%]	b.p. [°C]/torr	
		found	reported
$n\text{-C}_4\text{H}_9\text{-O-CH}_3$	94	70°C	70°C <sup>9</sup>
$n\text{-C}_6\text{H}_{13}\text{-O-CH}_3$	95	126°C	126°C <sup>9</sup>
$t\text{-C}_4\text{H}_9\text{-O-CH}_3$	99	55°C	55.2°C <sup>9</sup>
	92	129–131°C	130°C <sup>10</sup>
	93	134°C	134°C <sup>9</sup>
	97	170°C	170–171°C <sup>9</sup>
	96	60°C/1	125–122°C/20 <sup>8</sup>
	90	180°C/12	273°C <sup>9</sup>

<sup>a</sup> Yield of distilled product. The <sup>1</sup>H-N. M. R. spectra of all products were identical with those of authentic samples.

reaction mixture is easy and the quantitative consumption of dimethyl sulfate eliminates the problems connected with the toxicity of the reagent at the end of the reaction.

#### Methyl Ethers from Alcohols, Diols, or Phenols; General Procedure:

To a stirred solution of the alcohol, diol, or phenol (0.07 mol) in 1,4-dioxan (70 ml) or triglyme (70 ml) at 65°C (oil bath temperature) (40°C for 2-hydroxymethylfuran) is added crushed commercial potassium hydroxide (14 g for alcohols and phenols, 28 g for diols) containing ~15 weight % water. Then, dimethyl sulfate (0.07 mol for alcohols and phenols, 0.14 mol for diols) is added at a rate of 3 drops in 5 min. The progress of the reaction is followed by G.L.C. After completion of the reaction (1.5 h), the mixture is filtered to remove the solid material and the filtrate is distilled to give the pure methyl ether.

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