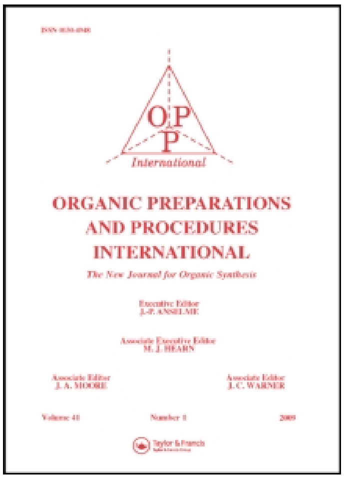

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O-METHYLATION OF POLYMER-SUPPORTED PHENOXIDES WITH DIMETHYL SULFATE

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O-METHYLATION OF POLYMER-SUPPORTED PHENOXIDES WITH DIMETHYL SULFATE

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The alkylation of phenols[1] using ion-exchange polymers benefits from the increased nucleophilicity of the polymer-supported anions. Although the O-methylation of polymer-supported phenoxides using methyl iodide is successful in some cases, it does not always result in high yields of products. Moreover, apart from inherent inconveniences in the use of methyl iodide (low volatility and greater cost of the reagent), the reaction may take a long time for completion.[2] We have found that dimethyl sulfate is much more effective than methyl iodide for the methylation of polymer-supported phenoxides.

$$R'\overset{+}{N}R_3\ ArO^- + (MeO)_2SO_2 \longrightarrow ArOMe + R'\overset{+}{N}R_3\ MeOSO_3^-$$

The O-methylation of a number of polymer-supported phenoxides was carried out in methanol, benzene and dioxane. The yields of products and the progress of the reaction were both dependent on the nature of the solvent (Table). In methanol, all the monohydric phenols except the sterically hindered 2,6-diisopropylphenol were methylated in excellent yields and in a very short time. The effect of bulky ortho substituents on the rate of the reaction was studied with thymol and 2,6-diisopropylphenol; unfortunately, all our attempts to prepare polymer-supported 2,6-di-t-butylphenoxides failed.[3] Both thymol and diisopropylphenol could be converted to the corresponding methyl ethers in relatively good yields, although introduction of two bulky substituents led to lowered yields. Conversion of dihydric phenols took longer time, apparently because of unfavorable interactions involved in the methylation of the second phenolic group, which remains largely as the sodium phenoxide. The yields of the methyl ethers were also moderate; these ethers were characterized by IR and ^{1}H NMR. The purity of the liquid ethers was checked by gas chromatography. The method has the potential of replacing even the conventional method of O-methylation of phenols using dimethyl sulfate,[4] since the reactions are simple and often yield nearly quantitative amounts of the very pure ethers.

TABLE. Methylation of Resin Phenoxides with Dimethyl Sulfate

	Solvent						mp or bp(°C)
	Methanol		Benzene		Dioxane		(lit.[5])
Entry	Yield (%)	Time (hrs)	Yield (%)	Time (hrs)	Yield (%)	Time (hrs)	
$C_6H_5O^-$	92	1	85	7.5	84	9	152-154 (154)
$MeC_6H_4O^-$(o)	96	1.5	93	8	87	9.5	169-171 (171)
$MeC_6H_4O^-$(m)	92	1.6	87	1.5	86	9	176-177 (177)
$MeC_6H_4O^-$(p)	95	1.4	90	8	85	8.5	175 (175)
1-Naphthoxide	98	0.4	92	1	88	3	164-166[a] (163-165)
2-Naphthoxide	95	0.33	84	7	82	8	72 (72)
p-Bromophenoxide	98	0.4	96	5	92	6	100[a] (98-100)
Thymolate	90	1.5	85	8	80	10	94-96[a] (94-97)
2,6-Diisopropylphenoxide	75	1	60	7	45	14	145-148[a] (146-149)
$^-OC_6H_4O^-$(o)	74	5	60	10	40	17	88-90[a] (86-89)
$^-OC_6H_4O^-$(m)	67	6	54	14	40	18	94-96[a] (94-95)

a) bps at 10 mm Hg

EXPERIMENTAL SECTION

The Amberlite IRA-400 phenoxide anions were prepared by the method of Salunkhe et al.[2] The capacity of the various resin phenoxides, as determined by the procedure of same authors, varied from 0.6-2.3 meq/g. All commercially available chemicals were purified by double distillation or by crystallization.

Alkylation of Resin-Phenoxides. General Procedure.- Amberlite IRA-400 2-naphthoxide anion (containing 15 mmol of 2-naphthol) in doubly distilled methanol (25 ml) was stirred with dimethyl sulfate (15 mmol) with TLC monitoring (ether-petroleum ether 1:4). After completion of the reaction (20 min.), the resin was removed by filtration and washed with methanol (10 ml). The filtrate and the washing were combined and the solvent was evaporated to yield 2-methoxynaphthalene as fine crystals (2.32 g, 98%), mp. 72°, lit.[5] 72° on crystallization of the crude product (benzene-chloroform 4:1). In experiments using different solvents, identical volumes of the solvents were maintained.

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