

Polymer Supported Reagents. Synthesis of *p*-Bromophenacyl Ethers

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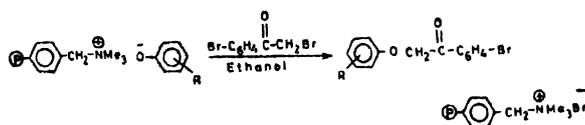
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Phenoxide supported on Amberlite IRA-400 on reaction with *p*-bromophenacyl bromide gave corresponding *p*-bromophenacyl ether in quantitative yield and purity.

HENDRICKSON has reported that the *p*-bromophenacyl ether can be synthesised according to the traditional method¹ but the problems associated with the classical procedure are slow reaction times¹, hydrolysis of the alkylating agents², low yields of the product and contamination of products with starting alkylating reagent. Durst³ has overcome some of these problems by carrying out the reaction using the potassium salt of an acid and dicyclohexyl-18-crown-6 as the solubilising catalyst under reflux conditions and Clark⁴ utilised potassium fluoride in glacial acetic acid for the preparation of phenacyl esters.

The reagents supported on insoluble polymers have found wide applications during the last decade or so in various fields, particularly, in organic synthesis⁵. In continuation of our work on polymer supported reagents⁶⁻⁸ and in view of the importance of *p*-bromophenacyl ethers as a protecting group⁹, a simple and efficient method is reported herein for the synthesis of the same in quantitative yield and purity under mild reaction conditions.



Experimental

A typical procedure for the preparation of polymer supported phenoxide: Commercial strongly basic anion-exchange resin in the chloride form (Amberlite IRA-400 (Cl⁻)) packed in a column was washed with 0.25 *N* aqueous sodium salt of phenol (prepared by dissolving 25 mmol of phenol in 100 ml 0.25 *N* NaOH) until complete removal of chloride ion. The resin was then successively washed with water and ethanol and finally dried in vacuum at 50° over P₂O₅ for 10 h. The exchange capacity was determined by passing aqueous 1 *M* NaCl solution (100 ml) through the resin (0.3 g) in a column.

The amount of phenoxide in the eluent was titrated 0.01 *N* HCl using methyl orange as an indicator.

A typical procedure for synthesis of p-bromophenacyl ether of phenol: Amberlite IRA-400 phenoxide form (5 g; capacity 1 mmol phenoxide anion/g of dry resin) in ethanol (15 ml) was stirred with *p*-bromophenacyl bromide (5.01 mmol) in a stoppered flask. The progress of the reaction was monitored by tlc. After completion of the reaction, the resin was removed by filtration and washed with ethanol. Removal of the solvent by distillation gave the corresponding *p*-bromophenacyl ether in almost pure form and in high yield (Table 1). The products were characterised by nmr, ir and samples.

TABLE 1

Phenol	Time h	<i>p</i> -Bromo- phenacyl ether yield (%)	Derivative M p. (lit.) °C
β-Naphthol	2	95	120 (120-1) ⁹
<i>p</i> -Hydroxybenzaldehyde	2	95	104 (103-4) ⁹
<i>o</i> -Nitrophenol	2	91	172
<i>p</i> -Nitrophenol	2	90	156-7
<i>o</i> -Chlorophenol	1	90	130-1
<i>p</i> -Chlorophenol	1	92	111
<i>p</i> -Hydroxymethylbenzoate	2	89	124
4-Hydroxycoumarin	1	89	225
4-Methyl-7-hydroxycoumarin	1	94	203-5

Results and Discussion

The method has the advantage in terms of yield and its simplicity. Interestingly, this method is inexpensive as the resin could be used repeatedly, since it can be regenerated to its initial activity by treating with a solution of hydrochloric acid. Reaction with catalytic amount of the resin does not give satisfactory results. Thus, the nucleophilicity of polymer-bound phenoxide ion is increased sufficiently to allow reaction with *p*-bromophenacyl bromide in a manner which is related to the principles of phase transfer technique with low molecular catalysts.

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