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BORIC ACID-CATALYZED ESTERIFICATION OF PHENOLS

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We have recently observed that the direct esterification of phenols, which usually fails even in the presence of strong mineral acids, is catalyzed by a combination of boric and sulfuric acids. For example, phenyl benzoate is produced in nearly quantitative yield when water is removed by azeotropic distillation from a refluxing toluene solution containing phenol, benzoic acid, and catalytic amounts of boric and sulfuric acids.

The esterification has been applied successfully to a variety of substituted phenols and aliphatic and aromatic carboxylic acids as shown in Table I.

Neither boric acid nor sulfuric acid alone catalyzes the reaction. Such compounds as butyl titanate cannot replace the boric acid; of the common mineral, organic, and Lewis acids investigated, only polyphosphoric acid can be substituted for the sulfuric acid.

TABLE I

Esterification of Phenols With Carboxylic Acids[a]

Product	Solvent	Reaction Time, Hr.	Isolated Yield, %
Phenyl benzoate	Toluene	8	94
p-Methoxyphenyl benzoate	Xylene	23	88
p-Nitrophenyl benzoate	Xylene	23	85
Phenyl butyrate	Xylene	17	86
Diphenyl isophthalate	Sulfolane/xylene	24	58
Diphenyl terephthalate	Sulfolane/xylene	23	87
Diphenyl tetramethyl-terephthalate[b]	Xylene	48	80
2-Naphthyl isobutyrate	Xylene	5	58

[a]In all cases the reaction was conducted by removing water by azeotropic distillation from a solution of the phenol and carboxylic acid in a solvent containing 1 to 5 mole % of boric and sulfuric acids. Products were isolated by appropriate crystallization or distillation.

[b]This compound, m.p. 265-266°C., had correct analysis for carbon and hydrogen.

We have found no reference to the use of catalytic amounts of boric acid or a combination of boric and sulfuric acids in esterifying phenols; the mechanism is not clear. The economy of the process, obviating the need for carboxylic chlorides, suggests that it may have general use in the preparation of phenyl esters.