FRIEDEL-CRAFTS ACYLATION WITH CARBOXYLIC ACIDS CATALYZED BY TOSIC ACID

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1 of 2

INTRODUCTION

Alkyl aryl ketones (Acetophenone, propiophenone and derivatives thereof) may be obtained by heating a carboxylic acid with certain aromatic compounds in the presence of (1) a volatile, organic compound which forms an azeotrope, i.e., a constant boiling mixture, with water and (2) a catalytic amount of an organic sulfonic acid, whereby the water of reaction is removed as an azeotrope from the reaction mixture. The carboxylic acid employed is not critical and may be selected from a wide variety of unsubstituted and substituted, aliphatic, cycloaliphatic and aromatic carboxylic acids containing from 2 to 20 carbon atoms. [...] Phenols and benzenediols, as well as ethers and esters thereof, may be acylated using methanesulfonic and toluenesulfonic acids. In the case of less reactive aromatic compounds such as alkylaromatic compounds, e.g., toluene and xylene, a more acidic sulfonic acid such as a perhaloalkylsulfonic acid, e.g., trifluoromethanesulfonic acid normally is required to achieve satisfactory reaction rates.

EXPERIMENTAL

EXAMPLE 1:

A mixture of p-toluic acid (22.2g, 0.163mol), p-xylene (100ml), and trifluromethanesulfonic acid (5ml, 0.056mol) was heated at reflux for 21 hours in a 300ml flask equipped with a Dean-Stark trap, after which time 3ml of water had been collected in the trap. The progress was measured with GC as well as by the amount of water collected. After 6 hours, 22% of the starting material had been converted to 2,5,4′-trimethylbenzophenone. The mixture was extracted with water, with 5% sodium hydroxide and again with water. Evaporation of the organic layer gave 24g (0.11mol) of 2,5,4′-trimethylbenzophenone, 66% of theory.

EXAMPLE1; MODIFIED:

The procedure in **Example 1** was repeated without a Dean-Stark trap. After 4 hours of reflux, only about 6% of the starting material had been converted to product. The amount of product was not increased significantly after refluxing an additional 6 hours.

EXAMPLE 2:

Benzoic acid (20g, 0.16mol), p-xylene (100ml), and trifluoromethanesulfonic acid (5ml) were heated at reflux in a 300ml flask equipped with a Dean-Stark trap. After 16 hours, the mixture was extracted with 100ml of 6% sodium hydroxide, washed with 100ml of water, dried over Mg sulfate and evaporated to give 15.4g (0.073mol) of 2,5-dimethylbenzophenone. The aqueous sodium hydroxide extract was acidified to give 8.1g (0.066mol) of unreacted benzoic acid.

EXAMPLE 3:

Hydroquinone (11.0 g, 0.1 mole), octanoic acid (30.2 g, 0.21 mole), heptane (110 mL), and methanesulfonic acid (10 mL, 0.14 mole) were heated at reflux (98°C.) for 5 hours in a 300 mL flask equipped with a Dean-Stark trap. During this time, 3 mL of water was collected. The sulfonic acid layer was separated, and the heptane layer was washed once with 50 mL of water and twice with 50 mL portions of saturated, aqueous sodium bicarbonate solution. The mixture was filtered to remove 5g of product, octanoylhydroquinone octanoate ester, while evaporation of the organic layer gave 17.3g. The total yield of octanoylhydroquinone was 22.3 g, 94% of theory.

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