

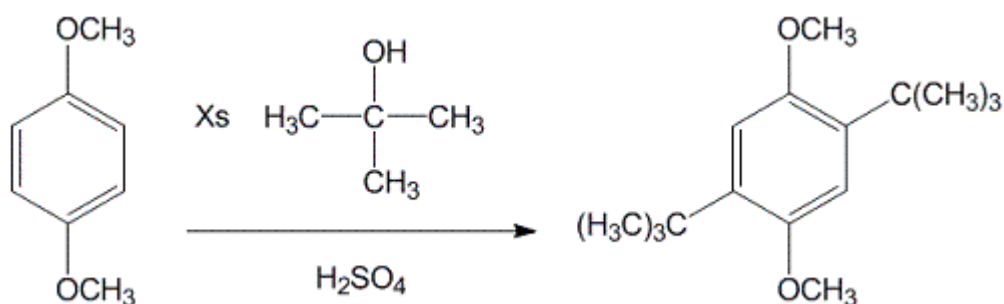
Electrophilic Aromatic Substitution #2

by John Kalman

Experiment Overview

p-Dimethoxybenzene reacts with excess *t*-butanol in the presence of sulfuric acid to give a high yield of 2,5-di-*t*-butyl-1,4-dimethoxybenzene, which is readily obtained in pure form by recrystallisation from methanol. The product is characterised by mp and proton NMR. The reaction is an example of a Friedel-Crafts alkylation. Students contrast the reaction with that of excess *m*-*p*-xylene with 1-bromopropane and aluminium chloride, the results of which are inferred from the gas chromatography trace supplied.

The experiment introduces students to the Friedel-Crafts Alkylation, one of the most important reactions of benzene and its derivatives. The experiment is straightforward and satisfying to perform, as the product is easy to purify and characterise.



Learning Experience

The experiment is effective in part because students are not distracted by difficult or complex manipulations in the laboratory. The student is exposed to a wide range of concepts related to electrophilic substitution reactions, including identifying suitable reagents to supply a particular alkyl group, the consequences of introducing an activating group (such as alkyl), alkyl rearrangements, steric hindrance, and reaction of an electrophile can compete with its rearrangement.

Level of Experiment

The experiment is performed at the University of Technology, Sydney, in first semester of second year. Acquisition and interpretation of the proton NMR spectrum has been added for the ACELL workshop – this would be suitable for second semester of second year.

Keyword Descriptions of the Experiment

Domain

organic chemistry

Specific Descriptors

electrophilic aromatic substitution, *p*-dimethoxybenzene, *t*-butanol

Course Context and Prerequisite Knowledge and Skills

Follows lectures on reactions of benzene, specifically Friedel-Crafts Alkylation.

Students are familiar with electrophilic reactions of benzene, including concepts of activating/deactivating groups, directing effects, and the rationalisations for these in terms of the reaction mechanism. The limitations of the alkylation reaction, namely polyalkylation and carbocation rearrangements, have also been described, and contrasted with what happens in acylation.

The practical skill of recrystallisation is the focus of an earlier experiment, and applied again in four experiments before this one.

Time Required to Complete

Prior to Lab: 15-30 min to complete prework

In Laboratory: 3 h, including acquisition of GC data

After Laboratory: 3-5 h to write full report

Experiment History

The experiment has been part of the laboratory component of *organic chemistry 1* at the University of Technology, Sydney, (UTS) since 1999. The method for the alkylation of *p*-dimethoxybenzene was taken from Williamson (1994). An experiment involving the alkylation of *p*-xylene had a long history in the Chemistry Department at UTS. The method quoted in the submitted experiment, and the GC result, are taken from this earlier experiment. The remainder of the text (introduction, prework, postwork, and juxtaposition with gc interpretation of *p*-xylene alkylation) was developed at UTS by the author of the educational analysis.

Since the practical work involved is fairly short, the experiment was extended (at Justin Read's suggestion) for the ACELL workshop by adding the GC and ¹H NMR analyses of crude and recrystallised product. These results will demonstrate the regiospecificity of the second alkylation step, and demonstrate the value of recrystallisation as a purification method.

References

Gilbert, J. C. & Martin, S. F. (1998). *Experimental Organic Chemistry* (2nd ed.). Fort Worth, TX: Saunders, pp. 395-403.

Mohrig, J. R., Hammond, C. N., Morrill, T. C., & Neckers, D. C. (1998). *Experimental Organic Chemistry*. New York, NY: WH Freeman, pp. 232-236.

Williamson, K. L. (1994). *Macroscale and Microscale Organic Experiments* (2nd ed.). Boston, MA: Houghton Mifflin, pp. 440-443.