Isobutylene Dimerization Repackaged as a Problem-Based Exercise

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INTRODUCTION

The dimerization of isobutylene produced by the dehydrogenation of tert-butyl alcohol was extensively studied in the 1930’s. This dimerization reaction has been commonly used as an example of alkene dimerization in organic chemistry textbooks and has been the basis of a preparatory laboratory exercise that allows students to verify the expected results. One limitation of this experiment as a preparatory exercise is that two isomeric cations are produced and analyzed as a mixture. Additionally, the reaction produces the less substituted acetone isomer as the major component of the product mixture. We have repackaged this experiment as a problem-based, culminating experience in our organic chemistry laboratory. Students are given a procedure for conducting the reaction and isolating the product, for which the composition and structures are not provided. Students then use a combination of GC-MS, IR, 1H NMR, 13C NMR, and molecular modeling to determine that the product contains a mixture of two isomeric acetones and to solve the structures of the two compounds. Additionally, students are asked to propose a reasonable stepwise mechanism for the transformation and to explain the unusual product distribution in the results from computations. The exercise gives students the opportunity to apply a range of instrumental techniques to a chemical reaction for which the product structures are not known to them.

THE EXERCISE

A. Procedure

1. A 15.0 mL sample of 2-methylpentane solvent was added slowly to 32 mL of 9 M sulfuric acid in a 100 mL round-bottomed flask. The reaction mixture was heated to a gentle reflux for 20 minutes. The heat was removed from the reaction flask and the reaction mixture was allowed to cool to room temperature. The two-phase reaction mixture was transferred to a separatory funnel. The lower acid layer was removed and the organic layer was washed with water (2 x 10 mL) and 5% sodium bicarbonate solution (1 x 20 mL). The organic layer was dried over sodium sulfate and purified by simple distillation. The fraction that distilled from 188-196 °C was isolated and analyzed.

B. Gas Chromatography-Mass Spectrometry

The sample was injected in a Varian 3900 GCMS using a 30 meter Varian CP-58 CB low bleed column and a constant temperature of 50 °C. The chromatogram clearly indicates the presence of two compounds in a ratio of 9:5 (Figure 1).

C. Mass Spectrometry

The mass spectrum of the major product gave a molecular ion of 112 amu and a major fragment of mass 57 amu from allylic cleavage of the C3-C3 bond (Figure 1). The mass spectrum of the minor product gave a molecular ion of 112 amu and major fragments at 97 from the allylic fragmentation of the C3-C3 bond, and 57 and 53 amu from the vinylic fragmentation of the C3-C3 bond (Figure 2).

D. Infrared Spectroscopy

The infrared spectrum of the product mixture provided strong indications of alkene functionality. There is a vinyl C=C stretch at 3070 cm⁻¹, an aliphatic C-H stretches from 2882-2925 cm⁻¹, and a C=C stretch at 1641 cm⁻¹. There is a prominent geminal dissociation signal at 892 cm⁻¹ from the major product and a small trisubstitution signal at 1079 cm⁻¹ from the minor product.

E. 1H NMR Spectroscopy

The 1H NMR spectrum was taken on a Bruker DPX-200 at 200 MHz using CDCl3, containing 0.3% TMS (Figure 3). All of the signals for both products are completely resolved. The signals present as clean singlets or as singlets with very small, indiscernible coupling. The major product shows a butyl signal at 0.53 ppm, an alkylic methyl signal at 1.77 ppm, an allylic methylene signal at 1.33 ppm, and two vinylic signals at 4.62 and 4.82 ppm. The minor product shows a methyl signal at 1.08 ppm, two allylic signals at 1.86 and 1.79 ppm, and a vinylic signal at 5.16 ppm.

The structure of the optimized carbocation intermediate indicates that H4 on methyl C12 is replaced with the empty orbital of saturate C13, while H3 and H2 on methyl C11 are at approximately a 22° angle from the C11-C12-C13 plane. A 360° coordinate scan of the C12-C11-C12-C13 tetrade ring indicates a 4.46a/mol barrier to rotation of H2 into a coplanar position relative to the empty C12 orbital.

Students are generally able to interpret much of the data with minimal supplemental instruction.

Microscale: Students determine that the reaction generates two products in a mixture of 9:5.

Mass Spectrometry: Students determine that the two products are isomers with a molecular weight of 112 amu. Most students generate a formula of C12H24O (one unsaturation), although some students will also consider C12H23O briefly. Students are not experienced enough with mass spectral data interpretation to use the fragmentation data to solve for the structures, but they are able to identify reasonable fragmentation events once the product structures are known.

Infrared Spectrometry: Students identify that the spectrum clearly indicates the presence of a C=C, although many students do not initially account for the geminal dissociation signal at 892 cm⁻¹. The trisubstitution signal at 892 cm⁻¹ is nearly always overlooked by students until the structure of the minor product is solved.

CONCLUSIONS

The preparation of isobutylene dimers has been successfully repackaged as a problem-based experiment for the organic laboratory. Students have found studying this alkene dimerization reaction to be rewarding and intellectually challenging. They are able to apply many of the laboratory skills that they have learned throughout the organic chemistry laboratory course.

The desired outcomes of the exercise include:

- reinforcement of basic laboratory techniques
- introduction to the analysis of mixed samples
- reinforcement of GC, MS, IR, 1H NMR, 13C NMR and molecular modeling data acquisition and analysis
- application of data analysis and critical thinking skills

REFERENCES


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