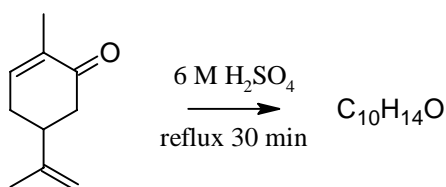


Acid-Catalyzed Isomerization of Carvone A Chemical Puzzle

Carvone is a polyunsaturated chiral molecule that is famous among organic chemists for its two distinctive odors: caraway and spearmint. Although carvone is naturally occurring and can be stored for long periods without decomposition, it cleanly rearranges to a more stable isomer when heated with acid. The goals of this experiment are to obtain this isomer, determine its structure using NMR and IR, and draw a multi-step mechanism for its formation. The experiment should appeal to you on several levels: the laboratory techniques are familiar, the structure puzzle is challenging, but not overly so, and the mechanism involves concepts and intermediates that you have been studying for the last few weeks. Have fun!



Procedure. Combine 1 mL of carvone and 10 mL 6 M aq. H_2SO_4 in a 50 mL round-bottom flask. Add a magnetic stir bar, attach a reflux condenser, and gently reflux the mixture¹ with rapid stirring for 35 minutes. Some coloring may occur.

Cool the mixture to room temperature and transfer it to your smallest separatory funnel.² Extract the reaction mixture with diethyl ether (2 x 5 mL), then wash the combined ether layers with saturated aq. NaHCO_3 (5 mL)³ and dry them over anhydrous Na_2SO_4 in a 25 mL Erlenmeyer flask.⁴ Use a disposable pipet to transfer the liquid from the spent drying agent to a clean, dry, pre-weighed 25 mL round bottom flask. Remove the solvent on a rotary evaporator. Weigh your “crude” product, obtain its IR spectrum, and submit an NMR sample (DAY.INI.ISO).

Separations. Carvone and its isomer are not very water-soluble. Don’t be surprised to see a distinct organic layer at the start of the experiment, and again at the end when the reaction mixture has cooled. Both of these compounds, along with any (colored?) organic by-products, will migrate to the organic layer along with small amounts of water and acid. The organic layers are washed with a weak base to remove all traces of acid from the organic layer. A stronger base than bicarbonate is not suitable (perhaps you will figure out why when the experiment is complete).

¹ Gentle reflux means the reflux ring should be maintained at or near the bottom of the condenser.

² 50 mL is an ideal size. If the funnel is larger than this, it will be too difficult to see the solvent interface. If it is smaller, it will be hard to control the gases liberated during the bicarbonate wash.

³ Approach this carefully. You are liberating a lot of gas in a very small volume.

⁴ Place enough drying agent in the flask to cover most of the bottom with a thin layer of solid. Swirl for several minutes to effect drying (the solids will clump). Use a disposable pipet to transfer the liquid to a second flask and repeat with fresh drying agent. If necessary, repeat again. Eventually you will obtain a “dry” solution that is not cloudy and in which the drying agent is dispersed instead of clumped.

Notebook. Make the usual entries in your notebook for this experiment. You can skip the hazard/disposal section and fill in the table of physical constants later (just leave room for it now).

Spectra. NMR and IR spectra of carvone are available at the course web page (see **News** section). It is worthwhile understanding these spectra. Partly so that you won't be misled by any carvone "impurity" that might be present in your product mixture, and partly because understanding the carvone spectra may help you work out the structure of the isomer.

The most distinctive signal in the IR spectrum is the strong absorption at 1680 cm^{-1} (C=O). A weaker band at 1650 cm^{-1} can be assigned to a C=C double bond stretching vibration. The strong band at 900 cm^{-1} may also be related to the alkene group. You should look up more information about this in the reserve materials – pay attention to how the substitution pattern of the alkene relates to the number, size, and position of low energy bands in the IR spectrum.

The NMR spectrum contains several noteworthy signals, some easily interpretable and some not. The ring protons have similar chemical shifts and are strongly coupled, so they produce a complex assortment of signals in the NMR spectrum, 2.2-2.6 ppm (these are true "multiplets"). We can do a little more with the methyl protons, ~1.7 ppm, but the expected doublet is actually more complicated than that, and it overlaps with the expected singlet. The alkene signals also contain some surprises. There are two singlets at ~4.7 ppm, and a multiplet at ~6.7 ppm. It would be helpful to look up some information about alkene chemical shifts and coupling constants (the lab manual contains useful tables for chemical shifts and coupling constants).

Report. Your report should contain a title, abstract, results and discussion, and experimental. For the most part, you can pattern these sections after your isopentyl acetate report. Two novel aspects of this report: 1) you undertook the experiment without knowing what it would yield, but you should know what you obtained by the time you write the report, so write your report accordingly, and 2) draw a mechanism for the isomerization reaction (see below for ideas). As always, attach your spectra to your lab report (and include appropriate expansions of your NMR spectrum so that coupling patterns and integrals can be read easily).

Mechanism. The isomerization reaction is triggered by acid, and carvone contains at least two weakly basic atoms that yield carbocations upon protonation:



Carbocations can undergo two reactions – 1,2 rearrangements and deprotonation – and both may play a role here.