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Semiquantitative Infrared Analysis of Diketones and Anhydrides in a Reaction Mixture

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ABSTRACT

The ozonolysis of a hydroxymethylene ketone yields a mixture of diketone and anhydride. Treatment of hydroxymethylene camphor with ozone affords, in addition to the expected camphor quinone, a surprisingly large amount of camphoric anhydride (56%) via Baeyer-Villiger reaction. Use of infrared absorption to analyze the relative amounts of camphor quinone and camphoric anhydride in a reaction mixture was studied by comparing peak heights of their carbonyl stretching bands.

INTRODUCTION

It has been shown (Yang and Pelletier 1968) that oxidative ozonolysis of the hydroxymethylene ketone (I) shown in Figure 1 yields a dicarboxylic acid. The synthesis involved treatment with ozone, peroxide, and base. If the peroxide and base treatments are omitted, straight ozonolysis yields the diketone (II) and anhydride (III) shown in Figure 1. That the dicarboxylic acid is not a precursor to the anhydride via dehydration was demonstrated by ozonation of the hydroxymethylene ketone in acetic acid-ethyl acetate solvent, yielding the mixture of anhydride and diketone. Other solvents (such as methylene chloride) also lead to mixtures, but with lesser amounts of the anhydride. It was concluded that anhydride formation resulted from a Baeyer-Villiger type oxidation of the α -diketone by a peracid generated during ozonolysis. Nonetheless, the yield of the seven-membered ring anhydride is surprisingly large.

Because of the extremely small amount of the starting hydroxymethylene compound, attention was directed toward analogous camphor compounds. Figure 2 shows several synthesis routes starting with camphor. The diketone, camphor quinone, can be made in high yield by treating camphor with selenium dioxide. Treatment of camphor with sodium and ethyl formate yields hydroxymethylene camphor. It has been shown that ozonolysis, followed by treatment with peroxide then base, produces camphoric acid in high yield. In fact, seven dicarboxylic acids have been synthesized by this method (Yang 1976).

Future synthesis attempts will be to make seven- and eight-membered ring anhydrides by the route demonstrated in Figure 2. Addition of a peracid should encourage the Baeyer-Villiger mechanism and cede high yields. Seven- and eight-membered ring anhydrides cannot be made by standard dehydration of straight chain dicarboxylic acids.

METHODS AND MATERIALS

Efforts to date have been directed toward use of infrared spectra to analyze the relative amounts of diketone and anhydride in the reaction mixture which results from straight ozonolysis of hydroxymethylene ketones without successive treatment with peroxide and base or with peracid. The infrared spectrum of the reaction mixture resulting from ozonolysis of compound I (Figure 1) was measured with a Perkin-Elmer Infracord spectrophotometer. All spectra were scanned in the region 4-7 microns to reveal carbonyl stretching frequencies of diketones and anhydrides.

Samples of d1-camphoric anhydride and d1-camphor quinone were secured from Aldrich Chemical Company. Potassium bromide pellets of each were measured on a Perkin-Elmer Model 21 infrared spectrophotometer. The instrument resolution at 6.5 microns is quoted by the manufacturer to be 17 cm^{-1} . Mixtures of known mole ratios of the two compounds also were measured in KBr discs. Mixtures were made so that the smallest quantities weighed were

approximately 10 milligrams which allowed three significant figures in the masses. Pellets made from these mixtures were 0.12 grams total mass, more than 99% of which was KBr. Mixing was done in vials on a mechanical shaker; pellets were pressed at 20,000 pounds per square inch for five minutes and their spectra determined immediately. Peak heights were estimated by the tangent baseline method (c.f. Conley 1966) for the semiquantitative determinations.

RESULTS AND DISCUSSION

Figure 1 shows a tracing of the spectrum obtained for the reaction mixture containing diketone II and anhydride III. The band at 1800 cm^{-1} is due to anhydride, that at 1730 cm^{-1} to diketone. The remaining doublet members from each species overlap and merge into the band at 1760 cm^{-1} . The peak height ratio for diketone/anhydride was found to be 2.8/1. To verify that the

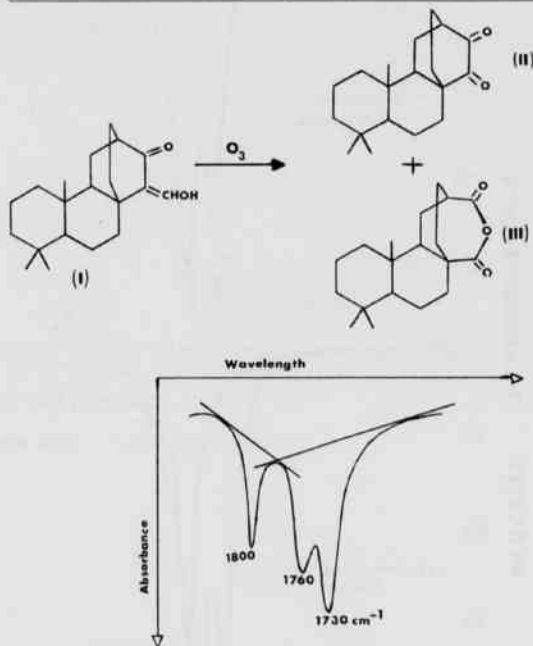


Figure 1. Reaction scheme and infrared spectra of ozonolysis reaction mixture.

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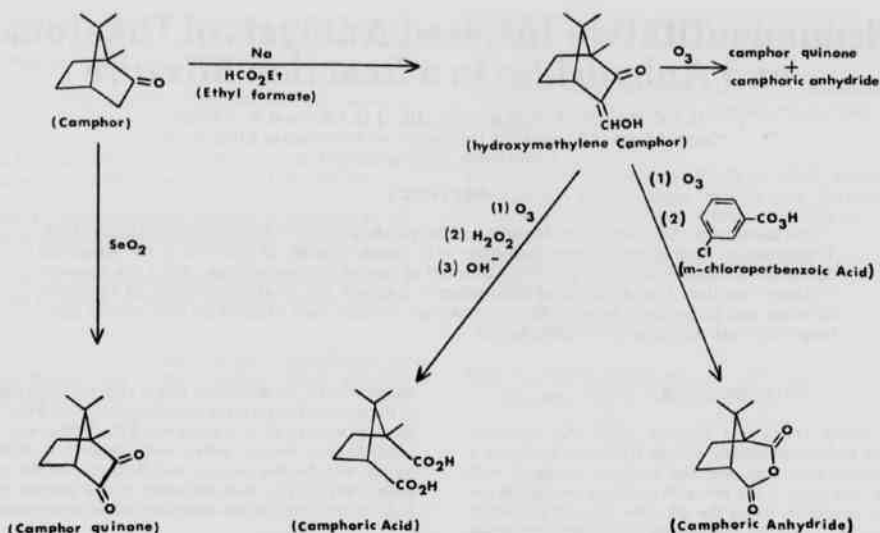


Figure 2. Synthesis routes of camphor derivatives.

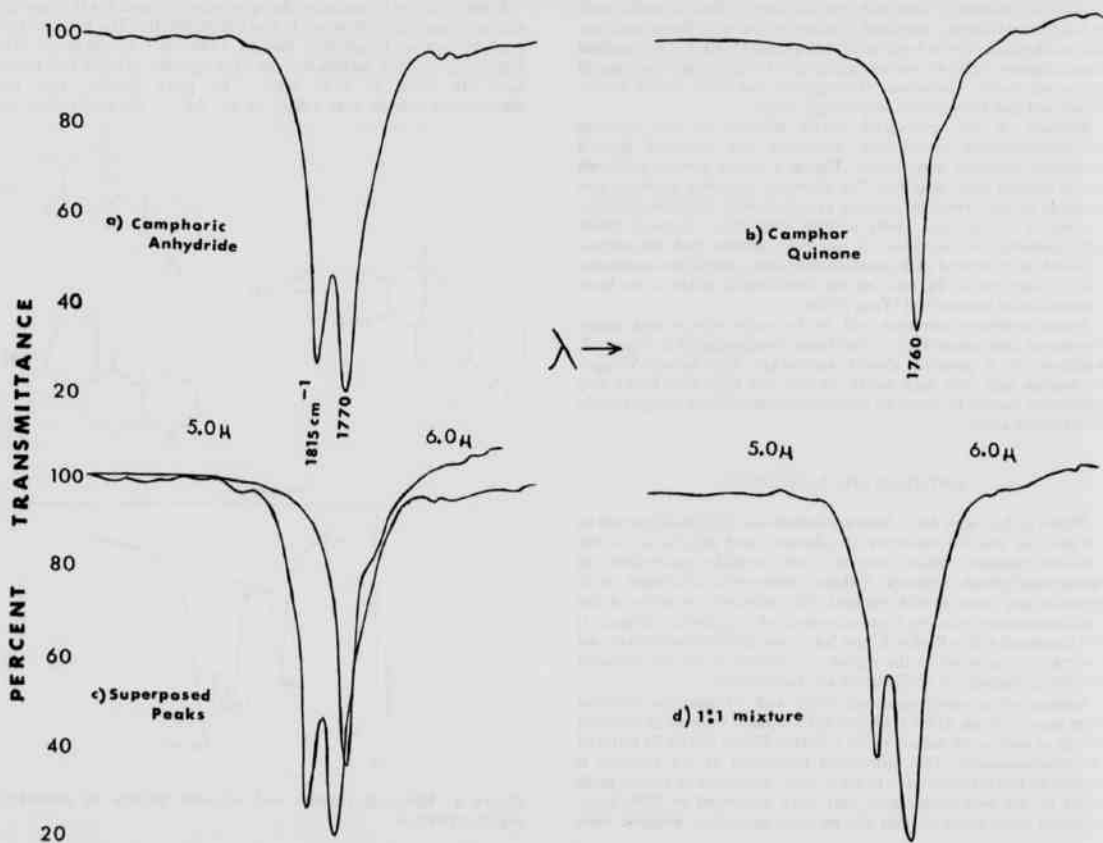


Figure 3. Infrared spectra of camphoric anhydride, camphor quinone, and 1:1 mixture.

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anhydride does not result from ozonolysis of the diketone, the mixture was recovered from the disc, subjected to excess ozone, and repressed into a KBr pellet. After over-ozonization, the peak ratio was found to be 2.7/1, which confirmed that the diketone is stable to excess ozone and lent credence to the Baeyer-Villiger mechanism for anhydride formation.

Shown in Figure 3, a and b, are the infrared spectra of camphoric anhydride and camphor quinone, respectively. A shoulder is observed on the red side of the camphor quinone band, but is not resolved as a distinct peak. Figure 3c shows the two bands superposed and reveals major overlap. The spectrum of a 1:1 mole ratio mixture of the two compounds is shown in Figure 3d. Such major overlap negated the possibility of using peak areas for analysis of the mixture. In fact, some doubt arose as to whether a ratio of the 5.5-micron camphoric anhydride peak height to the height of a peak due to overlapping bands would be useful for semi-quantitative analysis. The peak ratios, however, did yield the smooth working curve shown in Figure 4.

As a check on the reliability of the peak ratios, four different pellets of mixtures with 0.60 mole fraction camphoric anhydride were made and their spectra obtained. Resultant ratios were 0.752, 0.746, 0.763, and 0.737, yielding an average value of 0.750 with standard deviation of 0.011. This finding indicates that mole fractions can be obtained to two significant figures from the working curve.

Analysis of the reaction mixture revealed it to have $X(\text{camphoric anhydride}) = 0.53$, corresponding to 56% camphoric anhydride by mass. The identities of the two species were verified by chromatographic separation and elemental analysis of each.

ACKNOWLEDGEMENTS

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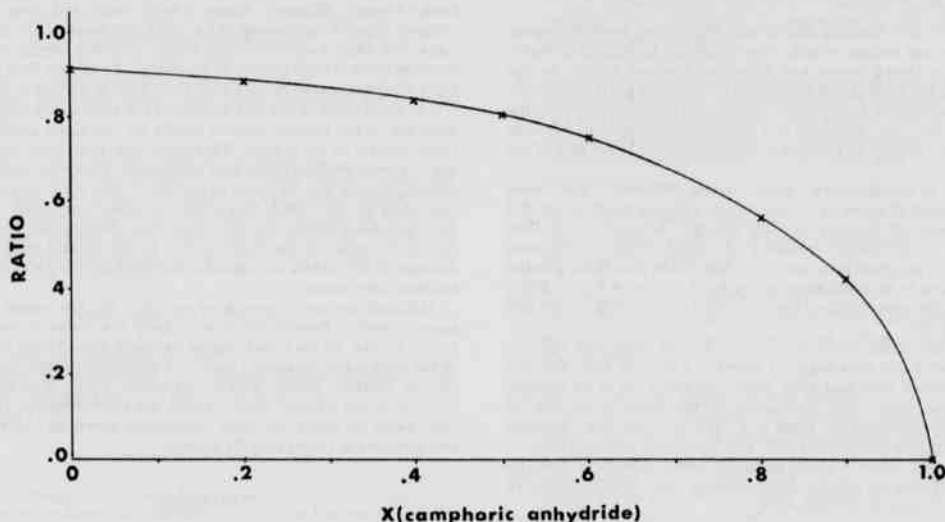


Figure 4. Ratio of peak intensities versus mole fraction camphoric anhydride.