[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

MECHANISM OF THE PYROLYSIS OF ESTERS[1]

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Received July 3, 1950

Although there has been considerable interest in the thermal decomposition of esters as a means of preparing olefins since Krafft (1) in 1883 explored this reaction, only a limited amount of work has been directed toward the mechanism of this high temperature decomposition.[3]

Pure *cis*- and pure *trans*-2-methylcyclohexyl acetates have now been pyrolyzed at 495° in a stainless steel tube in an atmosphere of nitrogen. The olefinic products from each pyrolysis were isolated in 75% yield and qualitatively and quantitatively analyzed from infrared absorption data. 1-Methyl- and 3-methyl-cyclohexenes were the only olefinic products found in the hydrocarbon fraction. The olefinic mixture resulting from the *trans*-ester consisted of 55% 1-methylcyclohexene and 45% 3-methylcyclohexene. From the *cis*-ester the mixture contained only 25% 1-methylcyclohexene and 75% 3-methylcyclohexene. There was no 4-methylcyclohexene found in either product.

DISCUSSION

Esters that undergo pyrolysis may be divided into two classes; first, esters with β-hydrogen atoms on the alkyl portion of the molecule and, second, esters without β-hydrogen atoms. Although a few workers (2) believe that all esters decompose thermally by the same mechanism, others (3) believe that the mechanism is not the same in the two cases. They base their belief on the contrasting conditions of pyrolysis and the products resulting. Pyrolysis of esters without β-hydrogens in the alkyl portion requires higher temperatures and the products are suggestive of a free radical type mechanism (3). However, if β-hydrogen atoms are available and the temperature of pyrolysis is optimum, only the expected olefins and acids result. Only esters belonging to the latter class were studied in this investigation.

Inasmuch as the reaction is stereospecific as shown by the difference in the ratio of the two olefinic products resulting from the pyrolysis of the isomeric esters, it was concluded that it is quite unlikely that the mechanism by which this pyrolysis proceeds is either an ionic mechanism as illustrated in "A" or a free radical mechanism as illustrated in "B". If the pyrolysis proceeded by either

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[1] Abstracted from a thesis presented to the Graduate Faculty of the University of Minnesota by G. G. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy, July 1949. Presented at the Pacific Northwest Regional Meeting of the American Chemical Society in Richland, Washington, June 9, 1950.

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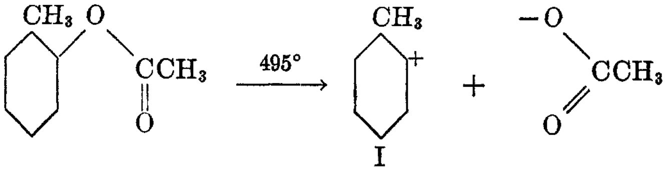
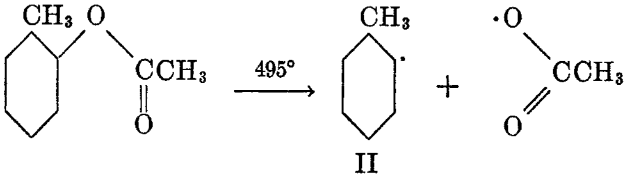
[3] Since this work was completed a paper on the same subject using different examples from ours but reaching the same conclusions was published by Alexander and Mudrak, *J. Am. Chem. Soc.*, **72**, 1810 (1950).

of these mechanisms the two expected olefins would have been formed in the same ratio from either isomeric ester.

A.



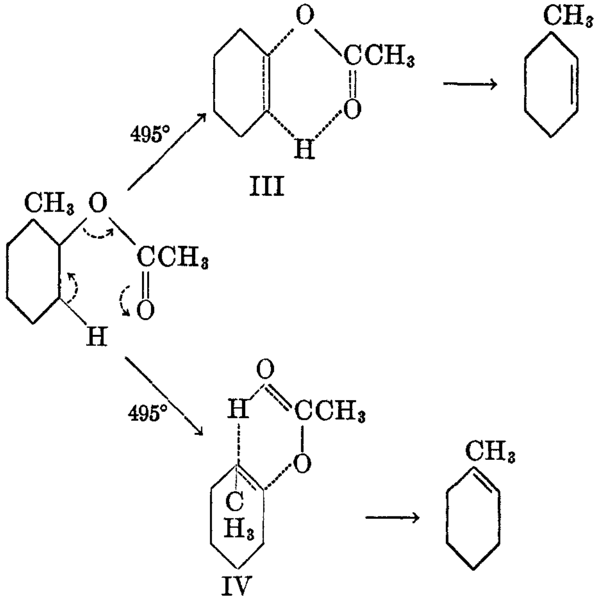
B.



If a carbonium ion such as indicated in I were formed during the pyrolysis it is likely that rearrangement would result from pyrolysis of esters of neopentyl type alcohols. Cramer and Mulligan (4) pyrolyzed the acetate of 3,3-dimethylbutanol-2 and noted no rearrangement products, the sole olefinic product being 3,3-dimethylbutene-1. Wibaut and Smittenberg (5) have reported the lack of isomerication in the pyrolysis of the acetate of 2,2-dimethyl-3-pentanol to 2,2-dimethylpentene-3.

A third possible mechanism (C) by which these esters may thermally decompose involves a transient cyclic intermediate (III, IV) similar to the one proposed by Hurd and Blunck (3). Here a hydrogen bridge would link the β-hydrogen of the alkyl group and the oxygen of the acetyl, and of course would be of importance only in the transition state.

C.



It appears credible from the information now available that the β-hydrogen is expelled simultaneously with the acetoxy group.

From this work on the pyrolysis of acetates of the isomeric 2-methylcyclohexanols it is apparent that a *cis*-elimination of the β-hydrogen and the acetoxy group is preferred over a *trans*-elimination. *cis*-2-Methylcyclohexyl acetate gave largely 3-methylcyclohexene while *trans*-2-methylcyclohexyl acetate gave approximately equal amounts of both isomers. The slightly larger quantity of 1-methylcyclohexene obtained from the *trans*-acetate would be expected from the stabilization resulting from hyperconjugation of the methyl group in the transition state.

EXPERIMENTAL

trans-2-Methylcyclohexyl 3,5-dinitrobenzoate (6, 7) was prepared from 2-methylcyclohexanol (Eastman Kodak, containing approximately 74% *trans*) with 3,5-dinitrobenzoyl chloride and pyridine. The *trans*-3,5-dinitrobenzoate was separated from the *cis*-isomer by carefully dissolving the more soluble *cis*-ester from the less soluble *trans*-ester with methanol and crystallizing each fraction from this solvent. From 122 g. (1.06 moles) of 2-methylcyclohexanol, 131 g. (40.5%) of pure *trans*-ester, m.p. 113.5–115° was obtained. Several other fractions, m.p. 70–94°, were collected whose melting points could not be changed by repeated crystallization.

trans-2-Methylcyclohexanol (7, 8, 9). A mixture of 123.5 g. (0.4 mole) of pure *trans*-2-methylcyclohexyl 3,5-dinitrobenzoate, 127 g. (2.27 moles) of potassium hydroxide, 1400 cc. of methyl alcohol, and 750 cc. of water was heated under reflux for two hours. The reaction mixture was concentrated by distillation and the product isolated by ether extraction. Vacuum-distillation through six inches of glass helices yielded 35 g. (85%) of pure *trans*-2-methylcyclohexanol, b.p. 60.7–61° (10.5 mm.), n_D^{20} 1.4611, n_D^{25} 1.4596, η^{25} 0.335 poise, d^{25} 0.9229.

cis-2-Methylcyclohexyl 3,5-dinitrobenzoate (6, 7) was prepared from 2-methylcyclohexanol obtained by the reduction of 2-methylcyclohexanone with Adams platinum oxide catalyst in acid medium. After two crystallizations from ethyl alcohol, a 57% yield of ester, m.p. 97–98°, was obtained.

cis-2-Methylcyclohexanol (7, 9) was obtained in 77% yield by the hydrolysis of the 3,5-dinitrobenzoate; b.p. 161.4°, n_D^{20} 1.4641, n_D^{25} 1.4620, η^{25} 0.170 poise, d^{25} 0.9307. Most of the *cis*-2-methylcyclohexanol used in this study was prepared by the catalytic reduction of 2-methylcyclohexanone with brown platinum oxide and hydrogen in glacial acetic acid containing approximately 5% concentrated hydrochloric acid. Since some of the 2-methylcyclohexanol so formed was esterified under the conditions of the reduction, it was necessary to hydrolyze the organic material before isolation of the *cis*-2-methylcyclohexanol. Distillation of the hydrolysate yielded 70% of *cis*-2-methylcyclohexanol, b.p. 43–45° 1–2 mm.), n_D^{25} 1.4620, η^{25} 0.171 poise, d^{25} 0.9310. From viscosity data this material was estimated to be at least 96% *cis*.

trans-2-Methylcyclohexyl acetate (8). A solution of 18 g. (0.23 mole) of acetyl chloride in 22 cc. of anhydrous chloroform was slowly added (two hours) to a well-stirred mixture of 25 g. (0.22 mole) of pure *trans*-2-methylcyclohexanol, 18 g. (0.23 mole) of anhydrous pyridine, and 79 cc. of anhydrous chloroform. The reaction was cooled with an ice-bath during the addition, then allowed to stand at room temperature for several hours. The chloroform solution was filtered to remove pyridine hydrochloride, washed once with water, twice with 5% sodium carbonate, dried over magnesium sulfate, and distilled. Distillation of the residue yielded 29 g. (84.6%), of pure *trans*-2-methylcyclohexyl acetate, b.p. 63–64° (11.5 mm.), n_D^{25} 1.4353.

cis-2-Methylcyclohexyl acetate (8). *cis*-2-Methylcyclohexyl acetate was prepared in the same manner as the *trans*-acetate. Distillation of the crude product produced 28.4 g. (83.3%), b.p. 68.5–69.5° (16 mm.), n_D^{25} 1.4376, of pure *cis*-2-methylcyclohexyl acetate.

Pyrolysis of trans-2-methylcyclohexyl acetate. Over a period of two hours 28.1 g. (0.18 mole) of pure *trans*-2-methylcyclohexyl acetate was dropped through a clean hot tube swept with a stream of nitrogen. The contact time in the tube was one to two minutes. The temperature of the tube was maintained between 490–500°. Any material not condensed with water condensers was caught in a Dry Ice trap. Following the addition of the ester the tube was swept with nitrogen for 10 minutes. The amber-colored olefin and acetic acid mixture, which was in two phases, was washed twice with small quantities of water, once with 5% sodium carbonate, and dried over potassium carbonate. Distillation produced 13 g. of clear liquid, b.p. 103–110°, n_D^{20} 1.4477, and 0.5 g. of high-boiling residue. The yield was 76.5% on the basis of pyrolyzed acetate. Very little carbon was found inside the tube.

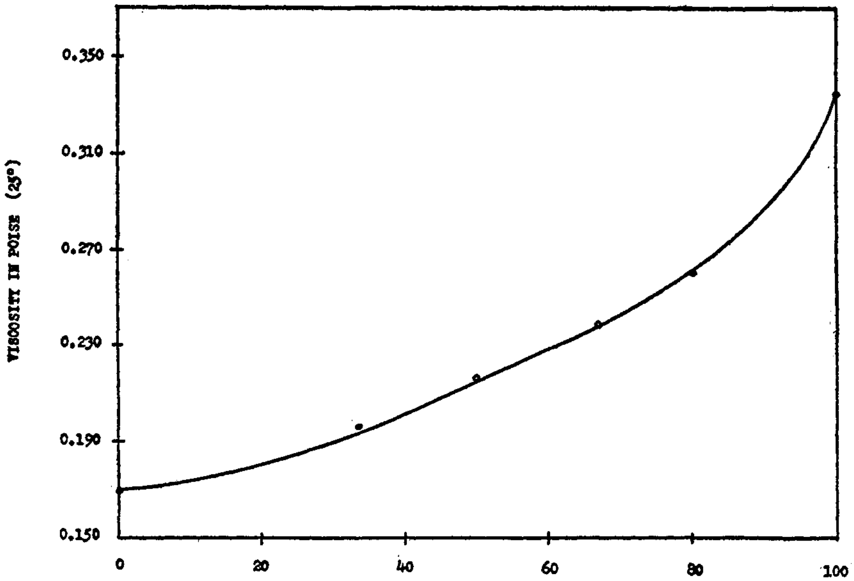


FIG. 1 *trans*-2-METHYLCYCLOHEXANOL, %

Pyrolysis of cis-2-methylcyclohexyl acetate. Pure *cis*-2-methylcyclohexyl acetate, 28 g. (0.18 mole), was pyrolyzed using the same procedure described above. Distillation of the olefinic product produced 12.2 g. of clear liquid, b.p. 100–105°, n_D^{20} 1.4458, and 1.5 g. of high-boiling residue. The yield was 75% on the basis of pyrolysed acetate.

Viscosity measurements. Viscosities were measured using 5 cc. of the sample in an Ostwald type viscosimeter Number 200. This model has a large capillary, and the time of flow for the compounds analyzed was between 167 and 330 seconds at 25°. The constant for the viscosimeter was determined using a 60% sucrose solution which has a viscosity of 0.439 poise at 25° (10). All substances were freshly distilled before measurements were taken. The viscosities agree well with those previously reported (8, 9). A plot of the per cent composition *versus* viscosity is given in Figure 1. The 2-methylcyclohexanol obtained from Eastman Kodak had a viscosity of 0.250 poise at 25°; this should contain approximately 74% *trans*-2-methylcyclohexanol.

Isomeric methylcyclohexenes. 1-Methylcyclohexene, b.p. 109–109.5°, n_D^{20} 1.4503, was prepared by distilling from iodine the tertiary alcohol, which resulted from the addition of methylmagnesium iodide to cyclohexanone (11, 12). 3-Methylcyclohexene, b.p. 100–100.8°, n_D^{20} 1.4442, was obtained through a series of reactions beginning with the bromination of cyclohexene using N-bromosuccinimide (13) and subsequent conversion of the allyl bromide to the cyclic olefin with methylmagnesium iodide (14). The third isomer, 4-methylcyclohexene (15), b.p. 102–103°, n_D^{20} 1.4418, was prepared by pyrolysis of the acetate of 4-methylcyclohexanol.

Analysis of the olefinic mixture from pyrolysis. Infrared absorption curves were taken of pure samples of the three isomeric methylcyclohexenes[4] (1-methyl-, 3-methyl-, and 4-methyl-cyclohexene) and of six mixtures of the 1-methyl and 3-methyl isomers on a Perkin-Elmer infrared spectrophotometer, model 12C, with a rock salt prism. By plotting the optical density at several of the peaks against concentration, curves were obtained which were used for the analysis of the pyrolysis products. The average of analyses from five absorption bands gave 75 ± 5% 3-methylcyclohexene and 25 ± 5% 1-methylcyclohexene from the pyrolysis of *cis*-2-methylcyclohexyl acetate and 45 ± 5% 3-methylcyclohexene and 55 ± 5% 1-methylcyclohexene from the *trans*-isomer. No 4-methylcyclohexene was found in either pyrolysis product.

SUMMARY

The acetates of *cis*- and *trans*-2-methylcyclohexanol have been pyrolyzed at 495°. A qualitative and quantitative analysis was made of the pyrolysis products. The reaction has proved to be stereospecific. A mechanism involving a quasi six-membered ring as the transition state is proposed for the thermal decomposition of esters containing β-hydrogens in the alkyl portion of the molecule.

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[4] The infrared absorption curves for these isomeric olefins have been published as 897, 898, and 899 in the Catalog of Infrared Spectrograms of the American Petroleum Institute, Research Project 44 at the National Bureau of Standards. We are indebted to Dr. Bryce Crawford and Mr. John Lancaster for the infrared analyses.