

THE PYROLYTIC DECOMPOSITION OF 5,5-DIMETHYL-3-CYANOHEX-1-YL METHACRYLATE
A STUDY OF THE THERMAL ELIMINATION OF ALLYLIC ESTERS

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(Chemistry)

Hamilton, Ontario

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AUTHOR: Leo Ka-Ming Lam, B.Sc. (McMaster University)

SUPERVISOR: Dr. J. Warkentin

By

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LEO KA-MING LAM, B.Sc.

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Submitted to the Faculty of Graduate Studies in Partial Fulfilment of the Requirements for the Degree Master of Science

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McMaster University

September 1963

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ACKNOWLEDGMENTS

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This allylic ester decomposed with difficulty. Under conditions which led to complete decomposition of 3-acetoxycyclohexene, 6,6-dimethyl-2-cyclohexen-1-ol acetate was virtually unreacted. Complete decomposition of the allylic acetate was achieved at about 600°C. The pyrolysis products consisted mainly of o-xylene, toluene, 5,5-dimethyl-1,3-cyclohexadiene and acetic acid. The aromatic compounds are thought to be formed from the less stable diene.

Partial decomposition of ester enriched with deuterium in the 4-position, permitted estimation of the isotope effect, k_H/k_D , for the pyrolytic elimination. The value obtained was about 2. Together with other experimental evidence, it indicates that the main mode of decomposition is 1,4-conjugate elimination and that allylic rearrangement, if it occurs at all, is unimportant.

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Synthesis of 4,4-Dideutero-6,6-dimethyl-2-cyclohexan-1-ol Acetate

General Discussion

Deuterium Exchange of 6,6-Dimethyl-2-cyclohexan-1-one

Synthesis of 4,4-Dideutero-6,6-dimethyl-2-cyclohexan-1-ol Acetate

Experimental Procedure Employed in the Thermal Decomposition of the Acetates

Separation and Characterization of Some of the Components in the Pyrolysates

General Discussion

Conditions for Complete Decomposition

Competitive Decomposition of 6,6-Dimethyl-2-cyclohexan-1-ol Acetate and 3-Isopropylcyclohexane

Preparation of 3-Isopropylcyclohexane

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various effects. Among them, steric, electronic, statistical and thermodynamic effects are the more important (1). One needs only to search the literature to find a multitude of contradictions as to how these effects influence the direction of elimination on pyrolysis of

HISTORICAL INTRODUCTION

Pyrolytic eliminations are important from both the practical and the theoretical point of view. Elimination reactions which proceed via an ionic intermediate in a polar solvent have preparative limitations because of the occurrence of rearrangement and substitution.

Pyrolytic elimination of esters and xanthates introduces unsaturation into a molecule with a remarkable freedom from such side reactions.

Stereochemically, the reaction has a high degree of cis-specificity.

It occasionally allows the formation of only a single product which might not be produced under other eliminating conditions. Pyrolytic

elimination reactions are of considerable interest from a mechanistic point of view.

Although the cis-stereochemistry of the process has been adequately established, the complete mechanism is not without

ambiguities. The nature of the transition state for 1,2-pyrolytic elimination has been the subject of controversy for many years. It

has incited extensive investigation and, as a result, more is known about the details of these reactions than of any other reactions

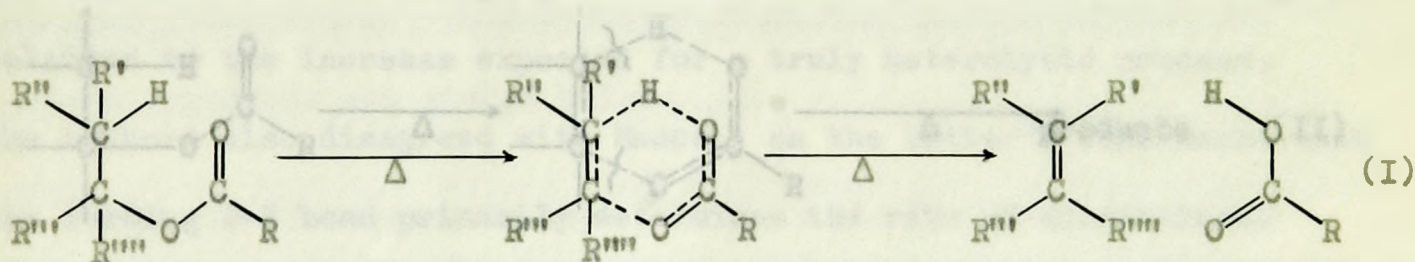
proceeding through cyclic transition states.

Among the many compounds that would undergo pyrolytic eliminations, carboxylic esters, especially acetates, have been most closely

studied. The course of the thermal cleavage of esters bearing a β -hydrogen atom in the alcohol portion has been shown to be subject to

various effects. Among them, steric, electronic, statistical and thermodynamic effects are the more important (1). One needs only to search the literature to find a multitude of contradictions as to how these effects influence the direction of elimination on pyrolysis of a certain ester if more than one way of eliminating the acid portion is possible. Another controversy is the possibility of both cis- and trans-eliminations being involved in cases where several products are obtained.

The currently accepted mechanism of the vapour-phase pyrolysis of esters was first proposed by Hurd and Blunck in 1938 (2). They postulated a quasi-six-membered cyclic transition state through which the reaction proceeds:

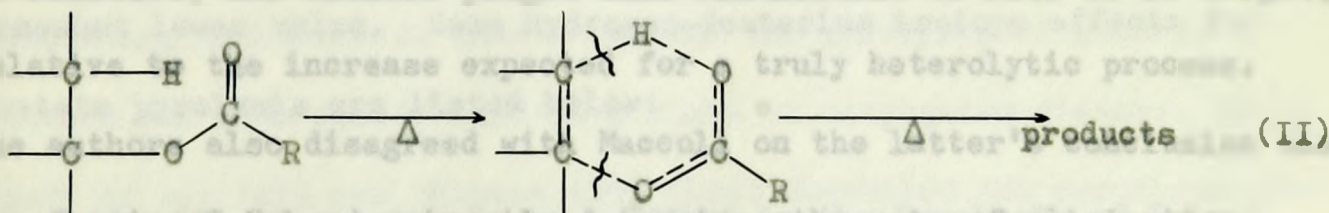


Since the reaction is conducted in the vapour phase, under relatively mild conditions, it is unlikely that an ionic type of intermediate is involved. This view is supported by the fact that the decompositions of esters and xanthates at high temperatures, in the absence of solvent, obey first-order rate laws and exhibit negative entropies of activation (3). Thus the elimination proceeds unimolecularly and motion is more restricted in the transition state than in the reactants.

However, the possibility that the ester decomposes into free radicals with subsequent elimination of acid, cannot be overlooked, especially

when esters are subjected to temperatures high enough to permit radical cleavage (4). Yet compounds sensitive to free radical attack such as 1,2-dimethylene-4-cyclohexene, 1,4-dimethylene-2-cyclohexene and 5-methylene-1,3-cyclohexadiene, etc. have been prepared by thermal decomposition of the corresponding esters (5). Thus one may conclude that esters may be pyrolyzed without appreciable interference from free radical processes.

A mechanism of the elimination involving a cyclic transition state requires at least some attraction between the carbonyl oxygen atom of the ester function and the β -hydrogen atom. The elimination of the carboxylic acid portion must involve two bond-breaking processes, namely the breaking of the C-O and the C-H bond (6):



Studies on the effect of substituents on the ease of these bond-breaking processes and on the effect of heavy isotopes on the reaction rates allow one to describe the transition state in some detail.

Maccoll (7) has collected relative rate data for the pyrolysis of primary, secondary and tertiary acetates and has shown that ethyl, *i*-propyl and *t*-butyl acetates react in the rate ratios 1:26:1660 at 400°C. This is in the order to be expected if heterolytic C-O bond-breaking is important, but the differences are less dramatic than one would expect for a carbonium ion mechanism. DePuy, King and Froemsdorf (6) obtained the relative rates for acetate pyrolyses as listed in Table I.

Table I. Relative Rates of Pyrolysis of Esters at 400°C

Compound	Relative rate
5-Nonyl acetate	1
α -Phenylethyl acetate	0.74 ± 0.02
β -Phenylethyl acetate	0.07 ± 0.006
α -Acetoxycyclohexanone	0.06

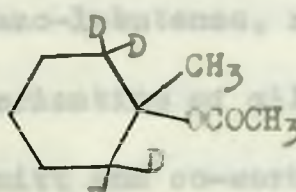
They argued that the amount of C-O heterolytic bond-breaking must be very small, for in any reaction involving appreciable carbonium ion character the α -phenylethyl acetate would certainly react much more rapidly than would α -acetoxycyclohexanone. Although it is 10 times as reactive, the authors judged this enhancement of rate to be slight, relative to the increase expected for a truly heterolytic process. The authors also disagreed with Maccoll on the latter's conclusion that the forming O-H bond primarily determines the rate of elimination.

Attempts have been made to gain an insight into the carbon-hydrogen bond-breaking process by studying the effect of increasing acidity of the β -hydrogen on the ease of pyrolysis. Strongly acidifying groups attached to the carbon bearing the hydrogen (e.g., C=O, NO₂) may favour its removal (8), but experimental data are not consistent (9). If the hydrogen is benzylic, then its removal is favoured yet the important effect of the phenyl group is not to acidify the hydrogen but to stabilize the incipient double bond (10). In unactivated cases the relative acidity of the hydrogen atom has little influence, as shown by the results for the pyrolyses of substituted 1,3-diphenyl-2-propanol

acetates (10) and of 1-methoxy-2-acetoxypropane (6). In both cases, reactions involved the removal of less acidic hydrogens producing the more stable olefins. This indicates that the stability of the olefin being formed is controlling the direction of the elimination.

The most direct measure of the importance of the breaking of the carbon-hydrogen bond in the transition state of a reaction can be obtained by studying the hydrogen-deuterium kinetic isotope effect (11). Curtin and Kellom (12) first obtained the kinetic isotope effect in acetate pyrolysis during the course of their study of the stereochemistry of the reaction, using the threo- and the erythro-2-deutero-1,2-diphenylethyl acetates. They arrived at a value of 2.8 ± 0.6 for the rate ratio k_H/k_D . DePuy, King and Froemsdorf (6) obtained a somewhat lower value. Some hydrogen-deuterium isotope effects for acetate pyrolysis are listed below:

Table II. Deuterium Isotope Effect in the Pyrolysis of Esters

Compound	Temperature °C	k_H/k_D	Reference
$C_6H_5CHDCH(OCOCH_3)C_6H_5$	400	2.8	12
	400	1.9	6
	500	1.7	6
$CD_3CD_2OCOCH_3$	500	2.1	13
$CHD_2CD_2OCOCH_3$	500	2.0	13

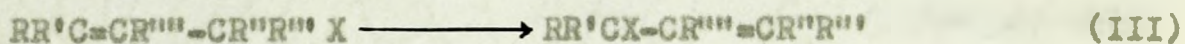
In most cases a value close to 2.0 was obtained for cis-1,2-elimination in acetate pyrolysis at 400 - 500°C.

The observation of a sizable deuterium isotope effect proves conclusively that the carbon-hydrogen bond is broken in the rate-determining step. The above k_H/k_D values further indicate a large amount of breaking of the carbon-hydrogen bond in the transition state, for the theoretical maximum value of k_H/k_D at this temperature, assuming loss of only one stretching vibration, is 2.1 (14). Hence it may be assumed that the transition state of the acetate pyrolysis reaction is best described as being one in which both the C-H and C-O bonds are to a large extent broken and a great deal of double bond character has developed. The process is highly concerted with only a small amount of charge separation.

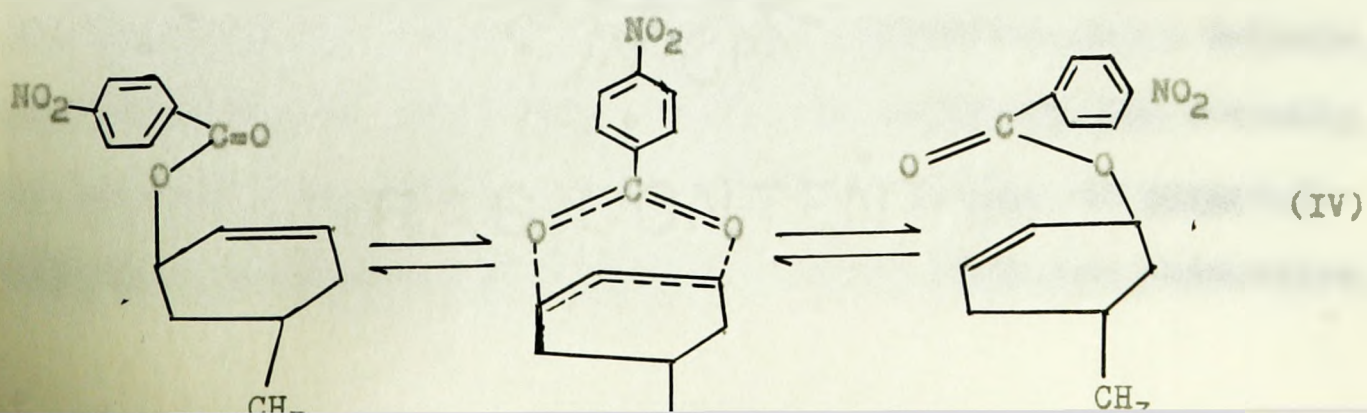
While pyrolysis of saturated acetates has been widely used for introducing unsaturation into a system, the pyrolysis of allylic acetates has been rarely used as a route to conjugated dienes. The report of van Pelt and Wilbaut (15) first described the pyrolysis of 4-acetoxy-2-hexene for the preparation of 2,4-hexadiene. Marvel and Williams (16) obtained 2-alkyl-1,3-butadienes and 3-cyano-1,3-butadiene by thermally decomposing 3-acetoxy-2-alkyl-1-butenes and 3-acetoxy-3-cyano-1-butenes, respectively. Recent work has indicated that isomerization of allylic esters during pyrolysis can be important. Grummitt and co-workers (17) have shown that a mixture of 1-cyclohexyl-1,3-butadiene and 1-cyclohexyliden-2-butene was obtained from the pyrolysis of either 1-cyclohexyl-3-acetoxy-1-butene or 1-cyclohexyl-1-acetoxy-2-butene. Marvel and Brace (18), as well as Bailey and Barclay (19) have reported isomerization of allylic esters during pyrolysis. Bailey and Goossens (20) explained the formation of

3-methylenecyclohexene on pyrolysis of 1-cyclohexenylmethyl acetate in terms of isomerization of the starting ester to 2-methylenecyclohexyl acetate before elimination. Baylouny (21) found that on pyrolysis of methyl cis-2-acetoxy-3-cyclohexen-1-carboxylate, the compound yielded three isomeric unsaturated esters: 2,4-; 1,3- and 2,5-cyclohexadiene carboxylates. He also found that diethyl 2-acetoxy-3-cyclohexen-1,1-dicarboxylate, on pyrolysis, gave as the main product, diethyl 2,4-cyclohexadiene-1,1-dicarboxylate. Isomeric diesters were also found.

Allylic rearrangement of the ester function, followed by cis-1,2-elimination of the acid portion, will conveniently account for the formation of the isomeric olefins found by the authors mentioned above. However, there is nothing in the experimental evidence that rigorously proves that the pyrolysis proceeded via prior rearrangement, rather than by direct 1,4-conjugate elimination. Allylic rearrangement (isomerization) of the type



in various solvent systems has been thoroughly studied by Burton and Ingold (22), Winstein and Young (23), Brande (24) and by others. The mechanism of the rearrangement has now been generally accepted as involving the 'internal return' of an 'ion pair' as shown below for the isomerization of 6-p-nitrobenzoyloxy-4-methyl-1-cyclohexene (25).



The ester group retains its configuration with respect to the methyl group. The ease and extent of the isomerization are determined mainly by the dielectric constant (the ionizing power) of the solvent and the ability of the ester group to accommodate an ionic charge (22). Thermal rearrangement of allylic esters in the vapour phase, however, has been observed only infrequently. Greenwood (26) has recently shown that isomerization of 2-acetoxy-trans-5-heptene to 4-acetoxy-trans-2-heptene or vice-versa occurred during pyrolysis of either of these isomeric acetates. The trans-configuration of the carbon-carbon double bond of these allylic acetates was essentially retained. He suggested that the isomerization proceeded intramolecularly and that the trans-conformation was the more favourable of the two principal conformations of an allylic ester having a trans alkene linkage.

Thus, it is possible that allylic esters undergo both direct 1,2-elimination and allylic rearrangement prior to 1,2-elimination. It is also conceivable, however, that allylic esters can undergo elimination from carbons 1 and 4. Several examples of the supposed 1,4-conjugate elimination have been described. Details of mechanism and stereochemistry have been discussed (27). Barnett and his co-workers (28) have studied elimination reactions in the 9,10-disubstituted 9,10-dihydroanthracene system. They worked with the 9,10-dihalo and the 9,10-dihydroxy compounds and they suggested that the reactions observed were 1,4-conjugate elimination with a definite cis-stereochemical preference. Cristol and co-workers (29) thermally decomposed the dibenzoates and the diacetates of cis- and trans-1,5-dichloro-9,10-dihydro-9,10-anthradiol. It was found that elimination

of the carboxylic acid portions were considerably faster with the trans-isomers than with the cis-compounds. The observed preference for cis-hydrogen over trans-hydrogen may be readily understood by recourse to a cyclic transition state analogous to those proposed for thermal 1,2-elimination. Furthermore, in order that the carbonyl oxygen atom and the hydrogen atom be within bonding distance, the preferred conformation of the meso-dihydroanthracene system would have to be that in which the central ring assumes the boat form. The same situation would be encountered in the cyclohexenyl system.

It was pointed out by Cristol that there were no experimental data to prove that the pyrolytic elimination observed in the 9,10-dihydroanthracene series were direct 1,4-elimination processes, although an attractive mechanism can be envisioned. In fact, all the results can be accommodated just as well by a mechanism involving allylic rearrangement in a first step followed by 1,2-elimination. It must also be pointed out that eliminations on the 9,10-dihydroanthracene system yield aromatic compounds, the corresponding anthracene derivatives. Resonance stabilization at the transition state may greatly promote such reactions. It seems probable that allylic esters, in which elimination can not produce an aromatic molecule, should pyrolyze less readily than the compounds studied by Cristol and Barnett. In any case, isolation of a conjugated diene does not demonstrate 1,4-conjugate elimination unless a two-step mechanism, involving allylic rearrangement, can be rigorously excluded. In view of the fact that alkyl carbon-to-oxygen bond cleavage would produce a stabilized allylic radical, a free radical mechanism can also not be

excluded on an a priori basis.

This work, concerned with the pyrolysis of the acetate of 6,6-dimethyl-2-cyclohexen-1-ol, was undertaken with a view to removing some of the existing ambiguities regarding thermal elimination in allylic esters. We have sought to clarify the mechanism of pyrolytic elimination in our system by answering the following questions:

- (1) How does the energy of activation for pyrolysis of 6,6-dimethyl-2-cyclohexen-1-ol acetate compare, qualitatively, with that for pyrolysis of 3-acetoxycyclohexene?
- (2) Can the isomeric ester 4,4-dimethyl-2-cyclohexen-1-ol acetate be detected among the ester residue resulting from incomplete pyrolysis of 6,6-dimethyl-2-cyclohexen-1-ol acetate?
- (3) How does the isotope effect for pyrolytic elimination in 6,6-dimethyl-4,4-dideutero-2-cyclohexen-1-ol acetate compare with that observed in a case where the elimination is unambiguously of the 1,2-type?
- (4) Are the products those expected from a conjugate elimination rather than from a free radical process?

The experimental results reported in the following section, by supplying answers to these questions, contribute to our understanding of the pyrolytic decomposition of allylic esters.

EXPERIMENTAL

The experimental work of this thesis is presented under the following main headings:

- (a) List of chemicals.
- (b) Synthesis of 6,6-dimethyl-2-cyclohexen-1-ol acetate.
- (c) Synthesis of 6,6-dimethyl-4,4-dideutero-2-cyclohexen-1-ol acetate.
- (d) Experimental procedure employed in the thermal decomposition of the acetates.
- (e) Separation and characterization of some of the components of the pyrolysates.
- (f) Preparation of unpyrolyzed acetate samples for deuterium analysis.
- (g) Estimation of the isotope effect from the deuterium analyses.

List of Chemicals

Acetic anhydride

The B.D.H. Certified Grade of acetic anhydride was used without further purification.

Acrolein

The Purified Grade of acrolein (Eastman Kodak Co.) was stabilized with hydroquinone. The cloudy, white liquid was first treated with solid sodium bicarbonate, then filtered into a distilling flask (30). Acrolein was distilled through a 1-foot, insulated Vigreux column. The colourless fraction which boiled at 52-54°C was kept in a brown glass bottle. A small amount of hydroquinone was added as a stabilizer.

Anhydrous ethyl ether

Stock ethyl ether was first dried with anhydrous calcium chloride. It was filtered and fine sodium wire was introduced directly into the liquid with the aid of a sodium press.

Cyclohexene

Cyclohexene (Eastman Kodak Co.) b.p. 82-83°C was dried with anhydrous sodium sulfate. It was filtered before use.

Deuterium oxide

Deuterium oxide was of purity greater than 99.5 per cent.

2,4-Dinitrophenylhydrazine

The Fisher Reagent Grade was used directly for the preparation of the Brady reagent (31). Freshly prepared Brady solution was used to prepare the 2,4-dinitrophenylhydrazones of ketones.

1,4-Dioxane

The reagent was distilled through a 1-foot, insulated Vigreux column after being dried with potassium hydroxide pellets. The boiling point was 101-102°C at 760 mm (32).

Lithium aluminum hydride

Lithium aluminum hydride was purchased from Metal Hydrides Inc., Beverly, Mass., U.S.A.

Methanol

Stock methanol was dried over anhydrous calcium sulfate and distilled. Methanol was collected over the range 64-65°C.

3-Methyl-2-butanone

3-Methyl-2-butanone (Matheson, Coleman and Bell Co.) was distilled through a 1-foot, insulated Vigreux column. The fraction boiling at 93-94°C at 760 mm was collected. It was dried over CaSO₄ before use.

Palladium black

The Fisher Purified reagent was used.

Selenous acid

The Fisher Certified reagent was used.

Semicarbazide hydrochloride

Semicarbazide hydrochloride (Eastman Kodak Co.) was used with no further purification.

Synthesis of 6,6-Dimethyl-2-cyclohexen-1-ol Acetate

General Discussion

The synthesis of 6,6-dimethyl-2-cyclohexen-1-ol acetate involved the following three steps:

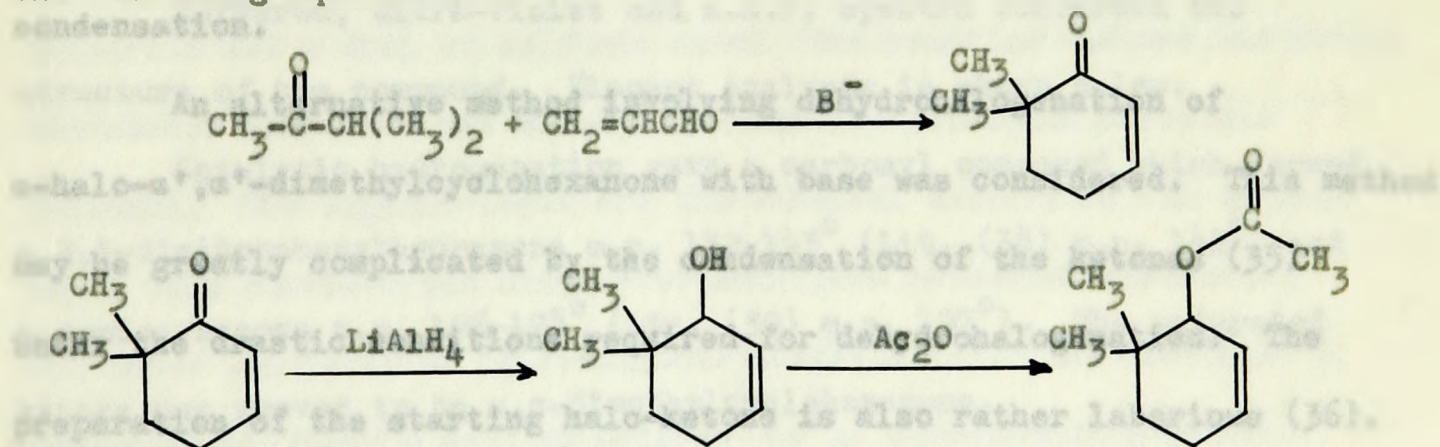
(i) the preparation of 6,6-dimethyl-2-cyclohexen-1-one

by Michael condensation of acrolein and 3-methyl-2-butanone,

(ii) the reduction of the ketone to the corresponding alcohol with lithium aluminum hydride,

(iii) the acetylation of the alcohol.

Schematically the synthetic process can be represented by the following equations:



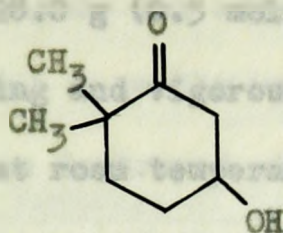
The preparation of 6,6-dimethyl-2-cyclohexen-1-one by the Michael condensation (33) of acrolein and 3-methyl-2-butanone was first performed by Colonge, Dreux and Thiers (34). Using methanolic

potassium hydroxide as the catalyst, these workers obtained a 12%

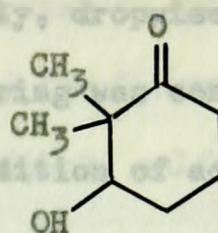
yield of the unsaturated ketone. However, the use of sodium methoxide

as the base and vigorous stirring of the reaction mixture for 10 hours increases the average yield to 40%.

There are at least two possible routes for the condensation, each leading to a different compound I and II depending on whether the



I



II

base abstracts a proton from the tertiary or the primary carbon alpha to the keto carbonyl group. It is clear that alcohol II, having no acidic hydrogen alpha to the hydroxy group, can not be easily dehydrated while I is readily converted to the product olefin. Compound II might regenerate the starting aldehyde and ketone by reversal of the condensation.

An alternative method involving dehydrohalogenation of α -halo- α',α' -dimethylcyclohexanone with base was considered. This method may be greatly complicated by the condensation of the ketones (35) under the drastic conditions required for dehydrohalogenation. The preparation of the starting halo-ketone is also rather laborious (36).

The reduction of 6,6-dimethyl-2-cyclohexen-1-one was accomplished with lithium aluminum hydride in anhydrous ether (37). The alcohol was acetylated without further purification.

A typical synthetic run is described on the following page.

* Analyzed by Dr. G. Miller and Dr. V. B. Strauss,
Stereochemical Laboratory,
154 University Ave.,
Berkeley, California.

Preparation of 6,6-Dimethyl-2-cyclohexen-1-one

To a 3-necked flask which contained 20 ml of sodium methoxide (2 g of sodium metal in 20 ml of methanol) was added 172.3 g (2.0 mole) of 3-methyl-2-butanone which had been previously cooled in an ice-bath. Acrolein, 28.0 g (0.5 mole) was added slowly, dropwise, to the solution with cooling and vigorous stirring. Stirring was continued for about 10 hours at room temperature after the addition of acrolein was completed. Aqueous hydrochloric acid solution was added to neutralize the base until the pH of the medium was about 7. The reaction mixture was then steam-distilled. The desired product was obtained by fractional distillation of the ethereal extract of the steam distillate. The fraction which boiled at 57° - 58° C at 12 mm weighed about 25 g; a yield of 40% (Lit. (34) b.p. 85 - 90° at 20 mm).

Infrared, ultra-violet and n.m.r. spectra confirmed the structure of the compound. Element analysis is shown below.

Catalytic hydrogenation gave a carbonyl compound which formed a 2,4-dinitrophenylhydrazone m.p. 142 - 143° (Lit. (38) m.p. 142°) and a semicarbazone m.p. 196 - 198° (Lit. (39) m.p. 197°). The saturated ketone was proved to be α,α -dimethylcyclohexanone.

Anal.* Calculated for $C_8H_{12}O$: C, 76.42; H, 9.68.

Found C, 76.55; H, 9.69.

* Analyst: Dr. G. Weiler and Dr. F. B. Strauss,
Microanalytical Laboratory,
164 Banbury Road,
Oxford, England.

Reduction of 6,6-Dimethyl-2-cyclohexen-1-one

Lithium aluminum hydride (0.56 g, 0.015 mole) was gently refluxed for $\frac{1}{2}$ hour in 50 ml of anhydrous ether. A solution of 5.6 g (0.045 mole) of 6,6-dimethyl-2-cyclohexen-1-one in 100 ml anhydrous ether was added slowly with stirring to the hydride suspension. A gentle reflux was continued for 2 hours. The metal complex was destroyed with wet ether and dilute sulfuric acid. The organic layer and the ethereal extract of the aqueous layer were combined and dried over anhydrous potassium carbonate. Ether was removed on a rotary evaporator. The alcohol was used to prepare the corresponding acetate without further purification.

Acetylation of 6,6-Dimethyl-2-cyclohexen-1-ol

Alcohol obtained from the lithium aluminum hydride reduction was gently heated, with stirring, for 20 minutes with 10 g of acetic anhydride and a drop of sulfuric acid. The reaction mixture was cooled and excess anhydride was decomposed with 10% potassium carbonate solution. The organic layer and the ethereal extract of the aqueous layer were combined and dried over anhydrous potassium carbonate. The ester was purified by fractional distillation. The fraction is collected at 76-77°C at 8 mm weighed 5.0 g, corresponding to an overall yield of 65%.

Infrared and n.m.r. spectra were in accord with the structural assignment.

Synthesis of 4,4-Dideutero-6,6-dimethyl-2-cyclohexen-1-ol Acetate

General Discussion

The hydrogen atoms attached to the 4-position of 6,6-dimethyl-2-cyclohexen-1-one are sufficiently acidic to undergo deuterium exchange. Thus, it is possible to prepare 4,4-dideutero-6,6-dimethyl-2-cyclohexen-1-ol acetate by reduction and acetylation of the deuterated ketone.

Deuterium Exchange of 6,6-Dimethyl-2-cyclohexen-1-one (40)

A round bottomed flask equipped with reflux condenser was charged with 6.2 g (0.05 mole) of 6,6-dimethyl-2-cyclohexen-1-one; 10 g (0.5 mole) of deuterium oxide and 0.25 g of potassium carbonate. The mixture was refluxed for 24 hours. The organic layer was separated and the aqueous layer was extracted with ether. The organic layer and the ethereal extract were combined, dried and distilled. Deuterio ketone was distilled in the range 57-58° at 12 mm.

Infrared and n.m.r. spectra confirmed the incorporation of deuterium. The infrared spectrum, however, shows absorption at 2250 cm^{-1} , clearly indicating the presence of vinyl deuterium (12). In the absence of the knowledge concerning the relative extinction coefficients of vinylic and allylic deuterium in the infrared, it is difficult to estimate the amount of vinylic deuterium in the system under discussion. It should be pointed out that considerable exchange of vinyl hydrogen had occurred and that the deuterium content in the 4-position was therefore lower than the analytical result would appear to indicate. This, however, would not affect the isotope effect calculation since the vinylic hydrogen can not be involved in the

reaction. The net change in deuterium content will then be independent of the amount of vinylic deuterium present.

Synthesis of 4,4-Dideutero-6,6-dimethyl-2-cyclohexen-1-ol Acetate

Deuterated 6,6-dimethyl-2-cyclohexen-1-one was reduced and the resulting alcohol was acetylated as described in the previous synthesis. Distilled water was used instead of dilute sulfuric acid to destroy the metal complex in the lithium aluminum hydride reduction process. This was done to avoid possible acid catalyzed exchange reaction.

Experimental Procedure Employed in the

Thermal Decomposition of the Acetates

The pyrolysis of acetate was carried out in a Pyrex tube of 25 mm diameter packed with one-eighth inch Pyrex helices. The packed section, which was 20 cm long, was heated to the desired temperature with a furnace about 12 hours prior to the pyrolysis. A thermocouple which extended to the centre of the helices packed section registered the temperature on a pyrometer*. Samples of esters weighing from one to two grams were introduced into the top of the vertically-mounted pyrolysis tube at the rate of about one drop in 5 seconds. Oxygen-free nitrogen was passed into the top of the tube at the rate of about 5 ml per minute. The pyrolysis products were swept from the reaction chamber by the slow stream of nitrogen and collected in a cold-trap. The apparatus for ester pyrolysis is shown in figure I.

* The Hoskins pyrometer (Hoskins Manufacturing Co., Detroit) was graduated in 10° divisions from 0-800°C. A maximum error of ±5°C is estimated for the temperature readings.

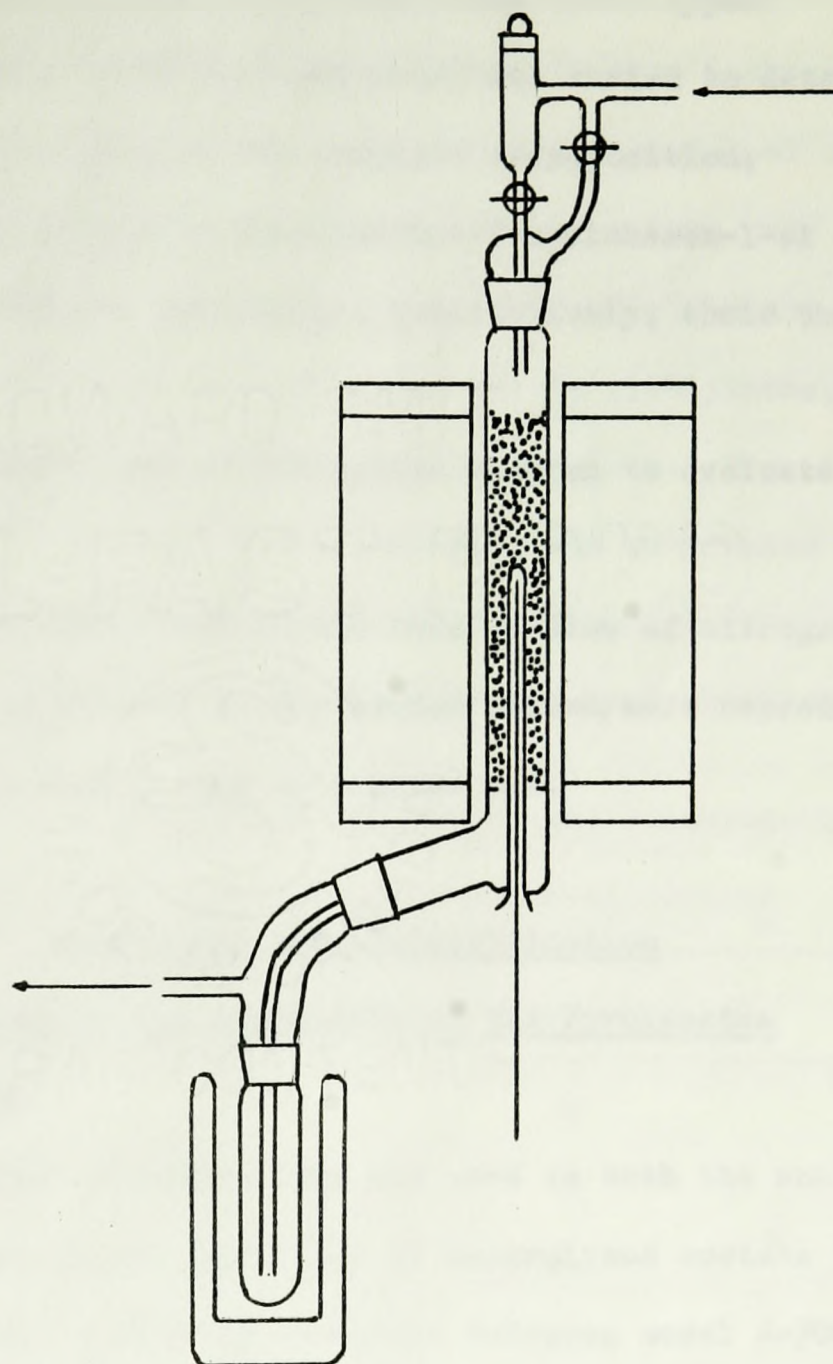


Fig. I. Apparatus for Vapour-phase Pyrolysis

Pyrolysis runs were of the following three types:

(i) exploratory runs in which temperature was varied to determine the minimum temperature required for complete decomposition,

(ii) pyrolysis of mixtures of 6,6-dimethyl-2-cyclohexen-1-ol acetate and 3-acetoxycyclohexene to compare, qualitatively, their thermal stabilities,

(iii) incomplete pyrolyses of deuterated samples to evaluate the isotope effect.

Experimental conditions, such as the rate of flow of nitrogen, and the rate of addition of acetate to the heated column, were reproduced as nearly as possible within runs of a given set.

Separation and Characterization

of Some of the Components of the Pyrolysates

General Discussion

Vapour-phase chromatography was used in both the analyses of the pyrolysates and in the isolation of unpyrolyzed acetate for the deuterium analysis. A Wilkens Aerograph Autoprep model A-700 instrument was employed. The instrument proved to be versatile enough for both analytical and preparative work. A 3/8" x 20' aluminum column, with SE-30 (silicon-gum-rubber) on 42/60 mesh Chromosorb P was used throughout this work. The column temperature was around 200°C depending on the sample being analyzed. For qualitative work, a sample of 2-3 μ l. was injected with a 10- μ l. syringe having a needle of 3 1/4 inch length. For preparative work, manual injections of about 0.1 ml samples were employed.

Conditions for Complete Decomposition

Temperature within the range 350-650°C were employed to pyrolyze 500 mg samples of 6,6-dimethyl-2-cyclohexen-1-ol acetate. This amount of acetate was added to the heated column over a period of 2 minutes. The pyrolysate was analyzed by vapour-phase chromatography. By comparing the chromatograms of the pyrolysates, it was easy to tell whether decomposition had taken place. When decomposition was detected, the per cent elimination was determined by titration with standard base of an aliquot of the product mixture. The following approximate values for the temperature effect were obtained:

Table III. Temperature Effect on the Decomposition
of 6,6-Dimethyl-2-cyclohexen-1-ol Acetate

Temperature °C	% Conversion (approx.)
350	0
400	0
450	40
500	70
550	80
600	100
650	100

The decomposition was complete when the temperature was around 600°C. The chromatograms showed that the pyrolysate was a mixture of at least four components. For partial decomposition at

lower temperatures, the chromatogram of the pyrolysate had exactly the same features as that obtained from a run to complete decomposition, except that the relative areas of the peaks of the components were different and, of course unpyrolyzed acetate was also detected. This implies that decompositions at high and lower temperatures give the same products in different relative amounts whether the process is complete or only partial.

An ultra-violet spectrum of the pyrolysate taken immediately after the pyrolysis had a λ_{\max} value of 257 m μ . It proved the presence of 5,5-dimethyl-1,3-cyclohexadiene (41) although the amount might have been small at high temperatures (no extinction coefficients were determined). For one of the total decomposition runs at 600°C, two larger components of the pyrolysate were separated by the preparative chromatographic method. These components in their pure state have been unambiguously identified as toluene and o-xylene by infrared, ultra-violet and n.m.r. spectrometry.

Competitive Decompositions of 6,6-Dimethyl-2-cyclohexen-1-ol

Acetate and 3-Acetoxycyclohexene

The experiment was designed to find out the difference, if any, between the energies of activation for thermal decomposition of the two allylic esters. The former acetate has no available β -hydrogen atoms while the latter has two and therefore can undergo direct 1,2-elimination on pyrolysis. An equimolar mixture of the two acetates was prepared and pyrolyzed. The pyrolysate was analyzed by vapour-phase chromatography. At temperatures between 300°C and 400°C,

3-acetoxycyclohexene was partially or totally decomposed (42) while 6,6-dimethyl-2-cyclohexen-1-ol acetate was found to be unchanged.

Preparation of 3-Acetoxycyclohexene (43)

Cyclohexene (82 g, 1 mole) and acetic anhydride (51 g, 0.5 mole) were gently refluxed with stirring. Selenous acid (20 g, 0.16 mole) was added to the hot mixture in small portions. The reaction mixture was refluxed for ten hours. The solution was cooled to room temperature and 200 ml of ether was added. The ethereal solution was washed five times with 10% K_2CO_3 solution, once with distilled water and then dried over anhydrous potassium carbonate. The product was obtained by fractional distillation of the ethereal solution. The fraction collected over 70-71°C at 14 mm had an infrared spectrum identical to that of 3-acetoxycyclohexene (44).

Preparation of Unpyrolyzed Acetate Samples

The Wilkens Aerograph Autoprep Model A-700 proved to be exceedingly useful in this work. Unpyrolyzed acetate from partial decomposition of deuterium enriched 6,6-dimethyl-2-cyclohexen-1-ol acetate was separated from the product mixture by a 3/8" x 20' aluminum column with SE-30 on 42/60 mesh Chromosorb P as the column packing material. These samples were repeatedly purified by the same procedure until only one peak was observed on the chromatogram. A typical run is described below:

A mixture of about 1:1 by weight of deuterio- and protio-acetates of 6,6-dimethyl-2-cyclohexen-1-ol was made up. Duplicate

deuterium analyses of this mixture were obtained.

A sample of about 1 g of this mixed acetate was accurately weighed on an analytical balance. It was then pyrolyzed at 450°C . The pyrolysate was diluted with 30 ml of pentane and extracted 5 times with about 5 ml portions of distilled water until the extract was neutral. The combined aqueous extracts were made up to 50 ml in a volumetric flask. Ten ml aliquots were titrated with 0.1 N standard sodium hydroxide solution to a phenolphthalein endpoint. The amount of acetic acid in the pyrolysate was then calculated and the per cent elimination was obtained.

After extraction, the ethereal solution of the pyrolysate was concentrated to about 2-3 ml. Unpyrolyzed acetate was isolated by vapour-phase chromatography at a column temperature of 180° and a flow rate of 200 ml per minute. With manual injections of about 0.2 ml samples, unpyrolyzed acetate was collected in a cold trap. Purity of the sample was checked by the same v.p.c. method with the detector at the highest sensitivity. The deuterium contents of the unpyrolyzed acetate samples were then analyzed in duplicate.

Estimation of Isotope Effect

General Discussion

The dependence of the rate constant on the zero-point energy difference between the activated complex and the reactants has been clearly shown in terms of the absolute rate theory of Eyring (45). The energy of a bond is a function of the vibrational frequency which in turn depends on the reduced mass of the atoms held together by the

bond in question. It can be shown that the vibrational frequency of a bond and hence the zero-point energy will be decreased if the reduced mass is increased by the substitution of a heavier isotope for one of the atoms forming the bond. On passing to the transition state the

difference between the energies of the heavier and the lighter form will be smaller. Therefore, the heavier form will require a larger activation energy to reach the transition state and should react at a slower rate if the isotopically substituted position is involved in the rate-determining step of the process. The theory of isotope effects has been discussed in detail by Bigeleisen (46,14).

Qualitative Estimation of Isotope Effect

If a mixture of normal and deuterated compound is subjected to the same reaction conditions, the isotope effect for the competitive reaction can be calculated from a knowledge of the change of isotopic content after a stoichiometrically measured fraction, f , of the initial mixture has reacted. Since the heavier form reacts at a slower rate, the change in isotopic content will be in the direction of increasing deuterium in the molecule. However, the extent of hydrogen exchange is not known. Hence, the exact amount of deuterium unreacted.

In table IV, duplicate analyses for deuterium are listed for both the initial and the recovered acetate samples for a typical partial decomposition of 6,6-dimethyl-2-cyclohexen-1-ol acetate at 450°C. Analyses of the recovered unpyrolyzed acetate sample show that its deuterium content was increased by a considerable amount (~ 30%). This indicates a strong preference for breaking a C-H bond

rather than a C-D bond in the rate-determining step of the elimination reaction.

is certain that a considerable portion of the labelled acetate contains

Table IV. Results of Analyses for Deuterium* compound

Description of sample	Sample No.	Deuterium content ‡	Mean values	% increase
Initial deuterium-enriched acetate	1	5.95 5.93	5.94	28.4%
Recovered unpyrolyzed acetate	2	7.61 7.64	7.63	

While it is clear that an isotope effect, k_H/k_D , exists for the pyrolytic elimination reaction of 6,6-dimethyl-2-cyclohexen-1-ol acetate, its exact magnitude could not be calculated readily due to complications arising from the following factors:

(a) Infrared spectra have clearly shown the presence of vinyl-deuterium in the molecule. However, the extent of vinyl hydrogen exchange is not known. Hence, the exact amount of deuterium incorporated at the 4-position could not be calculated.

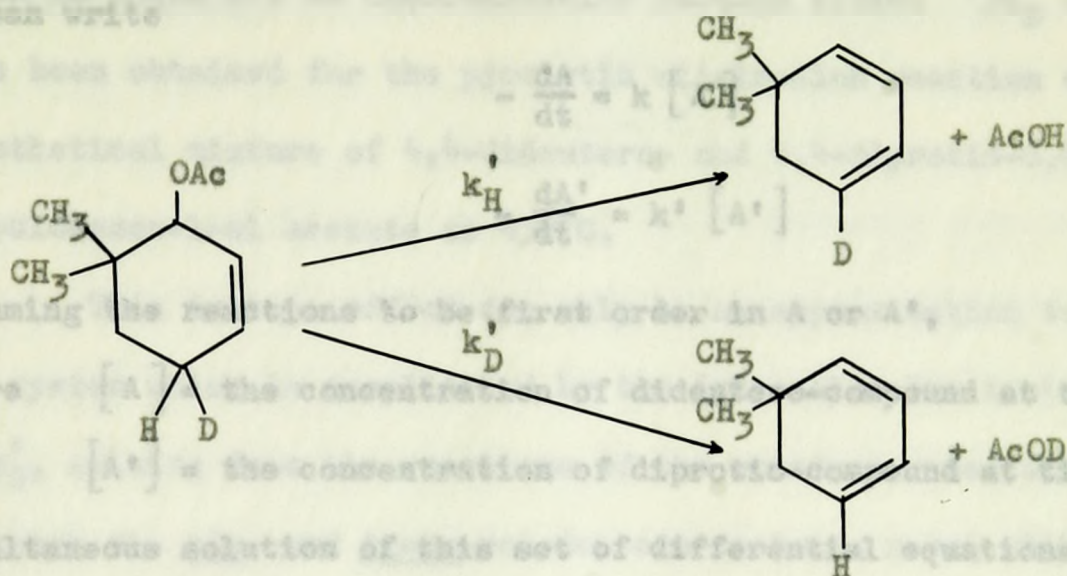
k_D = rate constant for decomposition of 4,4-dideuterated acetate.
An accurate calculation of the intermolecular isotope effect.

* Analyst: Josef Nemeth,
303 W. Washington St.,
Urbana, Ill., U.S.A.

‡ Entries corresponding to a given sample represent duplicate analyses and are expressed as atom per cent excess deuterium.

k_H/k_D and k_D/k_H would be required as well.

(b) Exchange of vinyl deuterium, together with the fact that the ketone was not exhaustively equilibrated with heavy water makes it certain that a considerable portion of the labelled acetate contains only one deuterium in the 4-position. The monodeuterated compound would react with different reaction rates depending on whether a hydrogen or a deuterium at the 4-position is cis to the acetoxy function.



An intramolecular isotope effect (47,48), therefore, exists in the reaction of such a system. The ratio, k'_H/k'_D , is expected to be different from k_H/k_D , the intermolecular isotope effect where

k_H = rate constant for decomposition of undeuterated acetate

k_D = rate constant for decomposition of 4,4-dideuterated acetate.

An accurate calculation of the intermolecular isotope effect, k_H/k_D , for this complicated system requires a knowledge of the distribution of deuterium among the various species in both reactants and products. A knowledge of the relationship between the two ratios k_H/k_D and k'_H/k'_D would be required as well.

equation. However, one can calculate the isotope effect from the results of analyses for deuterium as shown in Table IV if the system had contained only the dideutero- and the diprotio-acetates. For such a system consisting of only two isotopic species, say A and A', undergoing an isotopic competitive intermolecular reaction (49)



we can write

$$-\frac{dA}{dt} = k [A] \quad (III)$$

and

$$-\frac{dA'}{dt} = k' [A'] \quad (IV)$$

assuming the reactions to be first order in A or A',

where $[A]$ = the concentration of dideutero-compound at time t,

and $[A']$ = the concentration of diprotio-compound at time t.

Simultaneous solution of this set of differential equations with the boundary condition $A = A_0$ when $A' = A'_0$, yield

$$\left(\frac{k}{k'} - 1\right) \log\left(\frac{A'}{A'_0}\right) = \log \frac{R_{af}}{R_{a0}} \quad (V)$$

where $R_{af} = A/A'$ after fraction f of the chemical species

A has reacted, and

$$R_{a0} = (A/A')_0, \text{ the initial ratio.}$$

Since the fraction reacted, f, is given by the stoichiometric relationship

$$1 - f = \frac{A + A'}{A_0 + A'_0} = \frac{A'(1 + R_{af})}{A'_0(1 + R_{a0})}, \quad (VI)$$

equation (V) can be written

$$\left(\frac{k'}{k} - 1\right) = \frac{\log(R_{af}/R_{ao})}{\log \frac{(1-f)(1+R_{ao})}{(1+R_{af})}} \quad (\text{VII})$$

The method then consists of the determination of the isotopic ratio R_{ao} of the starting material and R_{af} after a stoichiometrically measured fraction, f , has reacted.

With $f = 40\%$ (from titration) and the deuterium analyses as shown in Table IV, an intermolecular isotope effect $k_H/k_D = 2$ would have been obtained for the pyrolytic elimination reaction of the hypothetical mixture of 4,4-dideutero- and 4,4-diprotio-6,6-dimethyl-2-cyclohexen-1-ol acetate at 450°C .

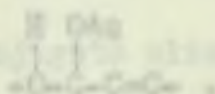
This isotope effect can only be an approximation to that of our system which is complicated by the intramolecular isotope effect, k'_H/k'_D , arising from the reactions of the monodeuterated acetates. Although the cis- and trans-monodeutero-acetates react with different rate constants, k'_D and k'_H , respectively, the relative amounts present before and after the reaction would not have an apparent effect on the deuterium analyses*. However, if $k'_H > k'_D$, more deuterium is lost as deutero diene than as deutero acetic acid. Hence the final deuterium analysis of our system which contains monodeuterated acetates is much lower than would have been expected for a system where the deuterium loss can be caused only by the reaction of the dideuterated species as

* If the system consisted of only monodeuterated acetates, the isotope effect, k'_H/k'_D , calculated from the deuterium content of the unpyrolyzed acetate should be equal to unity.

in the hypothetical system chosen for our calculation. We have therefore set a lower limit to the true isotope effect by the above calculation.

RESULTS AND DISCUSSION

The object of the present investigation is to establish that a sizeable isotope effect existed in the pyrolytic elimination reaction of 6,6-dimethyl-2-cyclohexen-1-ol acetate. Knowledge of the exact magnitude of this effect is not required for the conclusion sought in the present study.



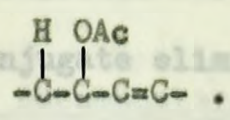
...likely, 1,2-elimination ...
 ...that involves a ...
 ...pyrolysis, allylic rearrangement can conceivably compete with the direct 1,2-elimination thereby producing isomeric acetates and, subsequently, isomeric dienes. It is interesting to investigate the course of thermal elimination on allylic acetates which have no available β -hydrogens and therefore cannot undergo direct 1,2-eliminations. Allylic isomerization followed by 1,2-elimination, then, would be the sole reaction path leading to the formation of conjugated dienes if no other mechanisms were possible.

Baylouny's work (21) on dimethyl 3-acetoxy-3-cyclohexene-1,1-dicarboxylate appears to be the only report in the literature to date on the pyrolysis of a β,β -disubstituted allylic acetate. However, in his work, the pyrolysis was done only incidentally to another study. There is no discussion concerning the mechanism of the reaction or of the conditions required for the decomposition. It is therefore desirable to further examine such systems having no available

RESULTS AND DISCUSSION

Preliminary Remarks

Thermal elimination in allylic acetates has been studied by several groups of workers (see Historical Introduction). The systems chosen for these studies are generally of the type:



On pyrolysis, allylic rearrangement can conceivably compete with the direct 1,2-elimination thereby producing isomeric acetates and, subsequently, isomeric dienes. It is interesting to investigate the course of thermal elimination on allylic acetates which have no available β -hydrogens and therefore cannot undergo direct 1,2-eliminations. Allylic isomerization followed by 1,2-elimination, then, would be the sole reaction path leading to the formation of conjugated dienes if no other mechanisms were possible.

Baylouny's work (21) on diethyl 2-acetoxy-3-cyclohexen-1,1-dicarboxylate appears to be the only report in the literature to date on the pyrolysis of a β,β -disubstituted allylic acetate. However, in his work, the pyrolysis was done only incidentally to another study. There is no discussion concerning the mechanism of the reaction or of the conditions required for the decomposition. It is therefore desirable to further examine such systems having no available

β -hydrogens, with a view to establishing the mechanism for pyrolytic elimination.

Cristol's work (29) on the cis- and trans-diacetates and dibenzoates of 1,5-dichloro-9,10-dihydro-9,10-anthradiol is similar in nature to the present investigation. An acetoxy function in the 9- or 10-position of this system resembles that of an allylic acetate with no β -hydrogens. Therefore, as in our system direct 1,2-elimination is excluded. Cristol interpreted the thermal elimination as involving, most likely, 1,4-conjugate elimination. There is no

evidence, however, that excludes a mechanism involving 1,3-rearrangement, followed by rapid 1,2-elimination. One might argue that, since allylic rearrangement in that system involves the sacrifice of considerable resonance energy, the alternative direct 1,4-elimination is more likely. Experimental support for such qualitative reasoning would be desirable. Even if 1,4-conjugate pyrolytic elimination had been demonstrated in the system studied by Cristol, one would still not be able to generalize the result to aliphatic and alicyclic allylic acetates for the following reason. The entities eliminated on pyrolysis of a 9-acetoxy-9,10-dihydroanthracene come from benzhydryl carbons so that the activation energy for such a process could be lowered due to resonance. We have confirmed this by showing, in competition experiments, that 6,6-dimethyl-2-cyclohexen-1-ol acetate required a higher temperature for decomposition than 5-acetoxycyclohexene. The latter, having β -hydrogens, can undergo direct 1,2-elimination. This result implies

The main reasons why 6,6-dimethyl-2-cyclohexen-1-ol acetate was chosen for this study were the following:

(a) the methyl groups should exert only a small electronic effect and, since they are identical groups, the steric factor should be simple, with no extra conformational effects.

(b) the unsaturated ketone, 6,6-dimethyl-2-cyclohexen-1-one, has been reported in the literature and is readily synthesized. The synthesis of the corresponding acetate is therefore not difficult.

(c) a study of molecular models revealed that the molecule can readily be brought into a conformation in which the carbonyl oxygen atom is within bonding distance of a hydrogen at C-4.

(d) Deuterium can be introduced into the 4-position of the molecule in order to study the isotope effect on the reaction.

Thermal Decomposition of

6,6-Dimethyl-2-cyclohexen-1-ol Acetate

Saturated aliphatic and alicyclic acetates are generally pyrolyzed at around 500°C. Allylic acetates with β -hydrogens are completely decomposed at about 400°C (1). The dibenzoate and the diacetate of trans-1,5-dichloro-9,10-dihydro-9,10-anthradiol decompose at 254° and 265°C, respectively (29). Complete decomposition of 6,6-dimethyl-2-cyclohexen-1-ol acetate, however, required a temperature of about 600°C which is much higher than a normal allylic acetate would require. We have confirmed this by showing, in competition experiments, that 6,6-dimethyl-2-cyclohexen-1-ol acetate required a higher temperature for decomposition than 3-acetoxycyclohexene. The latter, having β -hydrogens, can undergo direct 1,2-elimination. This result implies that, if the two-step mechanism is involved, the allylic rearrangement must be a process with high free energy of activation. Alternatively, if 1,4-elimination occurs, that process must have a considerably greater free energy of activation than direct 1,2-elimination.

Isotope Effect

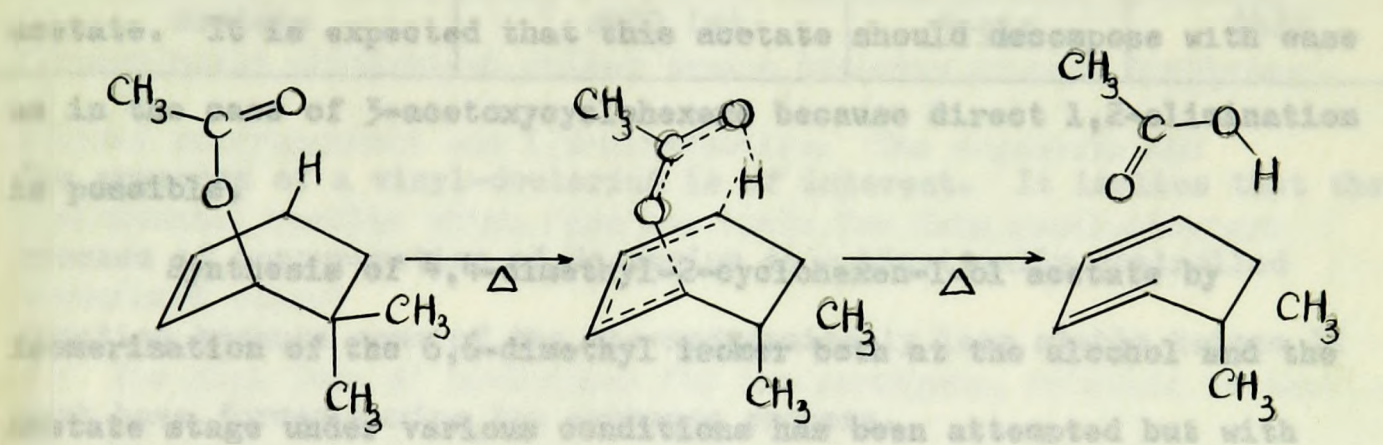
A choice between the alternative mechanisms can be made with a knowledge of the deuterium isotope effect in the decomposition of the 6,6-dimethyl ester. If a two-step mechanism is involved, there is no doubt that the first step, namely isomerization, must be the slow step. Since that step does not involve a C-H bond at C-4, the overall process should not be subject to an isotope effect. Direct 1,4-elimination, however, involves the removal of a hydrogen atom attached to C-4. It should exhibit a deuterium isotope effect of considerable size.

Absence of an isotope effect could also mean that elimination proceeds by a free radical mechanism. The presence of a sizable isotope effect indicates that a free radical mechanism is not important. The recovery of considerable amounts of acetic acid from the pyrolysates further demonstrates that acetoxy radical formation is unimportant. Acetoxy radicals have been shown to decompose into carbon dioxide and methyl radicals immediately upon formation (50). However, formation of acetic acid by a free radical mechanism would involve hydrogen abstraction by acetoxy radicals.

The existence of an isotope effect of considerable size indicates that neither isomerization nor radical formation can be rate-determining steps. The fact that an isotope effect, k_H/k_D , of the value about 2 was observed in this work implies that a process which involves C-H bond weakening at position 4, at the transition state, is important.

Mechanism of Elimination

With the above knowledge on the thermal elimination reaction of 6,6-dimethyl-2-cyclohexen-1-ol acetate, a mechanism that involves direct elimination of the elements of acetic acid from carbons 1 and 4 is proposed here.



This mechanism of elimination is an intramolecular 1,4-elimination through a cyclic eight-membered transition state. It can conveniently account for the observed deuterium isotope effect since a C-H bond is broken during the process. It is likely that, in such a process, the cis-hydrogen atom would be preferred since the trans-hydrogen cannot come within bonding distance of the carbonyl oxygen without gross distortion of the molecule. A model of a molecule of 6,6-dimethyl-2-cyclohexen-1-ol acetate shows that a boat-like conformation of the molecule with the acetoxy group occupying an axial position is the only conformation that can lead to 1,4-elimination of the acid element. The large increase in entropy required to achieve the necessary conformation may account for part of the enhanced thermal stability of the ester under discussion.

Table V. Other Points of Interest

The following points of some interest are suggested for future investigation:

Compound	Bands (cm^{-1}) ^a	Assignment	Reference
Deuterated 4,4-dimethyl-2-cyclohexen-1-ol acetate			

(1) It would be very desirable to study the thermal elimination reaction of the isomeric acetate, 4,4-dimethyl-2-cyclohexen-1-ol acetate. It is expected that this acetate should decompose with ease as in the case of 3-acetoxycyclohexene because direct 1,2-elimination is possible.

Synthesis of 4,4-dimethyl-2-cyclohexen-1-ol acetate by isomerization of the 6,6-dimethyl isomer both at the alcohol and the acetate stage under various conditions has been attempted but with little success. An alternative method of preparation, involving oxidation of 3,3-dimethylcyclohexene (51) with selenous acid in acetic anhydride, is suggested (43).

(2) It should also be of some interest to study the thermal decomposition of the methyl xanthate of 6,6-dimethyl-2-cyclohexen-1-ol. Allylic rearrangement of the xanthate would result in a dithiocarbonate. It should be interesting to compare the thermal stability of such compounds with that of the corresponding xanthates.

(3) Infrared spectra of the deuterated 6,6-dimethyl-2-cyclohexen-1-ol acetate show three modes of absorption between 2030-2350 cm^{-1} for C-D stretching (52). Their frequencies and assignments are listed in Table V.

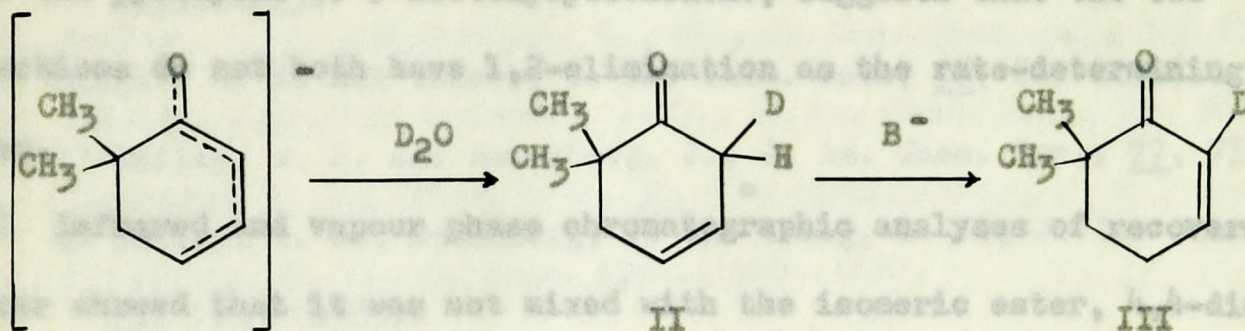
The details of the disproportionation steps involved might be worthy of investigation.

^a The letters A and B denote strong and medium bands, respectively.

Table V. Carbon-deuterium Absorption Bands

Compound	Bands (cm ⁻¹)*	Assignment	Reference
Deutero-6,6-dimethyl-2-cyclohexen-1-ol acetate	2250 (m)	2-vinyl	(12)
	2150 (s)	4- <u>trans</u>	(42)
	2100 (m)	4- <u>cis</u>	(42)

The presence of a vinyl-deuterium is of interest. It implies that the process of incorporation of deuterium is a kinetically controlled reaction because some of the thermodynamically less stable ketone II must have formed during the exchange process.



It would be expected to isomerize to the more stable form III.

This finding may be important in structural elucidation work, such as the determination of the number of exchangeable hydrogen atoms in an unsaturated ketone.

(4) The mechanism of formation of o-xylene and toluene from 6,6-dimethyl-2-cyclohexen-1-ol acetate is not clear. It is likely that these arise out of thermal aromatization reactions of 5,5-dimethyl-1,3-cyclohexadiene. The details of the disproportionation steps involved might be worthy of investigation.

* The letters s and m denote strong and medium bands, respectively.

CONCLUSION

It has been shown that vapour-phase pyrolysis of the acetate of 6,6-dimethyl-2-cyclohexen-1-ol is a one-step process involving 1,4-conjugate elimination rather than a two-step process involving allylic rearrangement and 1,2-elimination. The arguments and experimental results which form the basis for this conclusion are summarized below:

- (1) The high free of activation for the pyrolysis, relative to that for the pyrolysis of 3-acetoxycyclohexene, suggests that the two reactions do not both have 1,2-elimination as the rate-determining step.
- (2) Infrared and vapour phase chromatographic analyses of recovered ester showed that it was not mixed with the isomeric ester, 4,4-dimethyl-2-cyclohexen-1-ol acetate. Rate determining 1,2-elimination, following rapid allylic rearrangement, is thus excluded.
- (3) A substantial hydrogen-deuterium isotope effect ($k_H/k_D > 2$) exists in the decomposition of ester partially deuterated at position 4. This clearly indicates that a C-H bond at carbon 4 is included at the transition state.
- (4) The products obtained from the pyrolytic elimination reaction of 6,6-dimethyl-2-cyclohexen-1-ol acetate are not those expected from a free radical process.

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