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PYROLYTIC ELIMINATION OF ACETATES

ISOTOPE EFFECT, RELATIVE REACTIVITY AND MECHANISM[1]

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Abstract—By comparing the exo–endo olefin ratio in the pyrolysis of 1-methylcyclohexyl acetate and of 1-methylcyclohexyl acetate-2,2,6,6-d_4, the deuterium isotope effect for the acetate pyrolysis reaction has been determined to be 1·7 at 500° and 1·9 at 400°. These values are to be compared with the theoretical maximum values of 2·1 and 2·3 respectively. By carrying out competitive pyrolyses it has been possible to determine some relative rates of pyrolysis which show that no appreciable positive charge is developed in the transition state of the reaction. It is further shown that the presence of hetero substituents changes the pattern of the pyrolysis in a predictable way, and rules are formulated whereby the products to be expected from a given pyrolysis can be predicted. A convenient synthesis of cyclohexenone is described.

THE pyrolytic elimination of acetates to form olefins has been a very useful synthetic reaction, especially for the preparation of olefins from alcohols which rearrange under acidic dehydration conditions, and for the preparation of terminal olefins from primary acetates. The pyrolytic elimination of unsymmetrical secondary and tertiary acetates has been investigated by Bailey and co-workers[3] and it was claimed that these esters cleanly pyrolyze so as to form exclusively the olefin bearing the least number of alkyl groups (Hofmann rule[4]). It has recently been shown, however, that these results of Bailey were in error, that actually all pyrolytic acetate eliminations lead to mixtures of olefins, and that the most highly substituted olefin actually predominates in cyclic cases.[5–8]

Despite the fact that the more recent work has shown the pyrolysis to be less selective than the earlier reports, we have demonstrated that the products formed from a pyrolytic elimination can be rationalized in terms of statistical, steric and thermodynamic effects,[5] and it is the purpose of the present paper to discuss new experiments which help elucidate the details of the mechanism, and to present rules, firmly based on experimental data, which will enable the relative amounts of products to be expected from a given pyrolysis to be predicted. It is hoped that the acetate pyrolysis will then gain a place among the most common laboratory procedures.

Since the cyclic, *cis* character of the reaction is well recognized,[9] we shall confine

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[2] Procter and Gamble summer research fellow, 1957 and 1958.

[3a] W. J. Bailey and C. King, *J. Amer. Chem. Soc.* **77**, 75 (1955); [b] W. J. Bailey, J. J. Hewitt and C. King, *J. Amer. Chem. Soc.* **77**, 357 (1955).

[4] C. K. Ingold, *Structure and Mechanism in Organic Chemistry* p. 427 *et seq.* Cornell University Press, N.Y. (1953).

[5] D. H. Froemsdorf, C. H. Collins, G. S. Hammond and C. H. DePuy, *J. Amer. Chem. Soc.* **81**, 643 (1959).

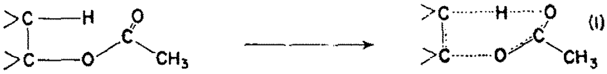
[6] W. H. Bailey and W. F. Hale, *J. Amer. Chem. Soc.* **81**, 647 (1959).

[7] E. E. Royals, *J. Org. Chem.* **23**, 1822 (1958).

[8] R. A. Benkeser and J. J. Hazdra, *J. Amer. Chem. Soc.* **81**, 228 (1959).

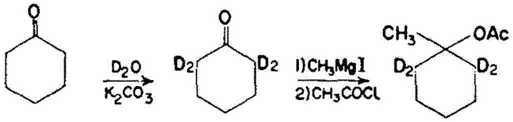
[9] E. R. Alexander and A. Mudrak, *J. Amer. Chem. Soc.* **73**, 59 (1951).

our discussion to a consideration of the two bond-breaking processes, namely the breaking of the C—H and the C—O bonds (equation 1). We will be most interested


(1)

in the timing of these two processes, and in the effect of substituents on the ease of such breaking. We shall then be able to describe the transition state in some detail.

If we examine first the carbon–hydrogen bond-breaking process, we are struck by the fact that for non-cyclic acetates the Hofmann product predominates. However, we have shown[5] that steric and statistical factors favor the formation of the least substituted olefins and that, *other conditions being equal, the ease of hydrogen removal in acetate pyrolyses is that predicted by operation of the Saytzeff rule*, i.e. 3° > 2° > 1°. If the hydrogen is benzyl, then its removal is favored,[10] but the effect of the phenyl is not to acidify the hydrogen but to stabilize the incipient double bond.[11] Strongly acidifying groups attached to the carbon bearing the hydrogen (e.g. C=O, NO_2) may favor its removal,[10a] but here experimental data are still contradictory.[12] We considered it of interest to examine the deuterium isotope effect in the acetate pyrolysis reaction, because the magnitude of this effect is generally considered to be a measure of the amount of bond-breaking in the transition state.[13] Curtin and Kellom[14] had arrived at a value of 2·8 ± 0·6 for this isotope effect, but because this value was determined only incidentally to another study the error was unavoidably large, and in addition the system in which it was determined (1,2-diphenylethyl acetate) might not be typical for aliphatic acetates. Kinetic experiments at the temperatures required for this reaction are difficult to perform, so we were led to study relative rates by an internal competition method. The synthetic aspects of the reaction are summarized in equation (2).



(2)

We pyrolyzed samples of 1-methylcyclohexyl acetate and its deutero analog (I) under identical conditions and determined the ratio of the olefinic products formed. These results are reported for 400° and 500° in Table 1. Making the reasonable assumption that the rate of pyrolysis into the exocyclic methyl group is the same in both compounds, it is possible to calculate the deuterium isotope effect quite easily. It is seen that by this method relatively large values for k_H/k_D are found, indicating that the carbon–hydrogen bond is being broken in the transition state. On the other hand they are significantly less than the theoretical maxima[15] at these temperatures

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[10a] W. J. Bailey and C. King, *J. Org. Chem.* **21**, 858 (1956); [b] C. G. Overberger, E. M. Pearce and D. Tanner, *J. Amer. Chem. Soc.* **80**, 1761 (1958).

[11] C. H. DePuy and R. E. Leary, *J. Amer. Chem. Soc.* **79**, 3705 (1957).

[12] See ref. 10*a*, footnote 11.

[13] K. B. Wiberg, *Chem. Rev.* **56**, 713 (1956).

[14] D. Y. Curtin and D. B. Kellom, *J. Amer. Chem. Soc.* **75**, 6011 (1953).

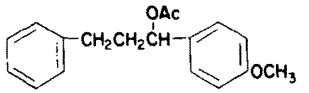
[15] If there were no C—H bond-breaking in the transition state then k_H/k_D would be unity. On the other hand if the hydrogen were transferred in the rate determining step, and the reaction were so concerted that the forming O—H bond exactly compensated for the breaking C—H bond, then only the mass differences would be important and k_H/k_D would be $\sqrt{2}$. The experimental value of 1·9 falls half-way between this value and the theoretical maximum for no bonding to hydrogen in the transition state.

which would perhaps imply that simultaneous O—H bond formation is significant. This is as would be expected for a highly concerted cyclic mechanism.

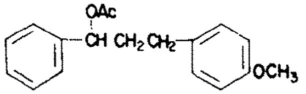
We next turned our attention to the breaking of the C—O bond. Maccoll[16] has collected relative rate data for the pyrolysis of primary, secondary and tertiary acetates and has shown that ethyl, i-propyl and t-butyl acetates react in the ratio 1 : 26 : 1660 at 400°. This is in the order to be expected if heterolytic C—O bond-breaking is important, but as Maccoll has also pointed out, at much reduced relative values than one would expect for a carbonium ion mechanism.[17] It is also the order to be expected on statistical, steric and thermodynamic grounds. We have already shown[11] that compound II, a *p*-methoxybenzyl acetate, pyrolyzes only about three times more rapidly than III, again a result inconsistent with the development of appreciable positive charge in the transition state. We have now obtained new results which substantiate this conclusion even more thoroughly. The relative rates given in Table 2 were obtained by pyrolyzing mixtures of acetates and determining the ratio of olefinic products by g.p.c. The results were very reproducible, but could only be determined accurately over a small temperature range. They show clearly that the amount of C—O *heterolytic* bond-breaking must be very small, for in any reaction which involved appreciable carbonium ion character the α-phenylethyl acetate would

TABLE 1. DEUTERIUM ISOTOPE EFFECT IN THE PYROLYSIS OF 1-METHYLCYCLOHEXYL ACETATE

	Temp °C	% Endo	% Exo	k_H/k_D	k_H/k_D max[13]
1-Methylcyclohexyl acetate	400	73	27		
1-Methylcyclohexyl acetate-d_4	400	59	41	1·9	2·3
1-Methylcyclohexyl acetate	500	73	27		
1-Methylcyclohexyl acetate-d_4	500	61	39	1·7	2·1



II



III

TABLE 2. RELATIVE RATES OF PYROLYSIS OF ESTERS AT 400°

Compound	Relative rate
5-Nonyl acetate	1
α-Phenylethyl acetate	0·74 ± 0·02[a]
β-Phenylethyl acetate	0·07 ± 0·006[a]
α-Acetoxycyclohexanone	0·06

[a] Corrected for differences in thermal conductivity of the olefins.

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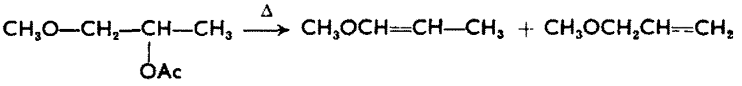
[16] A. Maccoll, *J. Chem. Soc.* 3398 (1958).

[17] The corresponding bromides pyrolyze to olefins with a rate ratio of 1 : 170 : 32,000.[16]

certainly react much more rapidly than would α-acetoxycyclohexanone. Actually it is only very slightly more reactive. It also suggests that it cannot be true that "it is the forming O—H bond that primarily determines the rate", as concluded by Maccoll,[16] for then β-phenylethyl acetate, with an activated hydrogen to be removed, would be the most reactive of the compounds studied.

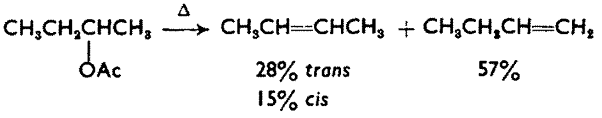
We may then summarize the results in the following way. The carbon–hydrogen bond is being broken in the transition state, as shown by the deuterium isotope effect, but the acidity of the hydrogen being removed is not of primary importance.[18] Substituents at both the carbon bearing the hydrogen and that bearing the acetoxyl exert an influence paralleling that which they will exert on the olefinic product, and consequently, other things being equal,[19] the more stable olefin predominates among the products. It may then 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, but one in which no appreciable charge separation is evident. This then places acetate pyrolysis in a category similar to pyrolyzes of vinyl ethers, as discussed by Maccoll.[16]

With this picture of the transition state firmly in mind, it is possible to predict, with a great deal of accuracy, the ratio of products to be expected in a given pyrolysis. For reasons that will presently become clear, we decided to examine the pyrolysis of 1-methoxyisopropyl acetate. The reaction is that expressed by equation (3), and it is to be compared with the pyrolysis of s-butyl acetate.[5]



$$\underset{\text{OAc}}{CH_3O{-}CH_2{-}\underset{|}{C}H{-}CH_3} \xrightarrow{\Delta} CH_3OCH{=}CH{-}CH_3 + CH_3OCH_2CH{=}CH_2 \qquad (3)$$

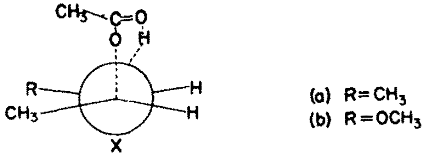
IV V VI



$$\underset{\text{OAc}}{CH_3CH_2\underset{|}{C}HCH_3} \xrightarrow{\Delta} \underset{\substack{28\%\ trans\\ 15\%\ cis}}{CH_3CH{=}CHCH_3} + \underset{57\%}{CH_3CH_2CH{=}CH_2} \qquad (4)$$

VII VIII IX

Statistically both primary olefins are favored over their internal isomers by a ratio of 3 : 2. The smaller amount of *cis*-2-butene than *trans*-2-butene formed was accounted for on the basis of eclipsing between the two methyl groups in the transition state leading to its formation (Xa). When R = OCH_3 (Xb) such eclipsing may be



X

slightly diminished and a slight increase in the *cis/trans* ratio might be expected, but differences in the two cases on statistical and steric grounds will be small. However,

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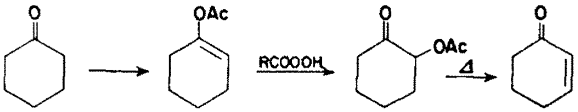
[18] This last will probably not be true for extremely acidic hydrogens (*vide supra*). If the hydrogen becomes sufficiently acidic the mechanism of the reaction may even change, as it does in the case of xanthate pyrolyses. [F. Bordwell and P. S. Landis, *J. Amer. Chem. Soc.* **80**, 6383 (1958)].

[19] i.e. Statistical and steric effects.

the methoxyl group will exert its influence by stabilizing the transition state leading to the formation of both *cis* and *trans* V in the same way that it stabilized the olefin in the vinyl ether being formed. Consequently one would predict that a somewhat greater proportion of internal olefins (V) would be formed on pyrolysis of the methoxy acetate than from the pyrolysis of s-butyl acetate. The actual results are in excellent agreement with these predictions, for pyrolysis of IV at 500° gave 47% primary olefin (VI) and 53% internal olefin (V) of which 30% was *trans* and 23% was *cis*. Bailey and Nicholas reported that the product of this pyrolysis was substantially pure primary olefin.[20]

Finally, we conclude our theoretical discussion with a consideration of the effect of temperature on the direction of elimination. Bailey and Hale[6] have pyrolyzed 1-methylcyclohexyl acetate and t-amyl acetate at temperatures from 220° to 600° and have arrived at the conclusion that as the temperature is lowered, Saytzeff elimination is favored, with the Saytzeff product predominating at the lower end of the temperature scale. These results are contrary to our own experience,[5] for we found no appreciable change in product composition as the temperature was lowered. For the deuterium isotope studies reported in this paper we measured the exo–endo product ratio again at 400° and found it to be 73–27, within 1 per cent of its value at 450° and at 500°, and not the 82–18 ratio reported by Bailey and Hale. The same ratio, 73–27, was also found at 350°.[5] We have pyrolyzed t-amyl acetate at 250° and have found no detectable olefinic product, either by g.p.c. or by bromine titration, and by using the Arrhenius parameters given[21] for the pyrolysis of t-butyl acetate it can be calculated that at 225° only 0·0035% yield of olefin would be expected. We therefore believe that another mechanism must be operating in their case at lower temperatures, and may be intruding even at 400°.[22]

With all the current discussion about the mechanistic aspect of the ester pyrolysis reaction, sight may be lost of its synthetic utility. In our experience the reaction is extremely simple, the yields are good and often quantitative, and the products easy to work up. Little charring or other decomposition has been observed. The pyrolysis



(5)

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[20] W. J. Bailey and L. Nicholas, *J. Org. Chem.* **21**, 648 (1956). Bailey and Hale[6] say "One could conclude that there are possible at least two sets of experimental conditions for the pyrolysis of esters which give slightly different results in the direction of elimination. One set of conditions appears to give the exocyclic isomer and to proceed in a selective manner according to the Hofmann rule. These highly elusive conditions, however, are not the normal operating conditions and at the present time cannot be defined." Bailey and Hale quote, in support of the above statement, the work of J. G. Traynham and O. S. Pascual, *J. Org. Chem.* **21**, 1362 (1956) who pyrolyzed 1-methylcyclohexyl acetate and who subsequently undoubtedly worked with a product which was at least rich in methylene cyclohexane. They neglect to state, however, that Traynham and Pascual *fractionated their products before use*. Since methylene cyclohexane boils nine degrees lower than 1-methylcyclohexene, it is not unlikely that they had mainly methylene cyclohexane for their further work. We do not believe that there are conditions likely to be found which will lead exclusively to Hofmann or exocyclic products.

[21] C. E. Rudy and P. Fugassi, *J. Phys. Chem.* **52**, 357 (1948).

[22] In this connection it may be significant that Bailey and Hale refer to the paper of W. J. Bailey and J. J. Hewitt, *J. Org. Chem.* **21**, 543 (1956) for the details of how the pyrolyses were carried out. In that paper the pyrolysis tube was cleaned after every run with nitric acid and distilled water. In our experience cleaning after every run is neither necessary nor desirable, but when the helices are cleaned in acid, *they must be washed free of residual acid with ammonia*, for it is not usually possible to wash glass free of acid with water. Traces of residual acid may account for the differences in results found at low temperature.

of α-acetoxycyclohexanone to cyclohexenone (equation 5) is a good example, and this sequence is, in our opinion, competitive with other available methods for the synthesis of this useful intermediate. This general method appears especially attractive for the preparation of higher homologs.

EXPERIMENTAL[23]

1-Methylcyclohexyl acetate-2,2,6,6-d_4. Cyclohexanone (49 g, 0·5 mole), D_2O (20 g, 1·0 mole) and K_2CO_3 (0·25 g) were heated at reflux for 24 hr, the solution was cooled and the layers separated. The ketonic layer was mixed with another portion of D_2O and K_2CO_3 and the procedure repeated. After six exchanges the ketone was distilled (30 g) and analyzed for deuterium. It showed 97·0 and 96·5% of the exchange calculated for the replacement of four hydrogens by deuterium. This cyclohexanone (14·3 g, 0·14 mole) was reacted with the Grignard reagent from CH_3I (24·6 g, 0·173 mole) and Mg (4·6 g, 0·19 atom) in 100 ml of dry ether. After working up in the usual manner the deutero 1-methylcyclohexyl alcohol was carefully distilled through a spinning brush column of approximately 15 theoretical plates. The product melted at 27–27·5°. It was acetylated with acetyl chloride and dimethyl aniline.[24] The acetate analyzed for 98% and 97·4% exchange of four hydrogens for deuterium.

Deuterium analyses. These were performed by burning the compound, purifying the water formed and analyzing for per cent deuterium oxide by the falling drop method following the procedure of Kirshenbaum.[25]

5-Nonyl acetate. The alcohol, prepared according to the method of *Organic Syntheses*,[26] was acetylated to give the acetate, b.p. 202–204°, lit.[27] 206–207°. It gave only a single peak by g.p.c. analysis.

Phenylethyl acetates. α- and β-phenylethyl acetates were prepared by acetylation of the commercially available alcohols. Their physical properties were in agreement with literature values.

α-Acetoxycyclohexanone. This compound was prepared by the method of Shine and Hunt.[28] Recrystallization from pentane gave a product of m.p. 35·5–36° (lit.[4] m.p. 35–36°).

β-Methoxyisopropyl acetate. Acetylation of the commercially available alcohol according to the directions of Bailey and Nicholas[20] followed by careful fractionation gave material of b.p. 145–146° (reported,[29] 145·5–146°).

Methyl allyl ether. Allyl bromide (34 g, 0·28 mole) was added dropwise with stirring to a solution of sodium (7·5 g, 0·33 mole) in 250 ml of dry methanol. After heating at reflux for 1 hr the product was distilled from the reaction flask and carefully fractionated. B.p. 42·5–43°, lit.[30] b.p. 42·5–43°.

Pyrolyses. The method and apparatus were as previously described.[5] Peak areas were determined by use of a planimeter. For the competitive pyrolyses equimolar mixtures of the esters and 5-nonyl acetate were passed through the column (for the case of β-phenylethyl acetate the molar ratios were 5 : 1) and the total reaction mixture was analyzed by g.p.c. Conversions were kept low (21–45% of the more reactive olefin) and the relative rates calculated as described by Lee.[31] Prior g.p.c. analysis of an equimolar mixture of pure 4-nonene (from pyrolysis of the acetate) and pure styrene gave a peak area ratio of 1·30 : 1. In the pyrolysis of α-acetoxycyclohexanone no correction was made for differences in thermal conductivity. The relative rates of the phenylethyl acetates are the average for three runs, that for acetoxycyclohexanone for a single run.

Pyrolysis of β-methoxyisopropyl acetate. The acetate was pyrolyzed in the conventional manner at 500° at the rate of 3 ml per min. A conversion of 57% was obtained, as determined by titration of the acetic acid liberated. The olefins were analyzed by g.p.c. The major peak (47%) had a retention time identical to that of an authentic sample of methyl allyl ether. The other two peaks (31% and

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[23] Melting and boiling points are uncorrected.

[24] T. D. Nevitt and G. S. Hammond, *J. Amer. Chem. Soc.* **76**, 4124 (1954).

[25] I. Kirshenbaum, *Physical Properties and Analysis of Heavy Water.* McGraw-Hill, New York (1951).

[26] *Organic Syntheses* Coll. Vol. II p. 179. John Wiley, New York (1943).

[27] B. A. Arbuzov and V. S. Vinogradova, *Bull. Acad. Sci. U.S.S.R.* 535 (1954).

[28] H. J. Shine and G. E. Hunt, *J. Amer. Chem. Soc.* **80**, 2434 (1958).

[29] A. A. Petrov, *J. Gen. Chem. U.S.S.R.* **14**, 1038 (1944).

[30] J. Irvine, J. MacDonald and C. Soutar, *J. Chem. Soc.* **107**, 351 (1951).

[31] T. S. Lee in *Techniques of Organic Chemistry* Vol. VIII, p. 101. Interscience Publishers, New York (1953).

22% respectively) were assigned to the *trans* and *cis* enol ether because a sample of the pyrolysate with 2,4-dinitrophenylhydrazine solution formed an immediate copious precipitate of the 2,4-dinitrophenylhydrazone of propionaldehyde, m.p. 153·5–154·5°, (reported[32] m.p. 155°). It was assumed that the larger peak, with the smaller retention volume, was the *trans* isomer by analogy with the butenes.

Pyrolysis of α-acetoxycyclohexanone. The pyrolysis was carried out in the conventional manner at 510°. The rate of addition was 0·5 ml per min and a conversion of 96% was obtained. The product was identified as cyclohexenone by its infrared spectrum and its retention volume on gas chromatography.

[32] C. Allen, *J. Amer. Chem. Soc.* **52**, 2957 (1930).