1-1-1969

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Recommended Citation
Wassenaar, Siek, "A kinetic study of the low temperature pyrolysis of hydrogen phthalate esters of some tertiary alcohols." (1969). *Electronic Theses and Dissertations*. 6076.
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A KINETIC STUDY OF THE LOW TEMPERATURE PYROLYSIS OF HYDROGEN PHTHALATE ESTERS OF SOME TERTIARY ALCOHOLS

BY

SIEK WASSENAAR

A DISSERTATION

Submitted to the Faculty of Graduate Studies through the
Department of Chemistry in Partial Fulfillment
of the Requirements for the Degree of
Doctor of Philosophy at the
University of Windsor

Windsor, Ontario
1969

THIS DISSERTATION HAS BEEN EXAMINED AND APPROVED BY:

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O Lord, how great
are thy works!

Ps. 92:5

ABSTRACT

Hydrogen phthalate esters were prepared from cis- and trans-1,2-dimethylcyclohexanol, cis- and trans-1-phenyl-2-methylcyclohexanol and 1-phenyl-2-methylcyclohexanol-2,6,6-d_3. A kinetic study of the thermal decomposition of these phthalate esters was made and rate constants and activation parameters were determined.

The 1,2-dimethylcyclohexyl hydrogen phthalates were pyrolyzed neat over an eight degree temperature range. From the positive entropy of activation (6 and 10 for trans and cis respectively) and previous isotope and product distribution work of this laboratory, it is postulated that the pyrolytic decomposition of these esters occurs via a free radical or ion pair mechanism. The product distribution at the pyrolysis temperature was determined and the difference in the amount of 1,2-dimethylcyclohexene from the cis (56%) and the trans (24%) is explained in terms of an anion proximity effect in the transition state.

The 1-phenyl-2-methylcyclohexyl hydrogen phthalate esters had to be pyrolyzed in solution because the melting points and decomposition points coincide. The negative entropy of activation (-11) for the trans ester is explained in terms of a solvent effect since the deuterated compound did not show an isotope effect. For the _cis_ compound a positive entropy of activation (+7) was obtained. The difference in activation entropies between the _cis_ and _trans_ isomers is explained in terms of the rate of decomposition and the effect of the solvent. A free radical or ion pair mechanism is also proposed for the decomposition of these compounds. The product distribution for the _cis_ and _trans_ isomers was found to be similar. A comparison with the product distribution obtained from the 1,2-dimethylcyclohexyl phthalate esters, shows that the phenyl group has a pronounced effect on the product distribution.

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Dr. K. G. Rutherford for his able and patient guidance in the course of these studies. He is also thankful to the other members of the department in particular Drs. J. L. Hencher and R. J. Walton whose help with the computer programme is appreciated.

The financial assistance provided by the Ontario Government in the form of Fellowships is also gratefully acknowledged.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure Page

Figure Page

CHAPTER I

INTRODUCTION

The pyrolytic elimination reaction in esters and xanthates (the Chugaev reaction) is known to result in the nearly exclusive abstraction of a <u>cis</u> - β hydrogen atom.[1] These eliminations have been visualized as proceeding by a highly concerted mode in which in the activated complex, little charge separation develops and some double bond character is thought to exist between the incipient olefinic carbon atoms (Fig. 1).

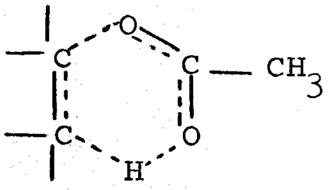

Fig. 1 - Transition State for the Concerted Cyclic Elimination of an Acetate Ester

An elegant demonstration of the <u>cis</u> nature of the ester pyrolysis has been provided by Curtin and Kellom.[2] They prepared <u>threo</u>- and <u>erythro</u>-1,2-diphenylethanol-2d by

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[1] C. H. DePuy and R. W. King, <u>Chem</u>. <u>Rev</u>., <u>60</u>, 431 (1960).

[2] D. Y. Curtin and D. B. Kellom, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>75</u>, 6011 (1953).

reducing cis- and trans-stilbene oxide with lithium aluminum deuteride (Fig. 2).

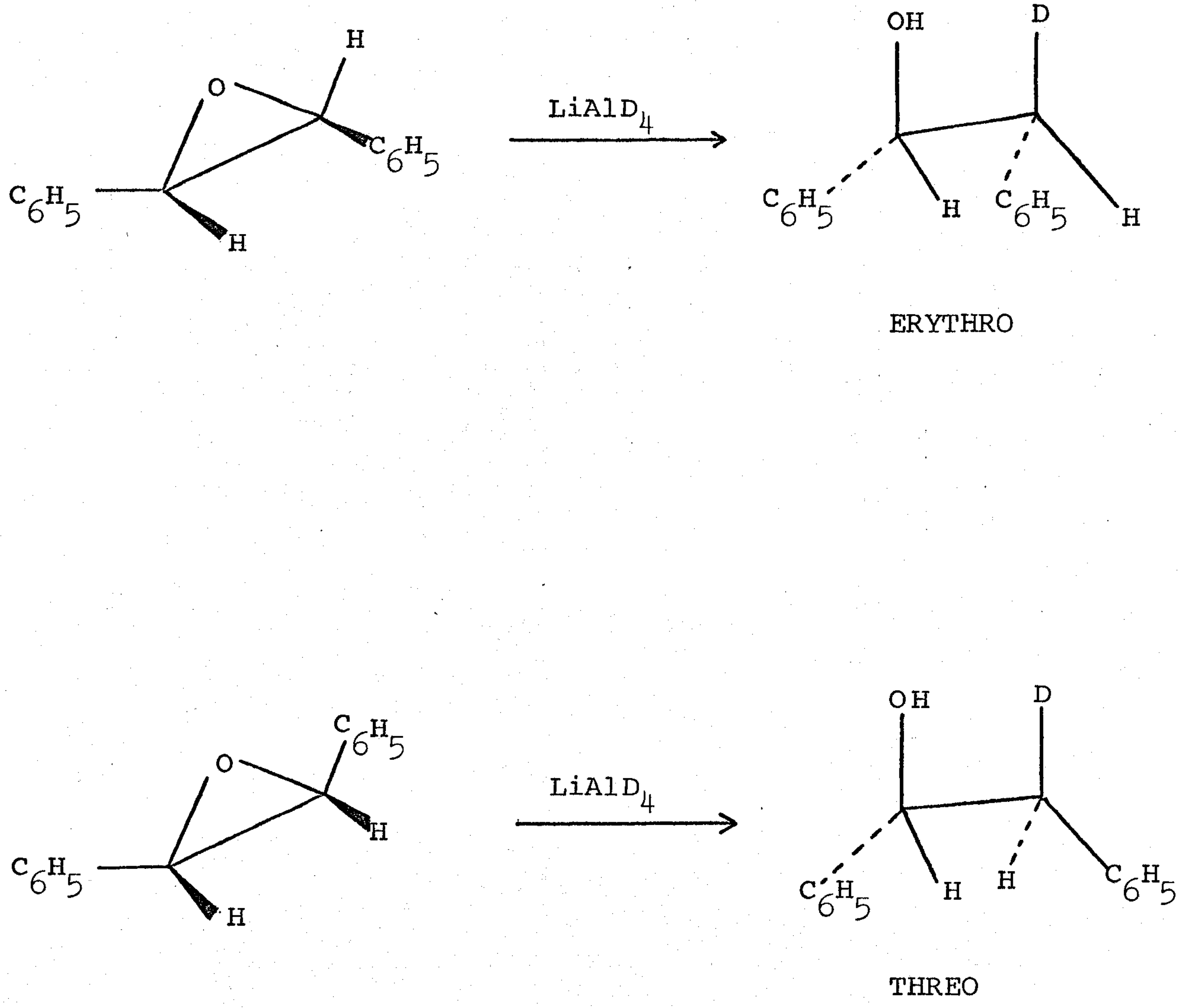

Fig. 2 - threo- and erythro-1,2-Diphenylethanol-2d

Pyrolysis of the acetates of both these alcohols yielded trans-stilbene (Fig. 3).

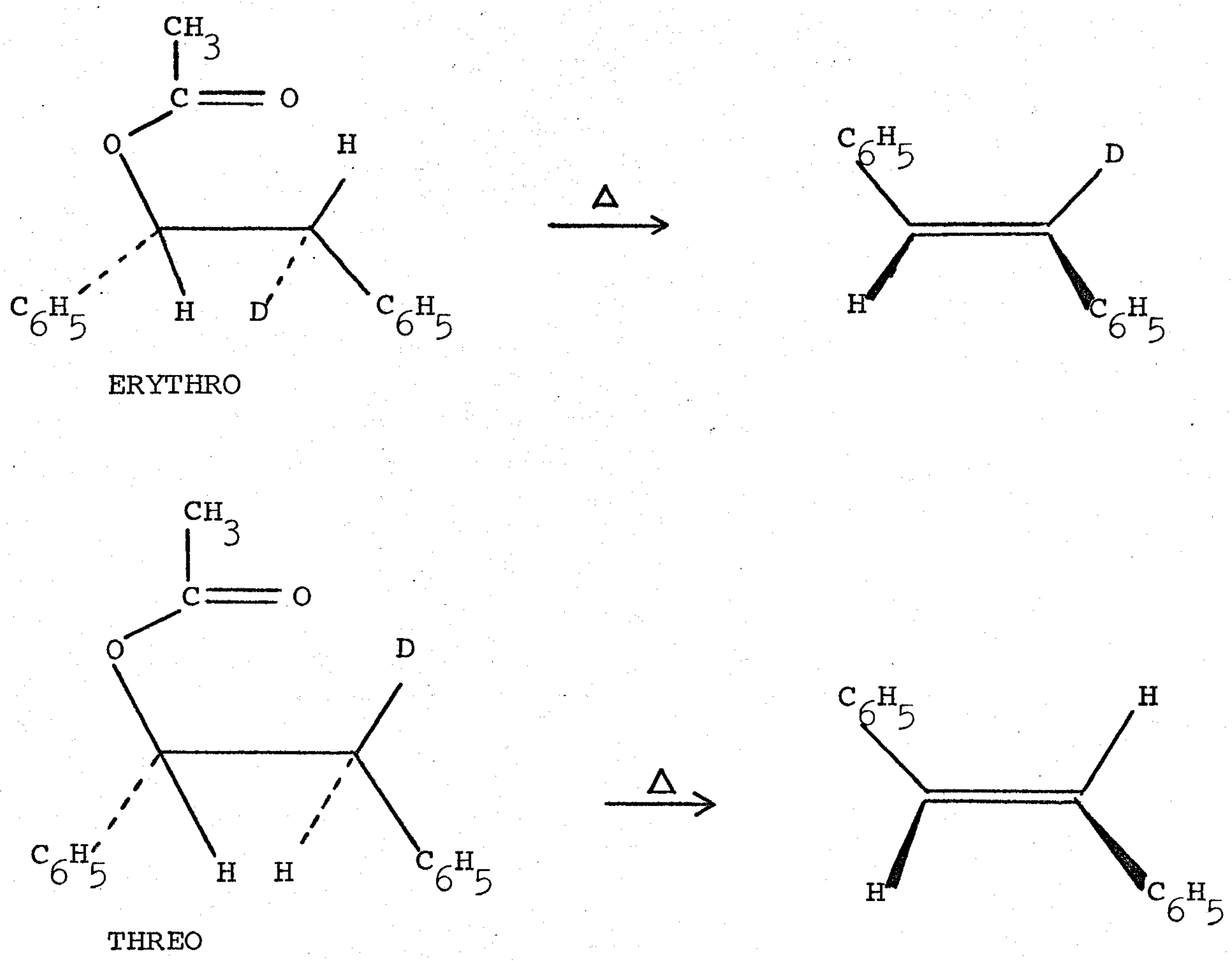

Fig. 3 - Pyrolysis of the Acetates of threo- and erythro-1,2-Diphenylethanol-2d

The stilbene from the erythro compound retained almost all of its deuterium (95.6%), whereas that from the threo isomer lost most of its deuterium (73.6%). These results are consistent with a cyclic mechanism.

The decomposition of cis-2-methylcyclohexyl acetate to yield mainly 3-methylcyclohexene[3, 4] and cis-2-phenylcyclohexyl acetate to give mainly 3-phenylcyclohexene[5] provides further evidence for a cyclic mechanism (Fig. 4).

The three factors of primary importance in determining the ratio of the products formed in the pyrolysis of aliphatic esters are: (a) the number of available hydrogen atoms in the different directions (statistical effect), (b) the repulsive interactions of groups in the transition state of the elimination process (steric effect) and (c) the relative stabilities of the olefinic products formed (thermodynamic effect).[6]

The high temperature pyrolysis of sec-butyl acetate exemplifies the statistical effect (Fig. 5). For elimination toward the methyl groups, there is a hydrogen atom cis to the acetoxy group in all rotational conformations. For

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[3] R. T. Arnold, G. G. Smith and R. M. Dodson, J. Org. Chem., 15, 1256 (1950).

[4] W. J. Bailey and L. Nicholas, J. Org. Chem., 21, 854 (1956).

[5] E. R. Alexander and A. Mudrak, J. Am. Chem. Soc., 72, 1810 (1950).

[6] C. H. DePuy and R. W. King, Chem. Rev., 60, 431 (1960).

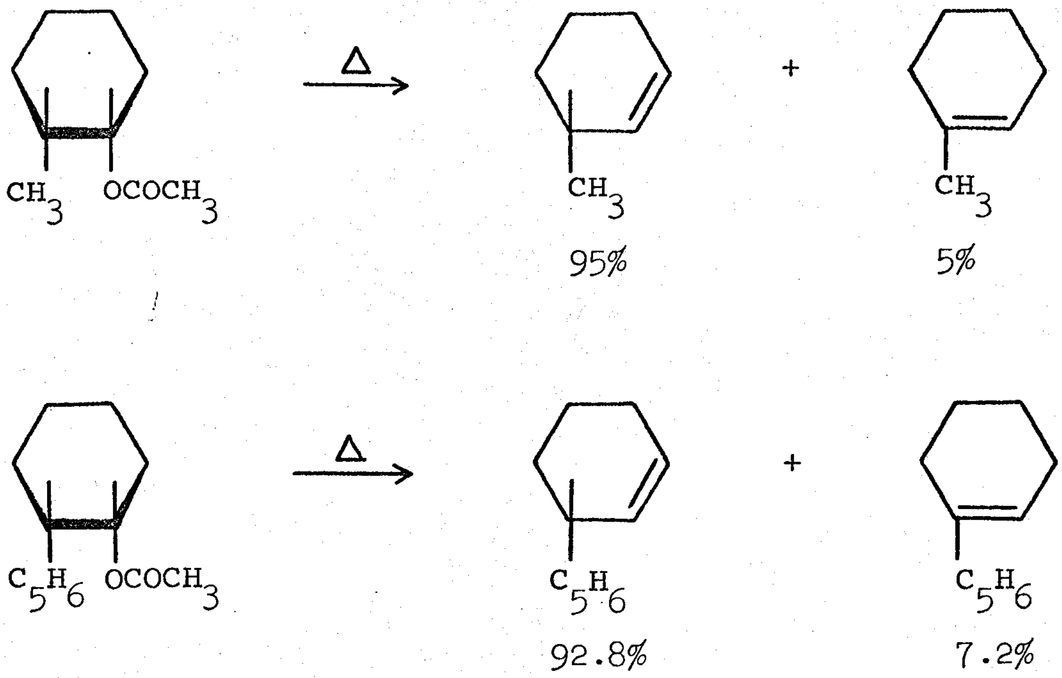


Fig. 4 - Pyrolysis of the Acetates of cis-2-Methylcyclohexanol and cis-2-Phenylcyclohexanol

elimination toward the methylene group, there is no cis hydrogen atom in one of the conformations. Statistically, the formation of 1-butene is favoured over 2-butene by a factor of 3:2, in excellent agreement with the experimental values of 57% and 43% respectively.

sec-Butyl acetate may also be used to demonstrate the steric effect. The pyrolysis of this acetate should yield cis- and trans-2-butene in equal amounts. However the amount of trans olefin produced is twice that of the

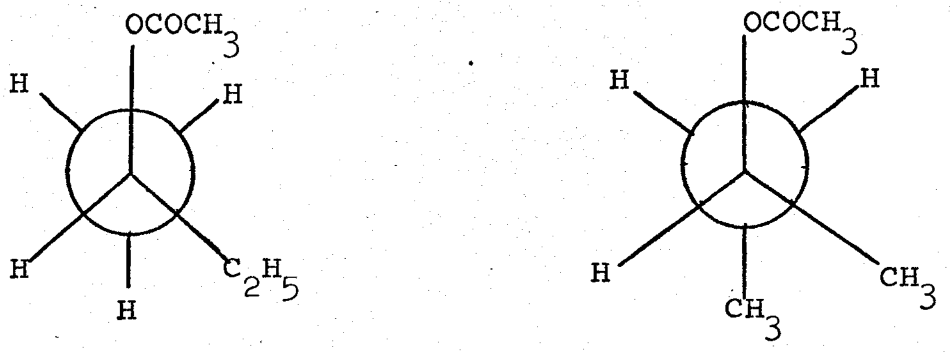
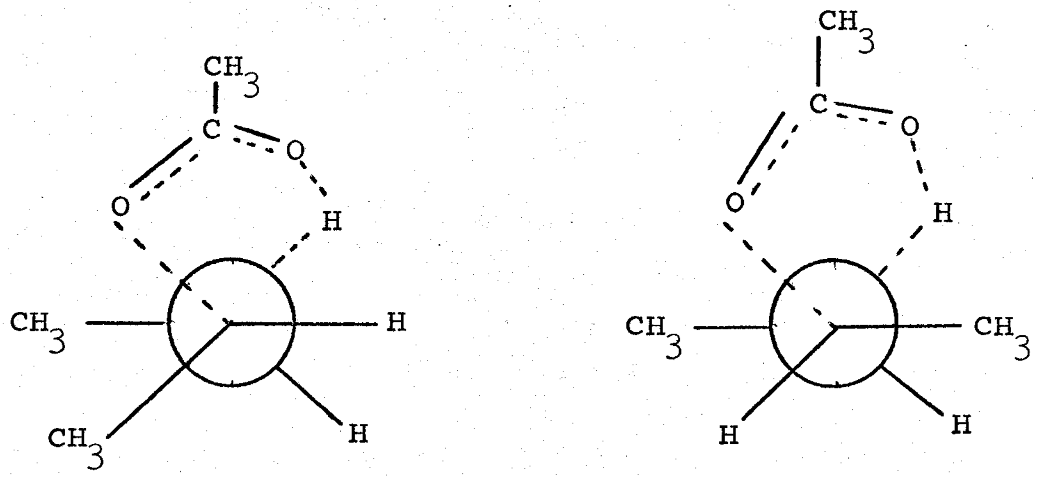


Fig. 5 - Possible Conformations in the Pyrolysis of *sec*-Butyl Acetate

cis isomer. It has been suggested that the methyl-methyl repulsion in the transition state leads predominantly (28%) to the *trans* olefin[7] (Fig. 6).



cis *trans*

Fig. 6 - Possible Transition States in the pyrolysis of *sec*-Butyl Acetate

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

The thermodynamic effect should favour the more stable internal olefins over their terminal isomers. Thus on statistical grounds 1-butene and trans-2-butene should be formed from sec-butyl acetate in the ratio of 3:1, because eclipsing effects are absent in both cases and there are three primary hydrogen atoms whose loss would lead to 1-butene and one hydrogen atom whose loss would give trans-2-butene. Experimentally, the ratio of the isomers is found to be approximately 2:1. The fact that more than the expected amount of the internal olefin was formed is attributed to its greater thermodynamic stability.

A concerted cis-cyclic mechanism as described previously explains the formation of the major portion of products in the pyrolysis of acetates, however, minor quantities of net trans elimination have been observed.[8] Again, Alexander and Mudrak[9] reported that the pyrolysis of cis- and trans-2-methyl-1-indanyl acetate yields only one olefin namely 2-methyl indene. Noteworthy is the fact that the trans-2-methyl-1-indanyl acetate was completely converted to products at 450°C, while the cis isomer required 650°C

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[8] H. R. Nace, Org. Reactions, 12, 57 (1962).

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

for the same quantitative conversion (Fig. 7). It is obvious that in the cis isomer no β hydrogen atom is available for a concerted cis elimination and although the cis compound is more stable it decomposes nevertheless to yield 2-methyl indene. The authors suggest that there must be another reaction path by which elimination can occur.

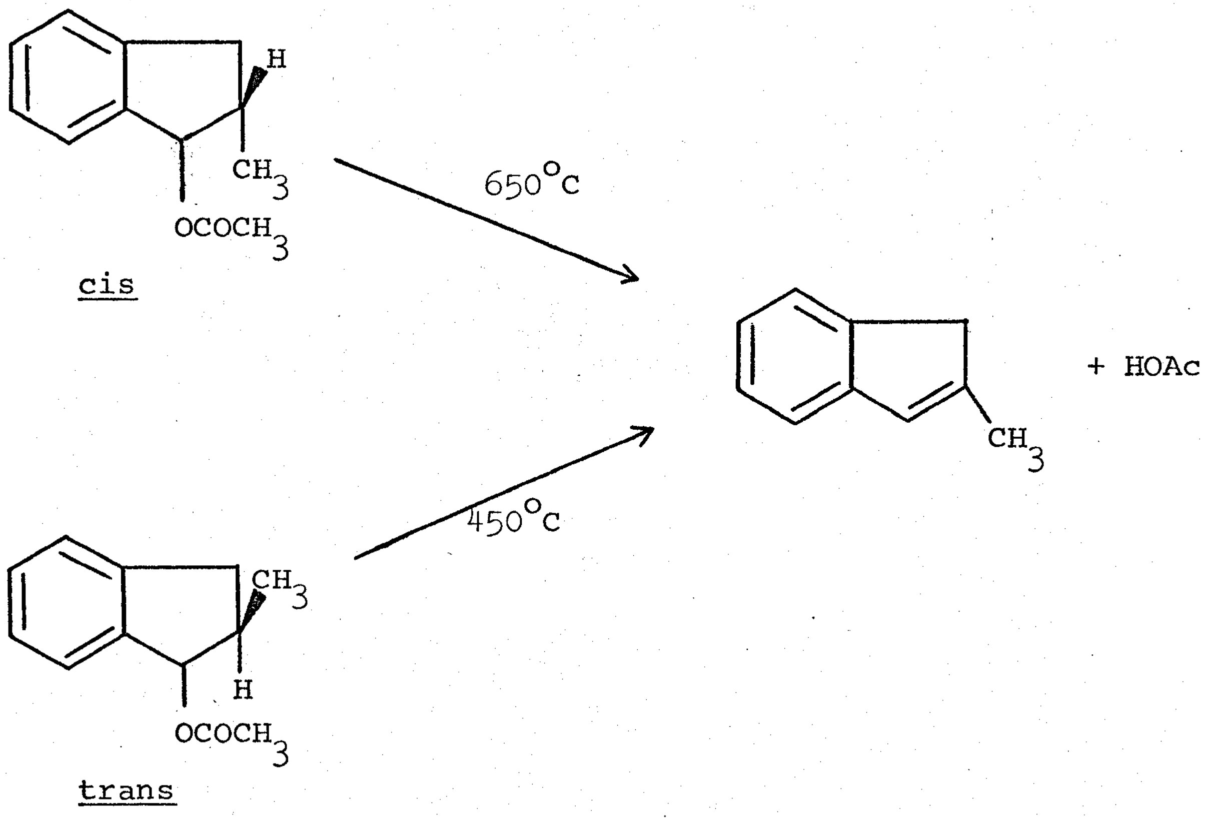

Fig. 7 - The Pyrolysis of cis- and trans-2-Methyl-1-indanyl Acetate

The pyrolysis of trans-1,2-dimethylcyclohexyl acetate (450°) does not yield any 1,2-dimethylcyclohexene.[10] The pyrolysis of trans-1,2-dimethylcyclohexyl hydrogen phthalate on the other hand yields 19% of 1,2-dimethylcyclohexene when decomposed at 140-150°.[11] This anomaly suggests strongly that acetates and phthalates may decompose by different mechanisms. Rutherford and Ottenbrite[12] have shown that a partial decomposition of ^{18}O enriched trans-1,2-dimethylcyclohexyl hydrogen phthalate results in the enrichment of ^{18}O in the alcohol portion of the undecomposed ester. The increase in excess of the normal ^{18}O abundance, represents approximately 17% exchange between the alkyl oxygen and carbonyl oxygen atoms (Fig. 8).

The ^{18}O exchange in the partial pyrolysis of trans-1,2-dimethylcyclohexyl hydrogen phthalate and the appearance of 19% of 1,2-dimethylcyclohexene in the complete pyrolysis of the same compound would seem to support the theory that carbonium ion character exists in the transition state of

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

[11] K. G. Rutherford and D. P. C. Fung, Can. J. Chem., 42, 2657 (1964).

[12] K. G. Rutherford and R. M. Ottenbrite, Can. J. Chem., 45, 679 (1967).

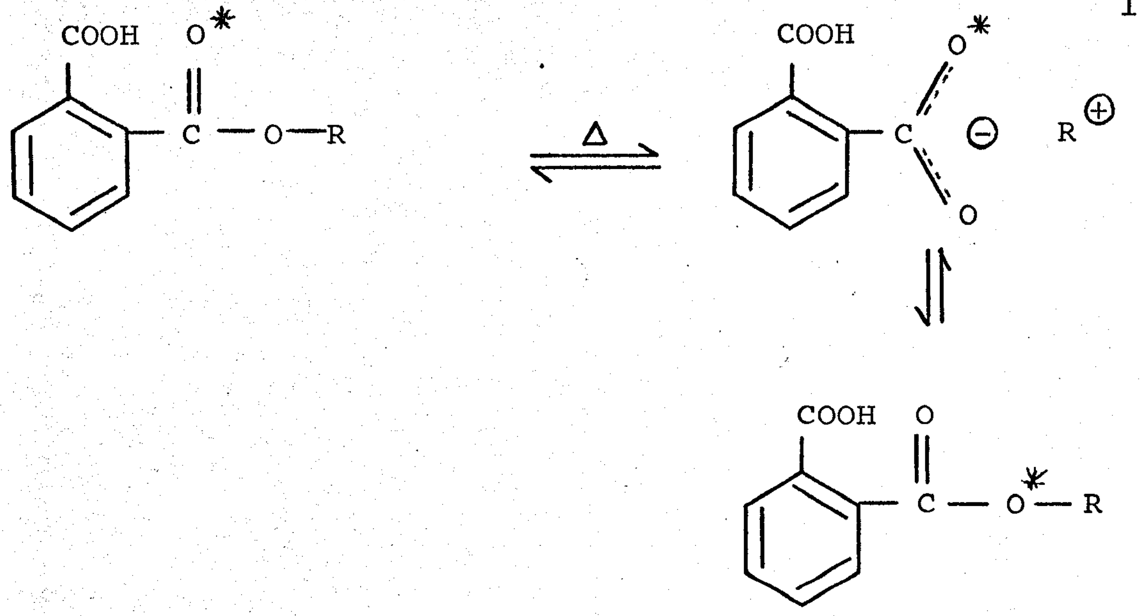

Fig. 8 - Exchange of ^{18}O between Carbonyl and Alkyl Oxygen in trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate

the pyrolysis of tertiary hydrogen phthalates which in general undergo decomposition at much lower temperatures than tertiary acetates.

The suggestion of an ion pair in the pyrolysis of esters is not new. Thus Bailey and Hale[13] did not exclude the possibility that a mechanism shift from ionic to cyclic may occur in the pyrolysis of tert-amyl and 1-methylcyclohexyl acetates as the temperature is increased from a liquid to a gas phase pyrolysis (200° to 500°).

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[13] W. J. Bailey and W. F. Hale, J. Am. Chem. Soc., 81, 647 (1959).

Briggs and Djerassi[14] suggest that in the pyrolysis of 2-methylcyclohexyl-S-methyl xanthates and acetates, the olefinic product from effective trans elimination may be accounted for by postulating heterolysis of the C-O bond yielding ion pairs, followed by direct proton loss or 1,2-hydride shift and subsequent proton loss from the cationic species (Fig. 9).

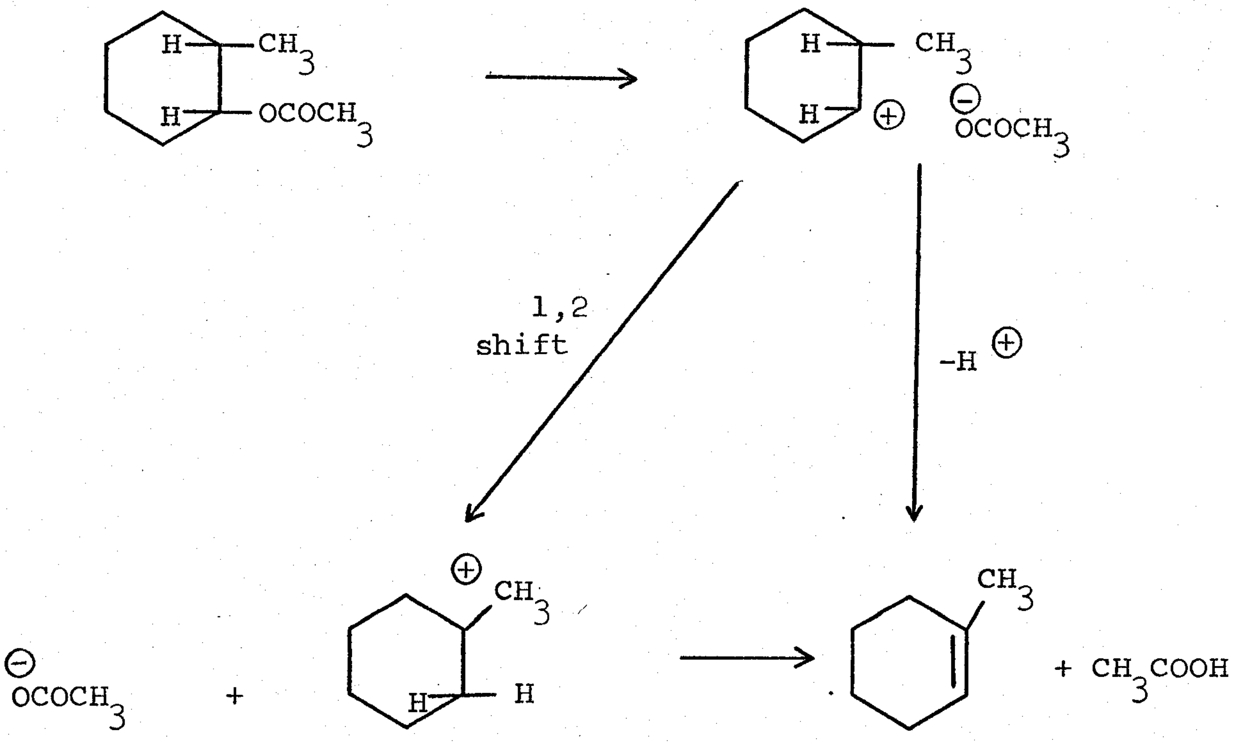

Fig. 9 - Possible Mechanism for the *trans* Elimination of *cis*-2-Methylcyclohexyl Acetate

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[14] W. S. Briggs and C. Djerassi, *J. Org. Chem.*, 33, 1625 (1968).

Kinetic studies on the pyrolysis of cholestanyl and cholesteryl acetate, xanthates and carbonate have also been reported in the literature.[15] Activation parameters are listed in Table I. The negative entropies of activation, though small, are cited as additional confirmation for a concerted cyclic process.

TABLE I

Activation Parameters of Cholesteryl Derivatives

Compound	$E_{exp.}$ kcal./mole	A 10^{-12} sec.$^{-1}$	$-\Delta S^{\ddagger}$ e.u.
3-β-Cholesteryl Acetate	44.1	5.1	3.6
3-β-Cholesteryl Ethyl Carbonate	41.0	2.4	4.3
3-β-Cholesteryl-S-Methyl Xanthate	32.7	2.4	4.7
3-β-Cholestanyl-S-Methyl Xanthate	33.8	2.0	5.0

Sixma and co-workers[16] postulate an ion pair mechanism for gas phase pyrolysis according to the scheme below

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[15] G. L. O'Connor and H. R. Nace, J. Am. Chem. Soc., 74, 5454 (1952); 75, 2118 (1953).

[16] J. C. Scheer, E. C. Kooyman and F. L. J. Sixma, Rec. Trav. Chim., 82, 1123 (1963).

(Fig. 10). The ion pair formed in the primary step may

$$\mathrm{ROAc}\ \underset{k-1}{\overset{k_1}{\rightleftharpoons}}\ \mathrm{R^{\oplus}\,{}^{\ominus}OAc}\ \xrightarrow{k_2}\ \mathrm{HOAc} + \text{olefin}$$

Fig. 10 - Proposed Decomposition Scheme for Acetates

either collapse to regenerate the original ester or decompose to alkene and acetic acid. The activation parameters for 28 acetates of primary, secondary and tertiary alcohols were calculated. The activation parameters of the most important compounds are listed in Table II. In general, the pyrolysis of primary acetates yields a more negative entropy of activation than in the case of secondary acetates, whereas for the tertiary acetates, the entropy of activation is positive. Indeed, of the six tertiary acetates listed by these workers, only one (2-methyl-2-pentylacetate) yielded a negative entropy of activation (-0.5) the other five cover the range from 1.2 to 6.5 e.u. Although the ionic mechanism is proposed by these workers, the energy of activation and entropy of activation are never mentioned in the discussion.

The observation that low temperature pyrolysis of

TABLE II

Activation Parameters of Selected Acetates

Acetate	$E_{exp.}$ (kcal./mole)	$\Delta S^{\ddagger}$ (e.u.)	T (^{o}C)
Ethyl	46.5	-7.0	487.8
n-Propyl	46.2	-7.6	486.4
iso-Propyl	45.2	-2.9	408.5
n-Butyl	44.5	-9.3	481.5
2-Butyl	47.0	+0.6	404.7
tert-Butyl	42.4	+2.6	322.7
n-Pentyl	44.9	-8.7	473.3
2-Pentyl	42.3	-5.9	409.3
tert-Amyl	43.1	+5.5	303.9
1-Methylcyclohexyl	44.0	+6.5	313.3

trans-1,2-dimethylcyclohexyl hydrogen phthalate yielded 1,2-dimethylcyclohexene (19%)[17] and the fact that ^{18}O appeared in the alcohol portion of the ^{18}O enriched ester when partially decomposed,[18] suggests strongly the operation of either an ion pair or radical mechanism. An investigation into the kinetics of pyrolysis of this compound and its epimer (which also undergoes decomposition at a similar low temperature) should prove interesting especially in view of the trend of activation parameters in the acyclic acetates. It was decided also to investigate the kinetics of pyrolysis of the cis- and trans-1-phenyl-2-methylcyclohexyl hydrogen phthalates to determine, if possible, the effect of the phenyl group.

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[17] K. G. Rutherford and D. P. C. Fung, Can. J. Chem., 42, 2657 (1964).

[18] K. G. Rutherford and R. M. Ottenbrite, Can. J. Chem., 45, 679 (1967).

CHAPTER II

RESULTS AND DISCUSSION

Synthesis of cis- and trans-1,2-Disubstituted Cyclohexanols

The reaction of methyl magnesium halide with 2-methylcyclohexanone yields predominantly trans-1,2-dimethylcyclohexanol.[1,2] This phenomenon is simply an extension of the rule of "steric control of asymmetric induction"[3] from the acyclic to the alicyclic system. That the minor product of the Grignard reaction was indeed cis-1,2-dimethylcyclohexanol, was shown by synthesizing this compound by an independent route.

The hydroboration of a double bond is known to result in the overall cis addition of the elements of water resulting in the formation of an alcohol. Brown and Zweifel[4] have shown that in the hydroboration of 1,2-

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[1] T. D. Nevitt and G. S. Hammond, J. Am. Chem. Soc., 76, 4124 (1954).

[2] A. V. Kamernitzky and A. A. Akhrem, Tetrahedron, 18, 705 (1962).

[3] D. J. Cram and F. A. Abd Elhafez, J. Am. Chem. Soc., 74, 5828 (1952).

[4] H. C. Brown and G. Zweifel, J. Am. Chem. Soc., 83, 2544 (1964).

dimethylcyclohexene a high yield (82%) of cis-1,2-dimethylcyclohexanol may be obtained. The Hydroboration of 1,2-dimethylcyclohexene, obtained by the acid dehydration of an isomeric mixture of 1,2-dimethylcyclohexanol, yielded a compound with identical spectra and glc retention time as the minor product from the Grignard reaction. This shows that indeed the minor product from the Grignard reaction is cis-1,2-dimethylcyclohexanol and hence the major product must be the trans isomer as would be expected from Cram's rule.

The reaction of methyl magnesium iodide with 2-methylcyclohexanone yielded 83% and 17% of trans- and cis-1,2-dimethylcyclohexanol respectively. Nazarov, Akhrem and Kamernitzky[5] reported finding 25% of cis-1,2-dimethylcyclohexanol using the same alkyl magnesium halide whereas Nevitt and Hammond[6] reported the presence of no more than 10% of the cis isomer in the crude mixture when methyl magnesium bromide was used to make the alcohol.

From Cram's rule it would be expected that the reaction

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[5] I. N. Nazarov, A. A. Akhrem and A. V. Kamernitzky, C. A., 52, 19979 (1958), [Izvest. Akad. Nauk., S.S.S.R., Otdel. Khim. Nauk., 631 (1958)].

[6] T. D. Nevitt and G. S. Hammond, J. Am. Chem. Soc., 76, 4124 (1954).

of 2-methylcyclohexanone with phenyl magnesium bromide would result in the production of an even lesser amount of the cis isomer than in the reaction with methyl magnesium iodide. The reaction of phenyl magnesium bromide with 2-methylcyclohexanone yielded two isomers (93% and 7%) and it is logical to assign the cis configuration to the isomer formed in the smaller amount since the steric strain in the transition state leading to the trans isomer is less than that leading to the cis isomer (Fig. 11).

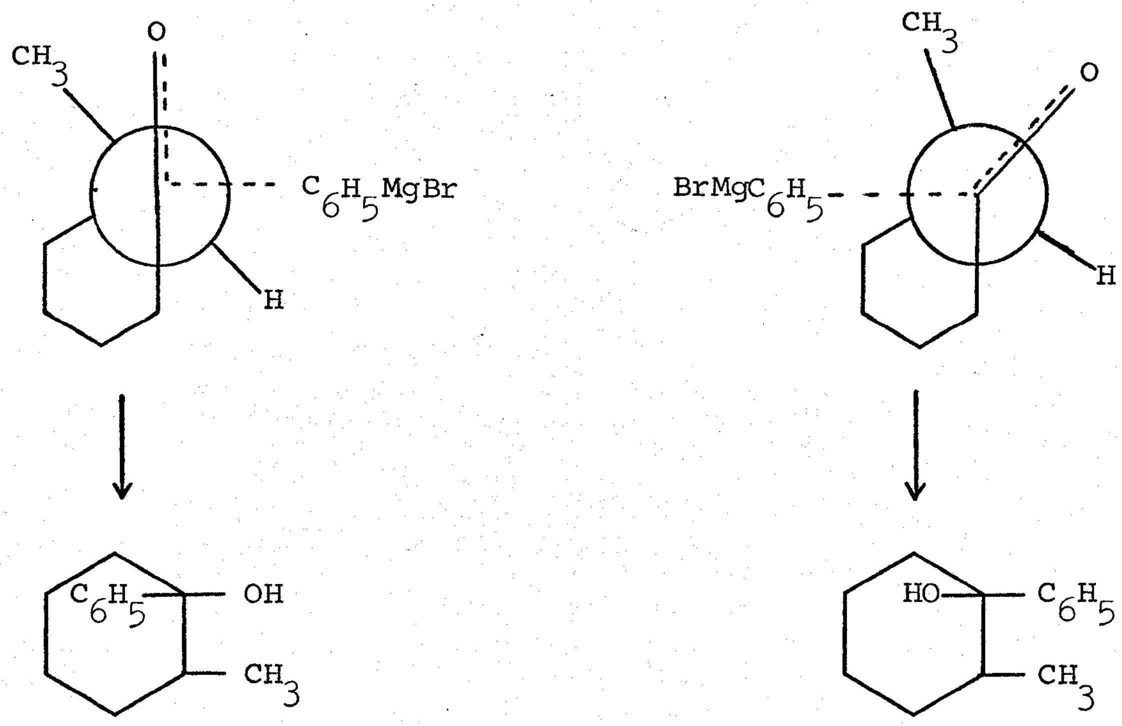

Fig. 11 - Transition States in the Nucleophillic Attack of Phenyl Magnesium Bromide on 2-Methylcyclohexanone Leading to cis and trans Alcohols

The reaction of 2-methylcyclohexanone with p-methoxyphenyl magnesium bromide yielded approximately the same amount of the _cis_ isomer as the reaction with phenyl magnesium bromide. The product distribution of the Grignard reaction as determined by glc analysis is listed in Table III.

The almost complete absence of the _cis_ isomer in the reaction of phenyl magnesium bromide with 2-methylcyclohexanone-2,6,6-d_3 is very surprising and difficult to explain.

TABLE III

Isomer Distribution of Tertiary Alcohols as Obtained in the Grignard Reaction

Alcohol	Product Distribution %	
	cis	_trans_
1,2-Dimethylcyclohexanol	17	83
1-Phenyl-2-methylcyclohexanol-2,6,6-d_3	0.2	99.8
1-Phenyl-2-methylcyclohexanol	7	93
1-(p-Methoxyphenyl)-2-methylcyclohexanol	8	92

Acid Dehydration of Tertiary Alcohols

The alcohols employed in the synthesis of the phthalate esters were dehydrated with acid to obtain olefins which were subsequently used for comparison with pyrolysis products. At low acid concentration (2.5% sulphuric acid in acetic acid), the least stable olefin (2-phenyl-3-methylcyclohexene) was found to predominate (76%) when 1-phenyl-2-methylcyclohexanol was dehydrated. This is in excellent agreement with results reported in the literature.[7] When the sulphuric acid concentration was increased to 15%, the amount of the least stable olefin dropped to 17%. The largest amount of 1-phenyl-2-methylcyclohexene observed was 83%.

Synthesis of Hydrogen Phthalate Esters

The synthesis of the esters was carried out by a well established procedure.[8] It was found that 1-(p-methoxyphenyl)-2-methylcyclohexyl hydrogen phthalate could not be made by this method. This compound was to be used to

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[7] E. W. Garbisch, Jr., J. Org. Chem., 27, 4243 (1962).

[8] K. G. Rutherford, J. M. Prokipcak and D. P. C. Fung, J. Org. Chem., 28, 582 (1963).

investigate the stabilizing and steric effect of the anisyl moiety in the pyrolysis of the phthalate ester. The addition of an ethereal solution of triphenylmethylsodium to an ethereal solution of 1-(p-methoxyphenyl)-2-methylcyclohexanol caused immediate discharge of the characteristic red colour of the base. The addition of water to the reaction mixture and subsequent isolation of the product yielded the original alcohol as determined by glc. The base then does remove the hydroxyl proton but does not cause any other reactions. When phthalic anhydride was added to a solution of the sodium salt of the alcohol, the reaction mixture became warm and the ether started to reflux which was also observed in the preparation of the other phthalate esters. The addition of water to this reaction mixture and subsequent examination of the ether layer yielded a liquid consisting of very little alcohol and mostly olefins. The ratio of the olefins found was the same as that found in the pyrolysis of <u>cis</u>-1-phenyl-2-methylcyclohexyl phthalate (12% 1-phenyl-2-methylcyclohexene and 88% 2-phenyl-3-methylcyclohexene). The ester decomposes in the ether as soon as it forms or it decomposes on the addition of water to the reaction mixture. Since very little alcohol was found in the reaction product, it is most likely that decomposition takes place in the warm ether solution. The product distribution suggests that the steric effect of the p-methoxyphenyl group is the same as that of the phenyl group. It appears that the carbonium ion stabilizing effect of the p-methoxyphenyl group is so great that the phthalate ester cannot be isolated. Pertinent to this is the observation made by Prokipcak[9] that the reaction of p-methoxybenzylchloride with sodium phenoxide does not yield p-methoxybenzylphenyl ether but p-methoxybenzyl-p-phenol on acidification of the reaction mixture (Fig. 12).

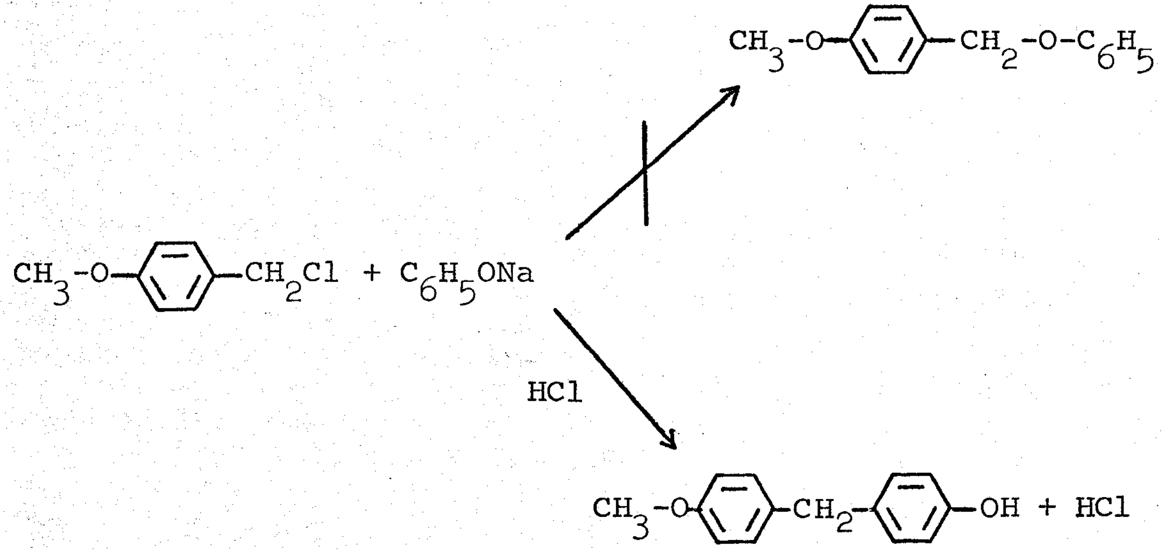

Fig. 12 - The Reaction of p-Methoxybenzylchloride with Sodium Phenoxide

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[9] J. M. Prokipcak, Private communication.

Kinetic Studies on the Thermal Decomposition of *cis*- and *trans*-1,2-Dimethylcyclohexyl Hydrogen Phthalate

The 1,2-dimethylcyclohexyl hydrogen phthalates are white crystalline solids with melting points of 99°C for the *cis*- and 126°C for the *trans*- compound. The decomposition points of these esters are high enough above the melting points (142°C for the *cis* and 146°C for the *trans*) to make neat liquid phase pyrolysis possible. The decomposition points refer to the temperature at which the appearance of a solid was noted in the molten sample and they do not refer to the so called "characteristic temperature." The latter is defined as the temperature at which a maximum is obtained from a plot of percentage yield divided by the pyrolysis temperature plotted against the pyrolysis temperature.[10]

Small samples were placed in test tubes which were then suspended in a heated oil bath. At set intervals, samples were removed and titrated with standard base. Rate constants and activation parameters were determined from the first order rate equation and from the absolute rate equation. Pertinent data is listed in Table IV.

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[10] G. G. Smith and W. H. Wetzel, *J. Am. Chem. Soc.*, *79*, 875 (1957).

The temperature range is of necessity rather small because of the narrow span in which the compounds decompose. The duration of the run at the highest temperature was about 17 minutes and at the lowest approximately 45 minutes. Decomposition at a temperature about ten degrees less than the lowest temperature listed was found to be impracticably slow. Whereas when the temperature was increased at the high end, the reaction was too fast to be followed.

The energy of activation is about ten kcals. lower than that reported for various tertiary acetates.[11] Since the phthalate is a much larger group than the acetate, there is probably a greater relief of steric strain on the expulsion of the phthalate moiety resulting in the lowering of the energy of activation. Again, it is well known that esters which on pyrolysis form strong acids, decompose faster than those which form weak acids. Thus Bailey and Hewitt have shown that in the pyrolysis of esters of methyl isobutyl carbinol, a straight line with positive slope results when the per cent pyrolyzed is plotted against the dissociation constant of the resulting acid.[12] The pyrolysis

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[11] J. C. Scheer, E. C. Kooyman and F. L. J. Sixma, Rec. Trav. Chim., 82, 1123 (1963).

[12] W. J. Bailey and J. J. Hewitt, J. Org. Chem., 21, 543 (1956).

of acetates and phthalates yields acetic acid and phthalic acid. Since the latter is the stronger acid, it may well contribute to the lowering of the energy of activation.

Also, the proton from the neighbouring acid group may well form a hydrogen bond with the alkyl oxygen of the ester or in the limit, transfer completely to this oxygen (Fig. 13). Any participation of the acid proton would make the phthalate a much better leaving group than acetate again resulting in a lower energy of activation for the pyrolysis of phthalates.

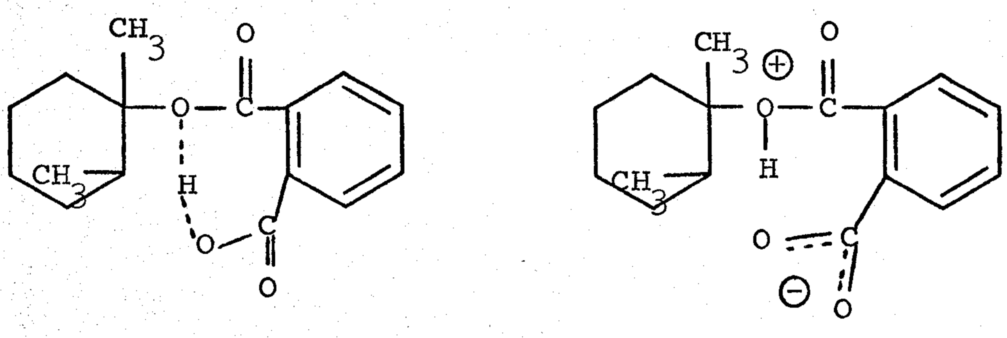

Fig. 13 - Possible Acid Proton Participation States in the Pyrolysis of 1,2-Dimethylcyclohexyl Hydrogen Phthalate

The entropy of activation was determined at each temperature of the experiment and averaged. The variation with temperature was insignificantly small and hence the entropy of activation was considered to be constant over the range of the experiment. The entropy of activation is seen to be positive and about the same as that determined for 1-methylcyclohexyl acetate.[13] On the basis then of the product distribution as determined by Rutherford and Fung,[14] the isotope work of Rutherford and Ottenbrite[15] and the positive entropy of activation as determined in this work, it is proposed that the pyrolysis of cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalate occurs by an ion pair or radical pair mechanism. This does not preclude that the reaction occurs at least in part by an irreversible homolytic or heterolytic bond cleavage.

First order rate constants were observed over the entire course of the reaction. The cis compound decomposed twice as fast as the trans at 125°C. This is not a spectacular increase and it appears that the steric requirements of the substituents of both the cis and trans esters are not vastly different in the transition state of the elimination.

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[13] J. C. Scheer, E. C. Kooyman and F. L. J. Sixma, Rec. Trav. Chim., 82, 1123 (1963).

[14] K. G. Rutherford and D. P. C. Fung, Can. J. Chem., 42, 2657 (1964).

[15] K. G. Rutherford and R. M. Ottenbrite, Can. J. Chem., 45, 679 (1967).

Product Distribution in the Pyrolysis of *cis*- and *trans*-1,2-Dimethylcyclohexyl Hydrogen Phthalate

The *cis* and *trans* esters were pyrolyzed at each temperature at which a kinetic experiment was performed and the product distribution was determined by glc. The results are listed in Table V. Only the high and low temperature results are noted since the product distribution did not change with temperature over the range of the experiment. The *trans* isomer yielded 24% of 1,2-dimethylcyclohexene and 30% of 2-methylmethylenecyclohexene whereas Rutherford and Fung reported a yield of 19% and 35% respectively. The increase in the thermodynamically more stable olefin cannot be attributed to isomerization because it has been shown that under the conditions of the experiment no isomerization takes place.[16]

On a purely statistical basis it would be expected that these esters would yield olefins in the ratio of 1:2:3 from free ion pairs (Fig. 14). From Table V it is clear, that experimentally, this distribution is not found. Furthermore, if the decomposition occurs *via* an ion or radical pair, introducing a large degree of planarity about the α carbon

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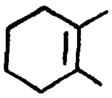
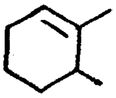
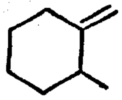
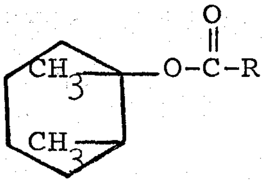
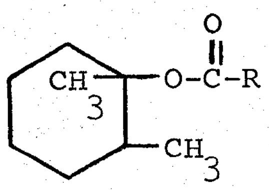
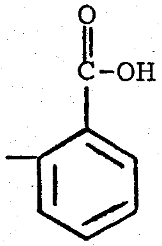
[16] K. G. Rutherford and D. P. C. Fung, *Can*. *J*. *Chem*., *42*, 2657 (1964).

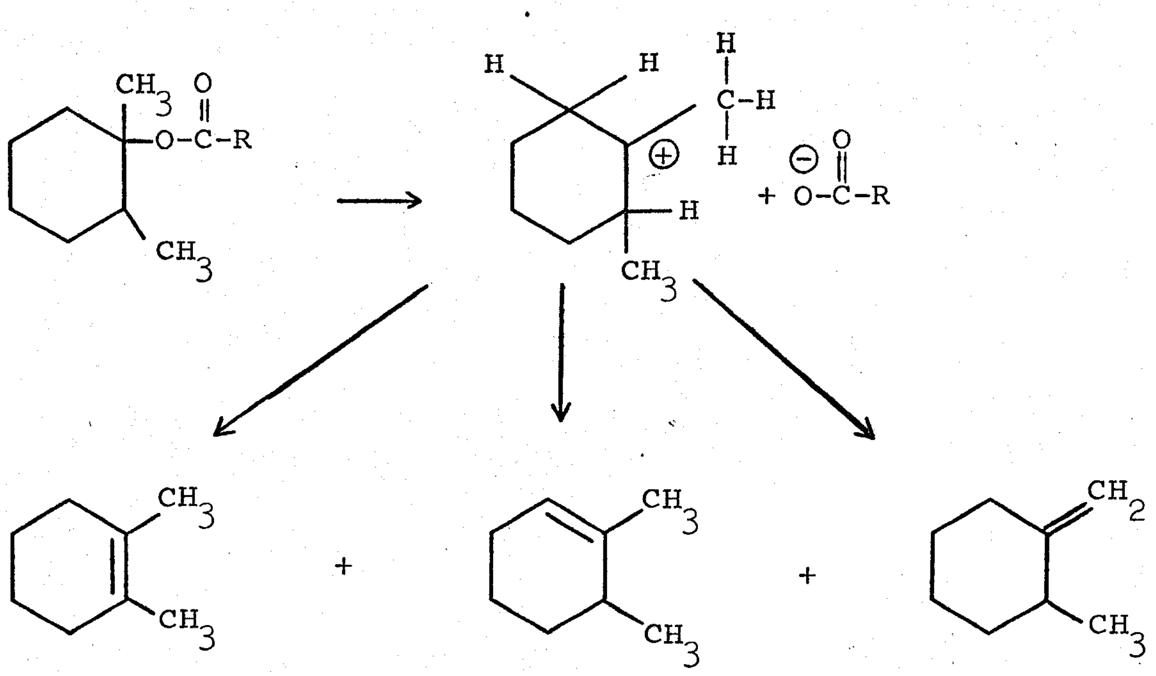
TABLE V

Pyrolysis of <u>cis</u>- and <u>trans</u>-1,2-Dimethylcyclohexyl Hydrogen Phthalates at Different Temperatures

Compound	Temp. (°C)	Duration (min)	Product Distribution %		
					
 cis	300	a	68	21	11
	120	90	56	20	24
	130	45	56	20	24
 trans	300	a	34	44	22
	125.7	90	24	46	30
	137.3	45	24	46	30

R = 

a The duration of the pyrolysis is not known because the sample was injected directly into the gas chromatograph.



1 2 3

Fig. 14 - Product Distribution in the Pyrolysis of 1,2-Dimethylcyclohexyl Hydrogen Phthalate from an Ionic Intermediate on a Statistical Basis

atom, the product distribution of the <u>cis</u> and <u>trans</u> isomers would be expected to be in close agreement. Again from Table V this is not in accordance with experimental findings. Perhaps the answer lies in nature of the ion or radical pairs which allow for preferential abstraction of the β protons by the anion (anion effect). Figure 15 depicts a possible transition state for the elimination in <u>cis</u>-1,2-dimethylcyclohexyl hydrogen phthalate. Removal of proton α results in an effective <u>trans</u> elimination. Protons marked <u>b</u> can

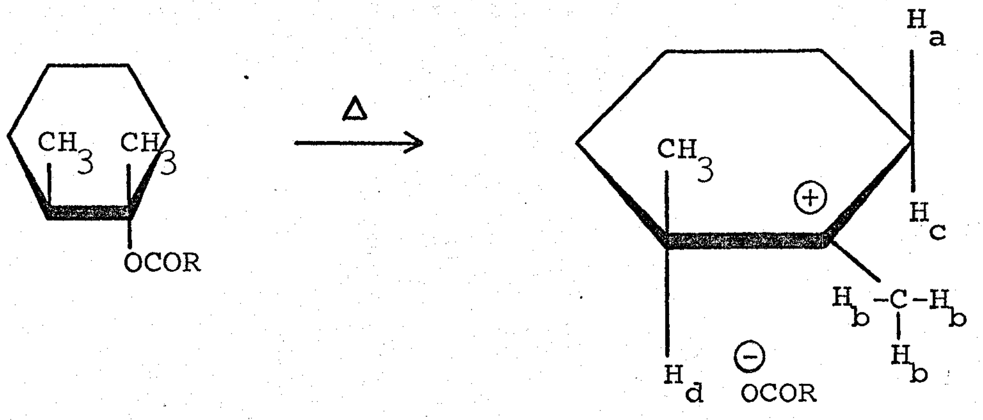


Fig. 15 - Possible Ionic Transition State for the Elimination in <u>cis</u>-1,2-Dimethylcyclohexyl Hydrogen Phthalate

bring about a cis or trans elimination whereas removal of protons c and d result in a cis elimination. Removal of protons b, c, and d will be enhanced by the anion which is in the proximity of these protons. Since the removal of proton d yields the most stable olefin, removal of c the second most stable and removal of any b protons the least stable olefin, it is not surprising that the product ratio is found to be in this order.

In the trans isomer, proton d is far removed from the anion (Fig. 16). The appearance of 1,2-dimethylcyclohexene (24%) is the result of effective trans elimination (removal of proton d). Proton c now receives the assistance of the anion rather than proton d and the amount of 2,3-dimethylcyclohexene is expected to increase over that found for the cis ester. This is indeed the case as can be seen from Table V.

The amount of 2-methylmethylenecyclohexane (24% and 30%) as obtained from both isomers does not show a great variation and this may be explained if it is assumed that the anion is equally close to the b protons in both isomers.

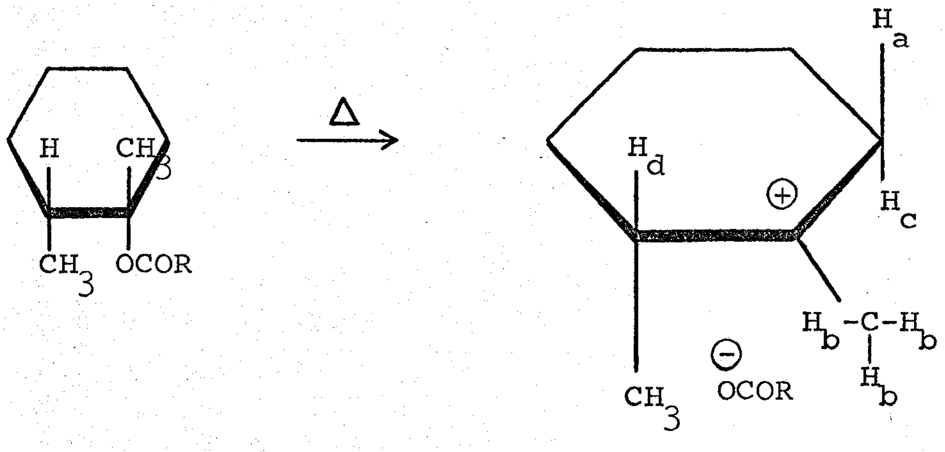


Fig. 16 - Possible Ionic Transition State for the Elimination in trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate

From Dreiding models it may be seen that in any conformation as the α carbon tends to planarize to the 120° bond angles of the carbonium ion, the anion is always closer to the d proton in the cis than in the trans isomer.

The breaking of the alkyl oxygen bond is still considered to be the slow step, hence rate controlling, however the proximity of the anion to the β protons and the stability of the olefin seem to govern the product ratio.

Kinetic Studies on the Thermal Decomposition of *cis*- and *trans*-1-Phenyl-2-methylcyclohexyl Hydrogen Phthalate

The esters of 1-phenyl-2-methylcyclohexanols are white crystalline solids whose melting points and decomposition points coincide. Since the melting point and decomposition point occur at the same temperature, the kinetics could not be performed on neat samples and the experiments had to be carried out in solution. The solvent chosen for this work was N,N-dimethylformamide since it has a fairly high boiling point (153.1°C), phthalic acid is soluble in it and can be titrated in the solution with dilute base.

A small quantity of the ester in pellet form was dissolved in the hot solvent. At set intervals, one ml. samples were removed and titrated with standard base to the phenolphthalein end point. Rate constants and activation parameters were determined and are listed in Table VI.

The temperature span and duration of the experiments were of the same order as those for the 1,2-dimethylcyclohexyl hydrogen phthalates. The values obtained for the cis ester fall in line with what would be expected for the operation of an ionic or free radical pair mechanism as proposed earlier.

For the trans compound a negative entropy of activation (-11) was obtained. This, at first glance, suggests the operation of a cyclic rather than an ionic or radical mechanism. If this compound does indeed decompose *via* a cyclic mechanism, an isotope effect is to be expected when the β protons are replaced by deuterium. The pyrolysis of trans-1-phenyl-2-methylcyclohexyl-2,6,6-d_3 hydrogen phthalate, in which the β protons have now been replaced by deuterium, yielded a rate constant very close to that obtained for the undeuterated compound (Table VI). The difference in the rate constants is approximately twice the standard deviation and probably does not constitute a real difference but is due to experimental error. In any case, if there is a real difference in the rate constant, it cannot be due to a primary isotope effect because it is far too small.

Since this experiment was carried out in solution, the part played by the solvent may not be negligible. The ester probably decomposes into radical or ion pairs which become solvated before they proceed to the products. The increase in the organization of the system caused by the solvolysis would result in the observance of an overall negative entropy for the system (Fig. 17).

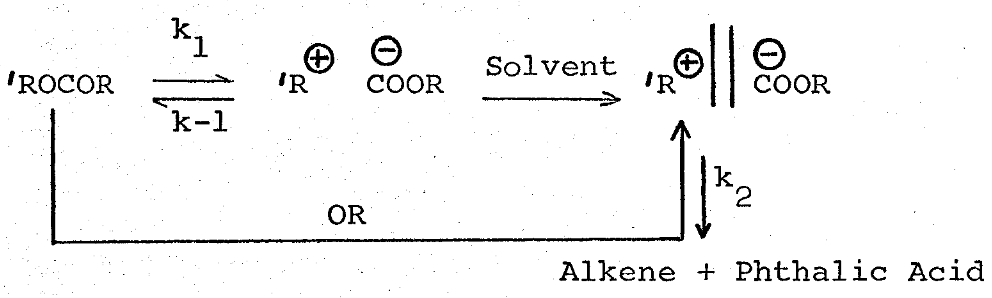


Fig. 17 - Proposed Scheme for the Pyrolysis of <u>trans</u>-1-Phenyl-2-methylcyclohexyl Hydrogen Phthalate in Solvent

The positive entropy of activation observed for the <u>cis</u> isomer may be rationalized by the suggestion that this compound decomposes too fast to generate solvent separated radical or ion pairs. In other words, it is proposed that this system does not gain the degree of organization obtained for the <u>trans</u> compound because the rate at which the radical or ion pairs proceed to the final product is too great to allow solvation. The <u>cis</u> ester decomposes indeed faster than the <u>trans</u> but it is difficult to estimate how much faster.

Product Distribution in the Pyrolysis of cis- and trans-1-Phenyl-2-methylcyclohexyl Hydrogen Phthalate

The cis- and trans-1-phenyl-2-methylcyclohexyl hydrogen phthalates were pyrolyzed at low temperatures and the product distribution determined by glc.

If the pyrolysis occurs via an ion pair intermediate, the ratio of olefins should be 1:2 for 1-phenyl-2-methylcyclohexene and 2-phenyl-3-methylcyclohexene respectively on a purely statistical basis (Fig. 18). Although the trend is in the right direction, only from one-third to one quarter of the expected amount of 1-phenyl-2-methylcyclohexene is observed (Table VII).

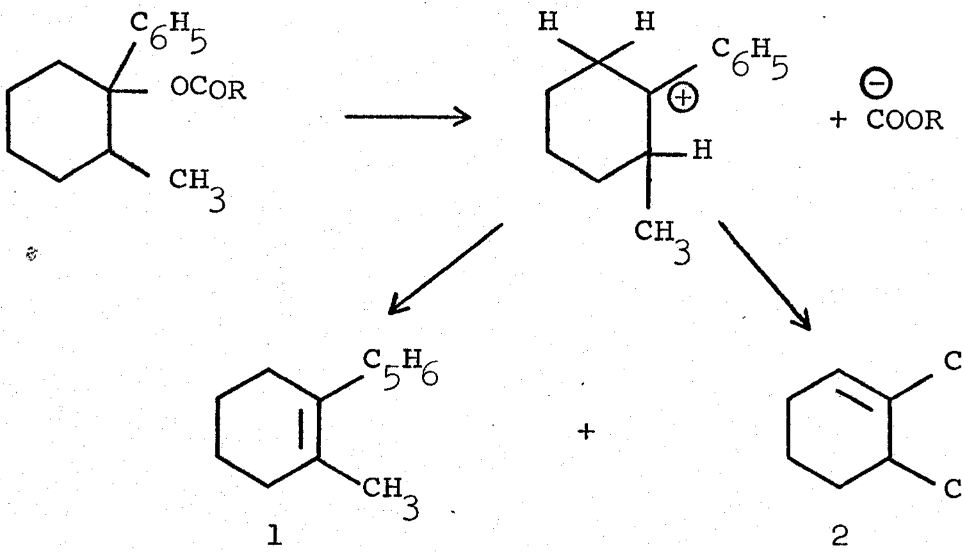
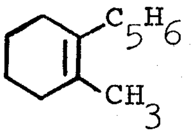
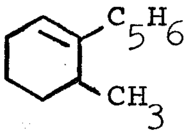
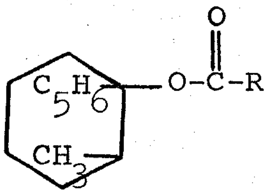
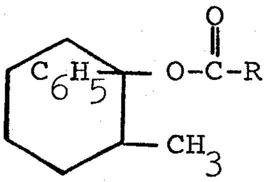
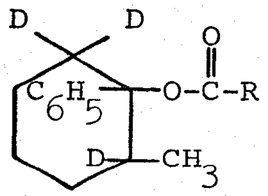


Fig. 18 - Product Distribution in the Pyrolysis of 1-Phenyl-2-methylcyclohexyl Hydrogen Phthalate from an Ionic Intermediate on a Statistical Basis

TABLE VII

Pyrolysis of *cis*- and *trans*-1-Phenyl-2-methylcyclohexyl Hydrogen Phthalates at Different Temperatures

Compound	Temp. (°C)	Duration (min.)	Product Distribution %	
				
 *cis*	115	a	11	89
	160	a	13	87
	290	a	25	75
	110	8	11	89
	126	3	12	88
 *trans*	140	a	7	93
	170	a	10	90
	290	a	19	81
	142	8	7	93
 *trans*	150	3	9	91

a The duration of the pyrolysis is not known because the sample was injected directly into the gas chromatograph.

The presence of 1-phenyl-2-methylcyclohexene from the trans isomer can only be the result of a trans elimination. Even though 1-phenyl-2-methylcyclohexene is the thermodynamically most stable isomer, its formation would be hindered by the cis effect of the methyl and phenyl group.

The anion effect, as proposed for the 1,2-dimethylcyclohexyl esters, also appears to be operative when the methyl group on the carbinol carbon is replaced by a phenyl group. As a result of the cis effect between the methyl and phenyl group, the anion abstracts the protons which lead to the formation of 2-phenyl-3-methylcyclohexene rather than those leading to the more stable 1-phenyl-2-methylcyclohexene.

As the pyrolysis temperature is increased, the proportion of the most stable olefin increases also for both 1-phenyl-2-methylcyclohexyl and 1,2-dimethylcyclohexyl ester. This is probably caused by the fact that at higher temperatures (300°) the molecules decompose faster overcoming the cis effect somewhat thus allowing less selectivity in the removal of a proton thereby increasing the thermodynamically more stable product.

Synthesis and Pyrolysis of 1-Phenyl-2-methylcyclohexyl Acetate

Although acetate pyrolysis is generally carried out at temperatures between 400°C and 500°C, it was decided to determine if 1-phenyl-2-methylcyclohexyl acetate could be pyrolyzed at a lower temperature. The acetate as prepared contained both the cis and trans isomers because acetic anhydride was used to decompose the Grignard complex. From previous work, it was shown that the cis isomer constitutes 7% of the mixture of isomeric alcohols. It seems reasonable then to expect approximately 7% cis acetate in the mixture. Pyrolysis was carried out at 290°, 220° and 170°C by direct injection into the gas chromatograph. The product distribution was the same at all three temperatures and 17% of 1-phenyl-2-methylcyclohexene and 83% of 2-phenyl-3-methylcyclohexene was found. The amount of 1-phenyl-2-methylcyclohexene is surprisingly high even in the presence of 7% of the cis isomer which is the only one that can lead to the most stable isomer by a cyclic mechanism. The product distribution is not too dissimilar from that found in the pyrolysis of the corresponding hydrogen phthalate where 13% and 10% of the most stable olefin were obtained from the cis and trans hydrogen phthalate respectively.

In view of the large amount of 1-phenyl-2-methylcyclohexene obtained, it would appear that further work on the pyrolysis of the acetates of *cis*- and *trans*-1,2-dimethylcyclohexanol and *cis*- and *trans*-1-phenyl-2-methylcyclohexanol is warranted.

CHAPTER III

EXPERIMENTAL

All infrared spectra were obtained using a Beckman IR 10 Infrared Spectrophotometer. All solutions were weight-weight per cent in the solvent specified. The nmr spectra were obtained using a JEOL C-60 nuclear magnetic resonance instrument and all solutions were weight-volume per cent in the solvent specified. The mass spectral analysis was performed by the Morgan and Schaffer Corporation, Montreal. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory, New York. Melting points and decomposition points were taken with an Electrothermal melting point apparatus and are uncorrected. The neutralization equivalents of the hydrogen phthalate esters were determined by dissolving a small amount of the ester (20-30 mg.) in ten ml. of a water-acetone mixture (50% water) and titrating the solution with standard sodium hydroxide (0.04 N) using phenophthalein as indicator. Appropriate corrections were applied for the acetone. All glc work was performed with an F and M 720 gas chromatograph. Peak areas were determined with a disc integrator. Preparative glc columns were all of the same dimensions (8 ft. x 0.5 in.) and packed with 10% silicone gum rubber SE-30 or LAC-728, on Diatoport W, 80-100 mesh.

Synthesis of Tertiary Alcohols

1,2-Dimethylcyclohexanol. Magnesium turnings (24.3 g.-1 mole) and anhydrous diethyl ether (500 ml.) were placed in a two-liter three-necked, round-bottomed flask which was equipped with a mechanical stirrer, a dropping funnel and a condenser (drying tube attached). A solution of methyl iodide (141.9 g.-1 mole) in anhydrous ether (200 ml.) was added dropwise at a rate sufficient to maintain reflux. After the addition of this solution, the reaction mixture was stirred at room temperature for one hour. A solution of 2-methylcyclohexanone (105.2 g.-0.94 mole) in anhydrous ether (150 ml.) was added to the reaction mixture at a rate which maintained gentle reflux. The reaction mixture was stirred for an additional hour after which the Grignard complex was hydrolyzed with a 5% volume-volume solution of hydrochloric acid. The ethereal layer was separated, washed three times with 5% sodium bicarbonate solution (100 ml. portions), three times with water (100 ml. portions) and dried over anhydrous magnesium sulphate. The drying agent was separated by filtration and the ether removed *in vacuo*. Glc examination (LAC-728 column) of the crude oil indicated the presence of 83% of the *trans*-1,2-dimethylcyclohexanol and 17% of the <u>cis</u> isomer[1] as well as unreacted 2-methylcyclohexanone. Purification with a Nester-Faust spinning band distillation apparatus (column 42 x 1 cm.) yielded four fractions. The first fraction (room temperature-68°/2cm.) was shown to be a mixture of alcohol and ketone. The second fraction (68-69°/2cm.) was pure <u>trans</u>-1,2-dimethylcyclohexanol as shown by glc analysis, n_D^{25} 1.4580 (reported[2] b.p. 86.8°/52mm., n_D^{25} 1.4588).

<u>Anal</u>. Calcd. for $C_8H_{16}O$: C, 74.90; H, 12.59.

Found: C, 74.99; H, 12.72.

Spectral data obtained for this compound is tabulated below.

<u>NMR</u>

Solution: Approx. 17% in $(CD_3)_2SO$.

Unresolved doublet	τ 9.2
Singlet	τ 9.0
Broad multiplet	τ 8.3-9.0
Singlet	τ 6.45

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[1] T. D. Nevitt and G. S. Hammond, <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>., <u>76</u>, 4124 (1954).

[2] T. D. Nevitt and G. S. Hammond, <u>loc</u>. <u>cit</u>.

The singlet at τ 6.45 is attributed to the hydroxyl proton from the integration curve and its disappearance on the addition of deuterium oxide.[3]

IR

Solution: Approx. 30% in CS_2.

Free OH stretching band $\nu_{max.}$ 3605 cm.$^{-1}$, 45% transmittance.

Hydrogen bonded stretching band $\nu_{max.}$ 3500 cm.$^{-1}$, 21% transmittance.

The third fraction (69°/1.9 cm.) was shown by glc analysis to contain a small amount of trans-1,2-dimethylcyclohexanol (6%) and the cis isomer (94%). The remainder in the distillation flask showed only one peak on glc analysis indicating pure cis-1,2-dimethylcyclohexanol. This material (3.5 g.) was transferred to a micro distillation apparatus and vacuum distilled (62°/1 cm.), n_D^{25} 1.4648 reported[4] b.p. 95.7°/53 mm., n_D^{25} 1.4628).

Anal. Calcd. for $C_8H_{16}O$: C, 74.90; H, 12.59.
Found: C, 73.78; H, 12.95.

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[3] R. H. Bible, Jr., Interpretation of NMR Spectra, Plenum Press, New York, 1965, p. 22.

[4] T. D. Nevitt and G. S. Hammond, J. Am. Chem. Soc., 76, 4124 (1954).

The spectral data for the *cis*-1,2-dimethylcyclohexanol is given below.

NMR

Solution: Approx. 20% in $(CD_3)_2SO$.

Doublet	τ 9.2, J = 5 c.p.s.
Singlet	τ 9.1
Broad multiplet	τ 8.3-9.0
Singlet	τ 6.1

The singlet at τ 6.1 disappeared on the addition of a few drops of deuterium oxide and hence is attributed to the hydroxyl proton.

IR

Solution: Approx. 30% in CS_2.

Free OH stretching band $\nu_{max.}$ 3600 cm.$^{-1}$, 60% transmittance.

Hydrogen bonded stretching band $\nu_{max.}$ 3400 cm.$^{-1}$, 13% transmittance.

Preparation of cis-1,2-dimethylcyclohexanol by the hydroboration of 1,2-dimethylcyclohexene. An isomeric mixture of 1,2-dimethylcyclohexanol was dehydrated with a 5% volume-volume sulphuric-acetic acid solution according to the method of Garbisch.[5] The crude olefinic yield was 7.3 g. (73%). Glc analysis (diisodecyl phthalate column) showed the product to consist of a mixture of isomers (13% and 87%). The isomers were identified from the nmr spectrum of the mixture.

NMR

Solution: Approx. 10% in $CDCl_3$.

Doublet	τ 9.04, $J = 6$ c.p.s.
Broad singlet	τ 8.45
Broad multiplet	τ 8.15

The doublet at τ 9.04 results from the coupling of methyl protons with a proton on an adjacent carbon atom resulting in the expected splitting order (6-8 c.p.s.).[6] From the integration curve, it was calculated that the olefin with a methyl group split by an adjacent proton accounts for approximately 10% of the mixture and hence the major component of the mixture is 1,2-dimethylcyclohexene and the minor component is 2,3-dimethylcyclohexene. Preparative glc was employed to separate the isomers (silicone gum

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[5] E. W. Garbisch, Jr., *J. Org. Chem.*, *26*, 4165 (1961).

[6] R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, 2nd. ed., John Wiley and Sons, Inc., New York, 1967, pp. 136-137, and 144.

rubber SE-30, temperature programmed at 2°/min. from 40-75°). This method did not give distinct peaks but a long sloping curve with a good indication where the compounds overlapped. The first part of the peak (9%) was discarded. The second part (58%) was collected and reinjected. The final fraction (33%) gave rise to only one peak (diisodecylphthalate column). This process was repeated until 1.95 gm. of pure 1,2-dimethylcyclohexene was obtained, n_D^{25} 1.4596 (reported[7] n_D^{25} 1.4587) which was subsequently used to prepare cis-1,2-dimethylcyclohexanol.[8]

The olefin (1.90 g.-1.72×10^{-2} mole) and a solution of sodium borohydride (0.270 g.-7.12×10^{-3} mole) in 10 ml. freshly distilled diglyme were placed in a wide mouth 50 ml. flask fitted with an addition funnel, thermometer and condenser (drying tube attached).[9] The reaction flask was placed in an ice-bath and the temperature maintained between 20-30° during the dropwise addition of freshly distilled boron trifluoride etherate (1.35 g.-9.45×10^{-3} mole). After stirring for 1.5 hr. at room temperature, 3 ml. of water was

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[7] G. S. Hammond and T. D. Nevitt, J. Am. Chem. Soc., 76, 4121 (1954).

[8] H. C. Brown and G. Zweifel, J. Am. Chem. Soc., 83, 2544 (1961).

[9] A. C. Cope, Organic Reactions, Vol. 13. John Wiley and Sons, Inc., New York, 1963, p. 29.

added cautiously followed by 3.8 ml. of 3N sodium hydroxide solution and 3.3 ml. of 35% hydrogen peroxide. Stirring was continued for 1.5 hr. after which the solution was extracted with 25 ml. of diethyl ether. The ether layer was washed with five 10 ml. portions of ice-water, dried with anhydrous magnesium sulphate and the solvent removed *in vacuo*. The crude material (1.65 g.-74.5% yield) was purified using preparative glc (LAC-728 column), n_D^{25} 1.4621 (reported[10] n_D^{25} 1.4628).

Anal. Calcd. for $C_8H_{16}O$: C, 74.90; H, 12.59.

Found: C, 74.90; H, 12.60.

Spectral data is recorded below.

NMR

Solution: Approx. 18% in $(CD_3)_2SO$.

Doublet	τ 9.2, *J* = 5 c.p.s.
Singlet	τ 9.07
Broad multiplet	τ 8.3-9.0
Singlet	τ 6.1

The singlet at τ6.1 disappeared on the addition of deuterium oxide.

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

IR

Solution: Approx. 30% in CS_2.

Free OH stretching band $\nu_{max.}$ 3600 cm.$^{-1}$, 60% transmittance.

Hydrogen bonded stretching band $\nu_{max.}$ 3400 cm.$^{-1}$, 15% transmittance.

1-Phenyl-2-methylcyclohexanol. A solution of phenyl magnesium bromide was prepared from magnesium turnings (24.3 g.-1 mole), bromobenzene (157.02 g.-1 mole) and 600 ml. anhydrous diethyl ether. By reacting the Grignard reagent with 2-methylcyclohexanone (112.17 g.-1mole), an isomeric mixture of 1-phenyl-2-methylcyclohexanol was obtained in 87% yield. Distillation of the crude product afforded a colourless oil b.p. 78-80° /0.25 mm., n_D^{25} 1.5360 (reported[11] b.p. 105-106°/1 mm., n_D^{25} 1.5359). Preparative glc (carbowax 20-M column) resulted in two well defined peaks 93% and 7% respectively. The major component (trans-1-phenyl-2-methylcyclohexanol) is a liquid (n_D^{25} 1.5334); the minor component (cis-1-phenyl-2-methylcyclohexanol) is a solid (m.p. 59-61°). The spectral data and analyses given below are for trans- and cis-1-phenyl-2-methylcyclohexanol

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[11] R. B. Carlin and H. P. Landerl, J. Am. Chem. Soc., 75, 3969 (1953).

respectively.

NMR (trans)

Solution: Approx. 17% in $(CD_3)_2SO$.

Doublet	τ 9.52, J = 5 c.p.s.
Broad band	τ 8.0-8.8
Singlet	τ 5.72
Multiplet	τ 3.0

The disappearance of the singlet at τ 5.72 on the addition of deuterium oxide characterizes this as being caused by the hydroxyl proton.

IR (trans)

Solution: Approx. 30% in CS_2.

Free OH stretching band $\nu_{\text{max.}}$ 3600 cm.^{-1}, 42% transmittance.

Hydrogen bonded stretching band $\nu_{\text{max.}}$ 3500 cm.^{-1}, 52% transmittance.

Anal. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53.
Found: C, 82.15; H, 9.38.

NMR (cis)

Solution: Approx. 15% in $(CD_3)_2SO$.

Doublet	τ 9.45, J = 7 c.p.s.
Broad band	τ 7.7-9.0

Broad singlet	τ 5.37
Multiplet	τ 2.65

The singlet at τ 5.37 disappeared on the addition of deuterium oxide which is indicative of the hydroxyl proton signal.

<u>IR</u> (<u>cis</u>)

Solution: Approx. 30% in CS_2.

Free OH stretching band $\nu_{max.}$ 3600 cm.$^{-1}$, 43% transmittance.

Hydrogen bonded stretching band $\nu_{max.}$ 3460 cm.$^{-1}$, 39% transmittance.

<u>Anal</u>. Calcd. for $C_{13}H_{18}O$: C, 82.06; H, 9.53.
Found: C, 82.04; H, 9.56.

<u>1-Phenyl-2-methylcyclohexanol-2,6,6-d$_3$</u>. The deuteration of the starting material (2-methylcyclohexanone) was carried out by an established procedure.[12] The deuterium oxide employed was supplied by Merck Sharp and Dohme and was 99.7% pure.

To a solution of 5% sodium carbonate in deuterium oxide, was added 18.6 g. (1.65x10^{-1} mole) of 2-methylcyclo-

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[12] E. Premuzic and L. W. Reeves, <u>Can</u>. <u>J</u>. <u>Chem</u>., <u>40</u>, 1870 (1962).

hexanone. After refluxing for 8 hr., the reaction mixture was frozen and the supernatant liquid decanted. This process was repeated four times after which the organic layer was extracted with petroleum ether (b.p. 30-60°), dried with anhydrous magnesium sulphate and the solvent removed *in vacuo*. Distillation of the product (161-162°) yielded 13.4 g. (70%) of 2-methylcyclohexanone-2,6,6-d_3. Pertinent spectral data is listed below.

NMR

Solution: Approx. 21% in $CDCl_3$.

Sharp unresolved triplet τ 9.05

Multiplet τ 7.8-8.9

Mass Spec

number of deuterium atoms	% of compound
0	0.3
1	0.4
2	8.7
3	90.6
4	0.0

Parent peak m/e 115.

A solution of phenyl magnesium bromide was prepared from magnesium turnings (2.1 g.-8.65×10^{-1} mole), bromobenzene (13.6 g.-8.65×10^{-1} mole) and 150 ml. of anhydrous ether. When 2-methylcyclohexanone-2,6,6-d_3 (9.95 g.-8.65×10^{-1} mole) was reacted with the Grignard reagent, 1-phenyl-2-methylcyclohexanol-2,6,6-d_3 (8.6 g.-51.5%) was obtained. Preparative glc analysis indicated the presence of 98.8% of the trans isomer and 0.2% of the cis. The data given below is for trans-1-phenyl-2-methylcyclohexanol-2,6,6-d_3 (n_D^{25} 1.5345).

Anal. Calcd. for $C_{13}H_{15}D_3O$: C, 80.77; H+D, 10.95.
Found: C, 80.70; H, 10.67.

NMR

Solution: Approx. 17% in $(CD_3)_2SO$.

Singlet	τ 9.54
Broad peak	τ 8.2-8.8
Singlet	τ 5.72
Multiplet	τ 3.0

IR

Solution: Approx. 30% in CS_2.

Free OH stretching band $\nu_{max.}$ 3605 cm.$^{-1}$, 39% transmittance.

Hydrogen bonded stretching band $\nu_{max.}$ 3500 cm.$^{-1}$, 45% transmittance.

1-(p-Methoxyphenyl)-2-methylcyclohexanol. To a solution of phenyl magnesium bromide prepared from magnesium turnings (6.08 g.-0.25 mole), p-bromo anisole (46.8 g.-0.25 mole) and 200 ml. of anhydrous ether, was added a solution of 2-methylcyclohexanone (28.1 g.-0.25 mole). The resulting complex was decomposed with 200 ml. of a saturated ammonium chloride solution. Fractional distillation of the product produced 28.2 g. (61%) of 1-(p-methoxyphenyl)-2-methylcyclohexanol, b.p. 124°/0.2-0.17 mm., n_D^{25} 1.5419. Glc analysis (LAC-728 column) gave two peaks corresponding to 95% and 5% of the trans and cis isomers respectively. The data given below is for the mixture of isomers.

Anal. Calcd. for $C_{14}H_{20}O_2$: C, 76.29; H, 9.17.

Found: C, 76.15; H, 9.04.

IR

Solution: Approx. 30% in CS_2.

Free OH stretching band $\nu_{max.}$ 3600 cm.$^{-1}$, 49% transmittance.

Hydrogen bonded stretching band $\nu_{max.}$ 3515 cm.$^{-1}$, 53% transmittance.

Acid Dehydration of Alcohols

The dehydration of the alcohols was performed according to the method of Garbisch[13] with slight modifications where deemed necessary.

An isomeric mixture of the alcohol under investigation, was dissolved in a solution of sulphuric acid in acetic acid. The solution was kept at room temperature for a certain time interval after which it was poured into a hexane-water mixture. The organic layer was separated and washed with a 5% sodium bicarbonate solution until basic to litmus and was then washed with water until neutral to litmus. The organic layer was subsequently dried with anhydrous magnesium sulphate and the solvent was removed *in vacuo*. The crude olefinic mixture was purified by vacuum distillation. The olefin distribution was determined by glc using a LAC-728 column or a diisodecyl phthalate column. The structure of the olefins was deduced from the nmr spectrum of the olefinic mixture in deuterated chloroform. The vinyl methyl group is found at τ 8.4-8.6. The methyl group on the allylic carbon is found at τ 9.1-9.2 and is coupled to a neighbouring proton (*J* = 7 c.p.s.). The nmr spectrum of the dehydra-

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[13] E. W. Garbisch, Jr., *J. Org. Chem.*, *26*, 4165 (1961).

tion products of 1-phenyl-2-methylcyclohexanol corresponds very well with that reported by Garbisch.[14] With the aid of the integration curve, it was determined what fraction of three protons was represented by the split methyl group on the allylic carbon atom by comparison with a section of the integration curve where the number of protons was known. This method is illustrated thusly: the nmr spectrum of the dehydration products of 1-phenyl-2-methylcyclohexanol showed an unresolved triplet centered at τ 2.95 caused by five aromatic protons. A doublet at τ 9.12 (_J_ = 7 c.p.s.) generated by coupled methyl protons, was also observed along with other peaks. The integration curve for the aromatic protons, was found to be 39 mm. high or approximately eight mm. per proton. The height of the integration curve for the split methyl protons, was five mm., hence, the split methyl protons represent 5/24 of a methyl group on an allylic carbon. From this calculation it is evident that the olefinic mixture is predominantly 1-phenyl-2-methylcyclohexene (80%) and the minor product is 2-phenyl-3-methylcyclohexene. The product ratios as determined from the nmr spectra, were found to be in reasonable agreement with the results of the

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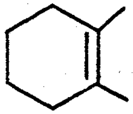
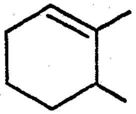
[14] E. W. Garbisch, Jr., _J. Org. Chem._, _27_, 4243 (1962).

glc analyses.

In Table VIII pertinent data for the dehydration of three tertiary alcohols is listed.

TABLE VIII

Acid Dehydration of Tertiary Alcohols[a]

Alcohol	% Concentration of sulfuric acid in acetic acid by volume	Product distribution %	
			
1,2-Dimethylcyclohexanol[b]	5	87	13
1-Phenyl-2-methylcyclohexanol	2.5	24	76
	15	83	17
	HCl/HOAc.[c]	82	18
1-(p-Methoxyphenyl)-2-methylcyclohexanol	5	83	17
	10	83	17

a Experiments were performed at room temperature for 20 minutes.

b The duration of this experiment was 45 minutes.

c A. F. Casy, A. H. Beckett and M. A. Lorio, Tetrahydron, 23, 1405 (1967). The acid ratio was 1:2 and the mixture was refluxed for 43 hours.

Synthesis of Hydrogen Phthalate Esters

The method used to convert the alcohols to the hydrogen phthalate esters studied in this investigation, was identical to that previously described by Rutherford, Prokipcak and Fung.[15] Pertinent physical data is listed in Table IX.

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[15] K. G. Rutherford, J. M. Prokipcak and D. P. C. Fung, J. Org. Chem., 28, 582 (1963).

TABLE IX

Hydrogen Phthalate Esters

	Average yield of acid phthalate %	Melting point °C	Dec. point °C	Neutralization equivalent		Carbon		Hydrogen	
				Calcd.	Found	Calcd. %	Found %	Calcd. %	Found %
cis-1,2-Dimethylcyclohexanol	60	98.5-99.5	142	276.3	276.7	69.53	69.09	7.31	7.49
trans-1,2-Dimethylcyclohexanol	80	125-127	146	276.3	276.2	69.53	69.13	7.31	7.26
cis-1-Phenyl-2-methylcyclohexanol	66	a	124	338.4	337.3	74.54	74.51	6.55	6.57
trans-1-Phenyl-2-methylcyclohexanol	85	a	142	338.4	338.6	74.54	74.42	6.55	6.63
trans-1-Phenyl-2-methylcyclohexanol-2,6,6-d_3	63	a	150	341.4	342.5	73.88	73.73	7.38[b]	7.19[c]

[a] Decomposed at the melting point.

[b] Calculated on the basis of 100% deuterium-hydrogen exchange.

[c] Determined as hydrogen.

Pyrolysis Studies of Hydrogen Phthalate Esters

Method A

Direct Injection of Esters into the Gas Chromatograph

A small amount of the desired hydrogen phthalate ester (100 mg.) was dissolved in approximately four drops of anhydrous diethyl ether and a few µl. of this solution was injected into the gas chromatograph. The following conditions were maintained for all experiments: detector temperature, 300°; detector current, 100 milliamperes; helium flow rate, 1 cc./sec.

In the case of the *cis*- and *trans*-1-phenyl-2-methylcyclohexyl hydrogen phthalate ester, a copper column (6-1/4 ft. x 1/4 in. o.d.) packed with 10% LAC-728 on 60-80 mesh Diatoport W was used. The column temperature was maintained at 100°. The temperature of the injector port was varied as indicated in Table X.

In the case of the *cis*- and *trans*-1,2-dimethylcyclohexyl hydrogen phthalate, a column (16 ft. x 1/4 in. o.d.) packed with 10% diisodecylphthalate on 60-80 mesh Diatoport W was used. The column- and injector port temperature were maintained at 100 and 300° respectively.

The resulting olefin distributions are summarized in Table X.

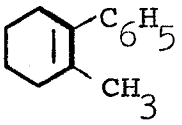
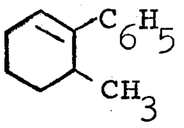
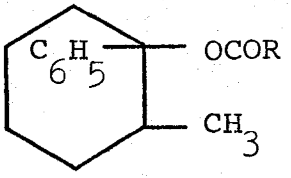
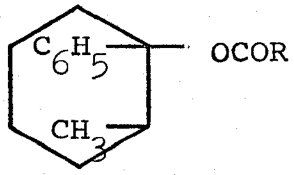
Method B

Decomposition of Esters by Immersion in an Oil Bath

A small amount of the hydrogen phthalate ester under investigation, was placed into a 5 ml. flask fitted with a condenser. The sample was immersed in an electrically heated oil bath maintained at the desired temperature. After a given time interval, the flask was removed from the bath and cooled rapidly. Petroleum ether (b.p. 30-60°) was then added through the condenser and the solid pulverized with a stirring rod. The solid was collected by suction filtration and washed with 1 ml. petroleum ether. Subsequent removal of the solvent in vacuo yielded a colourless liquid. The olefins obtained were subjected to glc analysis under conditions similar to those described in Method A. All olefins were identified by comparison with the retention times of the known dehydration products of an isomeric mix-

TABLE X

Pyrolysis of Hydrogen Phthalate Esters by Direct Injection into the Gas Chromatograph

Hydrogen Phthalate Ester	Injection Port Temperature °C	Product Distribution %	
			
	140	7	93
	170	10	90
	290	19	81
	115	11	89
	140	12	88
	160	13	87
	290	25	75

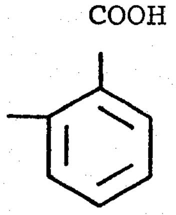
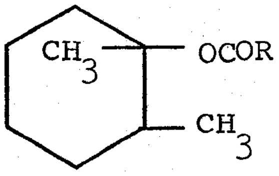
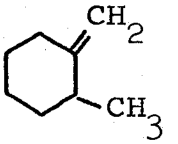
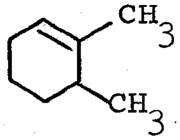
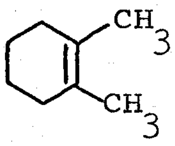
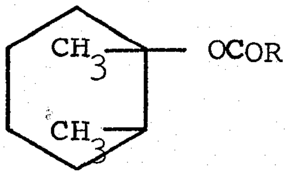
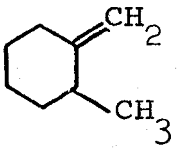
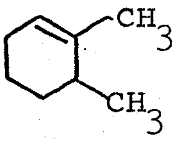
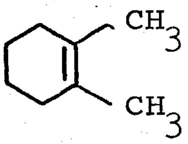
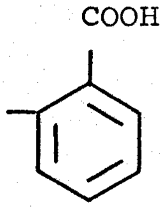
R = 

TABLE X (Cont'd)

Hydrogen Phthalate Ester	Injection Port Temperature °C	Product Distribution	
	300		22%
			44%
			34%
	300		11%
			21%
			68%

R = 

ture of the parent alcohols.

In the case of trans-1-phenyl-2-methylcyclohexyl hydrogen phthalate, 0.107 g. was pyrolyzed yielding 79% of the expected amount of olefins. Glc analysis generated two well defined peaks. Similarly the pyrolysis of cis-1-phenyl-2-methylcyclohexyl hydrogen phthalate (0.099 g.) yielded 50% of the expected amount of olefins.

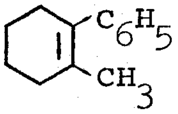
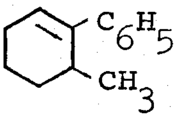
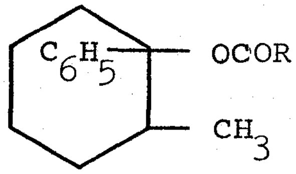
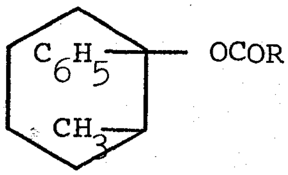
The addition of phthalic acid (1.52×10^{-1} g.-9.15×10^{-4} mole) in the pyrolysis of trans-1-phenyl-2-methylcyclohexyl hydrogen phthalate (9.17×10^{-2} g.-2.72×10^{-4} mole) resulted in a 46% yield of the calculated amount of olefins.

The pyrolysis of cis- and trans-1,2-dimethylcyclohexyl hydrogen phthalates was performed by placing 25 mg. of the ester in a 1x7 cm. test tube and suspending the samples in a constant temperature oil bath. After complete pyrolysis, the samples were extracted with petroleum ether (b.p. 30-60°) and the solution subjected to glc analysis as in method A.

In Table XI, the temperature and duration of the pyrolysis along with the olefin distribution are summarized.

TABLE XI

Pyrolysis of Hydrogen Phthalate Esters in an Oil Bath

Hydrogen Phthalate Ester	Oil Bath Temp. °C	Time Min.	Product Distribution %	
				
	142	8	7	93
With Phthalic Acid Added	142	30	7	93
	110	8	11	89

R =

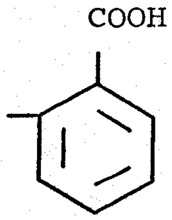
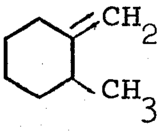
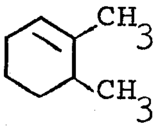
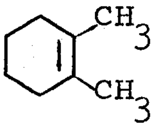
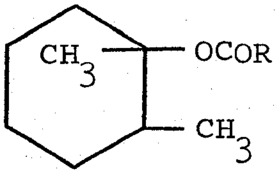
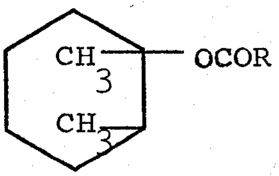
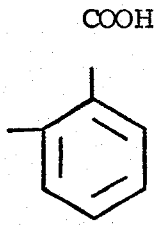


TABLE XI (Cont'd)

Hydrogen Phthalate Ester	Oil Bath Temp. °C	Time Min.	Product Distribution %		
					
	125.7	90	30	46	24
	137.3	45	30	46	24
	120	90	24	20	56
	130	45	24	20	56

R = 

Method C

Decomposition of Esters in a Melting Point Tube

A small amount of the desired compound was placed in a melting point tube (2 mm. o.d.x10 cm.) to a depth of circa 1 cm. The tube containing the sample was placed in an Electrothermal Melting Point Apparatus previously heated to the decomposition point of the ester under investigation. When all observable reaction had ceased, the tube was removed from the apparatus and cooled under a stream of cold water. Petroleum ether (b.p. 30-60°, 10 μl.) was then added and the solid pulverized with a stainless steel wire. The tube was cut to a length of about 3 cm. and placed in a centrifuge for several minutes. Small amounts (3-4 μl.) of the supernatent solution were removed with a syringe and analyzed by glc as described previously. The resulting olefins were identified by comparison with the retention times of the known dehydration products of an isomeric mixture of the parent alcohols. However, the retention times of the olefins which resulted from the pyrolysis of _trans_-1-phenyl-2-methylcyclohexyl-2,6,6-d_3 hydrogen phthalate, were compared with the retention times of the undeuterated olefins produced by the acid dehydration of an isomeric mixture of 1-phenyl-2-methylcyclohexanol.

The following hydrogen phthalate esters were investigated in this manner: cis- and trans-1-phenyl-2-methylcyclohexyl, trans-1-phenyl-2-methylcyclohexyl-2,6,6-d_3.

Table XII summarizes the duration and temperature of the pyrolysis as well as the distribution of the olefins.

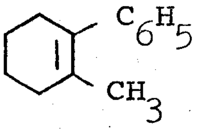
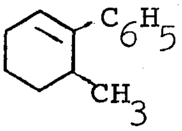
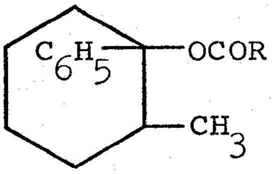
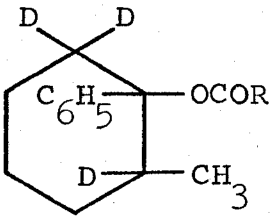
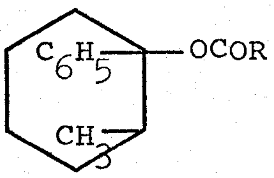
Kinetic Studies

For those hydrogen phthalate esters which melted before they decomposed, pyrolysis was carried out on neat samples. Hydrogen phthalate esters which decomposed at their melting points, were pyrolyzed in a solution of N,N-dimethylformamide. The experimental procedure for the former compounds will be described first.

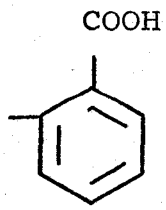
An accurately weighed sample (20 or 25 mg.) of the hydrogen phthalate ester to be studied, was placed in a 75x10 mm. test tube. The samples (20-30) were then suspended in a constant temperature oil bath preheated to the desired temperature with a Haake-All Purpose Constant Temperature Circulator. After an initial waiting period (1-2 min.) to ensure constant temperature, samples were removed at set intervals and immediately placed in ice-water. The samples were transferred to 25 ml. Erlenmeyer flasks with

TABLE XII

Pyrolysis of Hydrogen Phthalate Esters in a Melting Point Tube

Hydrogen Phthalate Ester	Temp. °C	Time Min.	Product Distribution %	
				
	143	2	5	95
	150	3	9	91
	126	3	12	88

R =



five 1 ml. portions of tetrahydrofuran and titrated with standard sodium hydroxide solution (0.014-0.016 N) with phenolphthalein as indicator; a blank correction was applied for the tetrahydrofuran.

From the weight of the hydrogen phthalate ester used, the number of equivalents may be calculated, however, pyrolysis had already started before the first sample was removed from the oil bath because of the initial waiting period (1-2 min.) to ensure temperature equilibrium. Zero time concentrations were calculated as shown below.

Setting: M_H = equivalents of hydrogen phthalate ester from the weight of the sample used.

M_{H1} = equivalents of ester left at any time after pyrolysis had started.

M_{Ho} = equivalents of ester consumed.

N_B = normality of base.

V_B = volume of base used to titrate M_H.

V_{B1} = volume of base used to titrate M_{H1} and phthalic acid formed.

V_{Bx} = volume of base to be subtracted from V_{B1} to find M_{H1}.

V_{Bc} = volume of base corrected to zero time.

At any time after the introduction of the sample into the oil bath, $V_{B1} > V_B$ and $(V_{B1} - V_B) \times N_B = M_{Ho}$

Substituting: $M_H - M_{Ho} = M_{H1}$

$$(V_{B1} - V_B) = V_{Bx}$$

$$V_{B1} - V_{Bx} = V_{Bc}$$

$$V_{Bc} \times N_B = M_{H1}$$

The above calculation was employed to determine the number of equivalents of the hydrogen phthalate ester present after the initial waiting period. The removal of the first sample signified the start of a run. The value of V_{Bx} was subtracted from all subsequent amounts of base used to titrate the samples.

The hydrogen phthalate ester is a mono basic acid which on pyrolysis produces a dibasic acid. From the amount of base consumed, the number of moles of ester remaining may be calculated as shown below.

Setting: A = hydrogen phthalate ester.

B = phthalic acid.

C = olefin.

a = number of equivalents of A.

x = number of equivalents of B.

y = number of moles of C.

N_B = normality of base.

V_B = volume of base used.

$(a - x)$ = number of equivalents of A left at any time t.

Now: $A \xrightarrow{\Delta} B + C$

$$a \xrightarrow{\Delta} o + o \quad \text{at, } t = o$$

$$(a - x) \xrightarrow{\Delta} 2x + y \quad \text{at, } t = t$$

$(a - x)$ and $2x$ are titrated simultaneously

hence: $a - x + 2x = a + x = N_B \times V_B$

and $x = (N_B \times V_B) - a$

therefore $a - x = a - [(N_B \times V_B) - a]$

$$a - x = 2a - (N_B \times V_B)$$

Since N_B, V_B and a are known quantities, $(a - x)$ may be calculated readily.

The hydrogen phthalate esters which decomposed at their melting points were pyrolyzed in N,N-dimethylformamide. The solvent was stirred for three hr. with freshly dried anhydrous magnesium sulphate (300°, 3 hr.) and distilled under reduced pressure. The centre cut (b.p. 53-55°/

2.8 cm.) was collected and used in all subsequent experiments.[16] The solvent (35 ml.) was pipeted into a 100 ml. 3 necked flask fitted with an electric stirrer, condenser and rubber septum with a hypodermic syringe. A certain amount of the ester (0.4-0.5 g.) was pressed into a pellet at 8000 p.s.i. with a Carver Laboratory Press. The apparatus was heated in the previously described oil bath and when the desired temperature was reached, the condenser was removed momentarily and the accurately weighed pellet of hydrogen phthalate ester introduced into the flask. After an initial waiting period (1-2 min.) to ensure complete dissolution of the ester, one ml. samples were removed at set intervals by means of the hypodermic syringe and placed into 25 ml. Erlenmeyer flasks containing five ml. ice cold tetrahydrofuran. The samples were titrated with standard base against phenolphthalein indicator. Blank corrections were applied for the solvent.

Correction factors and calculations were the same as previously described for neat pyrolysis, however an extra

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[16] Arthur L. Vogel, Elementary Practical Organic Chemistry, Longmans, Green and Co., Inc., London, 1958, p. 692.

correction factor was needed with this method. The solvent was measured at room temperature but the samples were removed at the temperature at which the experiments were performed thereby changing the concentrations. The expansion of the solvent was determined for each temperature at which the experiment was performed by placing a small graduated glass tube containing some solvent in the oil bath and observing the change in volume on heating. The per cent change was found and this figure was used to determine the initial concentration of the hydrogen phthalate ester.

The rate constant was calculated using the first-order rate equation $\ln E_L = - kt + \ln E_o$

Where: E_L = hydrogen phthalate ester left at any time t.

E_o = hydrogen phthalate ester at time zero.

k = rate constant, (sec.$^{-1}$).

t = time (sec.).

The line of best fit was found from a regression calculation of $\ln E_L$ on t.[17]

---

[17] Appendix I

The frequency factor and experimental activation energy were calculated from the Arrhenius equation $k = A\ e^{-E_{exp.}/RT}$ in the form $\ln k = - E_{exp.}/RT + \ln A$.[18]

Where: k = rate constant ($sec.^{-1}$).

$E_{exp.}$ = experimental activation energy ($cal.\ mole^{-1}$).

R = gas constant ($cal.\ deg.^{-1} mole^{-1}$).

T = absolute temperature (deg.).

A = frequency factor ($sec.^{-1}$).

The quantity $- E_{exp.}$ is equal to the slope of the line resulting from a plot of $\ln k$ against $1/RT$ where as $\ln A$ is found from the intercept on the y axis. Again a regression calculation of $\ln k$ on $1/RT$ was employed to determine the line of best fit. A combination of the absolute rate equation $k = Ke(k^1T/h)\ e^{\Delta s^{\ddagger}/R}\ e^{-E_{exp.}/RT}$[19] with the Arrhenius equation $k = A\ e^{-E_{exp.}/RT}$ yields $A = Ke(k^1T/h)\ e^{\Delta s^{\ddagger}/R}$ which can be rearranged to give $\Delta s^{\ddagger} = R \ln (h/e\ k^1\ T) + R \ln A$

---

[18] G. L. O'Connor and H. R. Nace, J. Am. Chem. Soc., 74, 5454 (1953).

[19] S. Glasstone, K. J. Laidler and H. Eyring, The Theory of Rate Processes. McGraw-Hill Book Co., Inc., New York, 1941, p. 295.

Where: k, $E_{exp.}$, R, T and A are as defined previously.

K = transmission coefficient and considered to be unity.

k^1 = Boltzmann constant (erg. deg.$^{-1}$ molecule^{-1}).

h = Planck constant (erg. sec. molecule^{-1}).

$\Delta s^{\ddagger}$ = entropy of activation (cal. deg.$^{-1}$ mole^{-1}).

As before, ln A is the intercept on the y axis.

The cis and trans-1,2-dimethylcyclohexyl hydrogen phthalate esters were pyrolyzed neat. Kinetic and thermodynamic data are listed in Table XIII.

TABLE XIII

Pyrolysis of cis- and trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate Ester

Compound	Temp. ^{o}C	Rate Constant k, $sec.^{-1} x10^{+5}$	Stand. Dev. of k, $sec.^{-1} x10^{+5}$	Energy of Activation $E_{exp.}$ Kcal./mole	Arrhenius A, $sec.^{-1} x10^{-13}$	Entropy of Activation $\Delta S^{\ddagger}$ e.u.	Number of Points	% Completion	Correlation Coefficient
trans	125.7	56.70	1.05	32.7 ± 1.6	47.51	6 ± 4[a]	20	71	-0.9969
	131.5	106.68	1.74				25	79	-0.9969
	134.4	148.34	1.80				24	91	-0.9983
	137.3	176.37	4.2				26	82	-0.9952
cis	120.0	60.61	1.55	33.7 ± 0.5	343.8	10 ± 1[a]	27	80	-0.9919
	123.6	89.85	1.18				27	78	-0.9978
	125.8	116.74	2.88				24	80	-0.9934
	130.0	176.14	2.89				26	90	-0.9968

[a] This is the probable error. See Appendix 1.

Fig. 19. The amount of trans-1,2-dimethylcyclohexyl hydrogen phthalate ester remaining, was plotted against the time on semi-logarithmic paper. The total number of points for each run along with the correlation coefficient is listed in Table XIII. The different symbols indicate the operating temperature in centigrade degrees as follows:

■ , 125.7; ▲ , 131.5; ○ , 134.4; ● , 137.3.

Figure 19

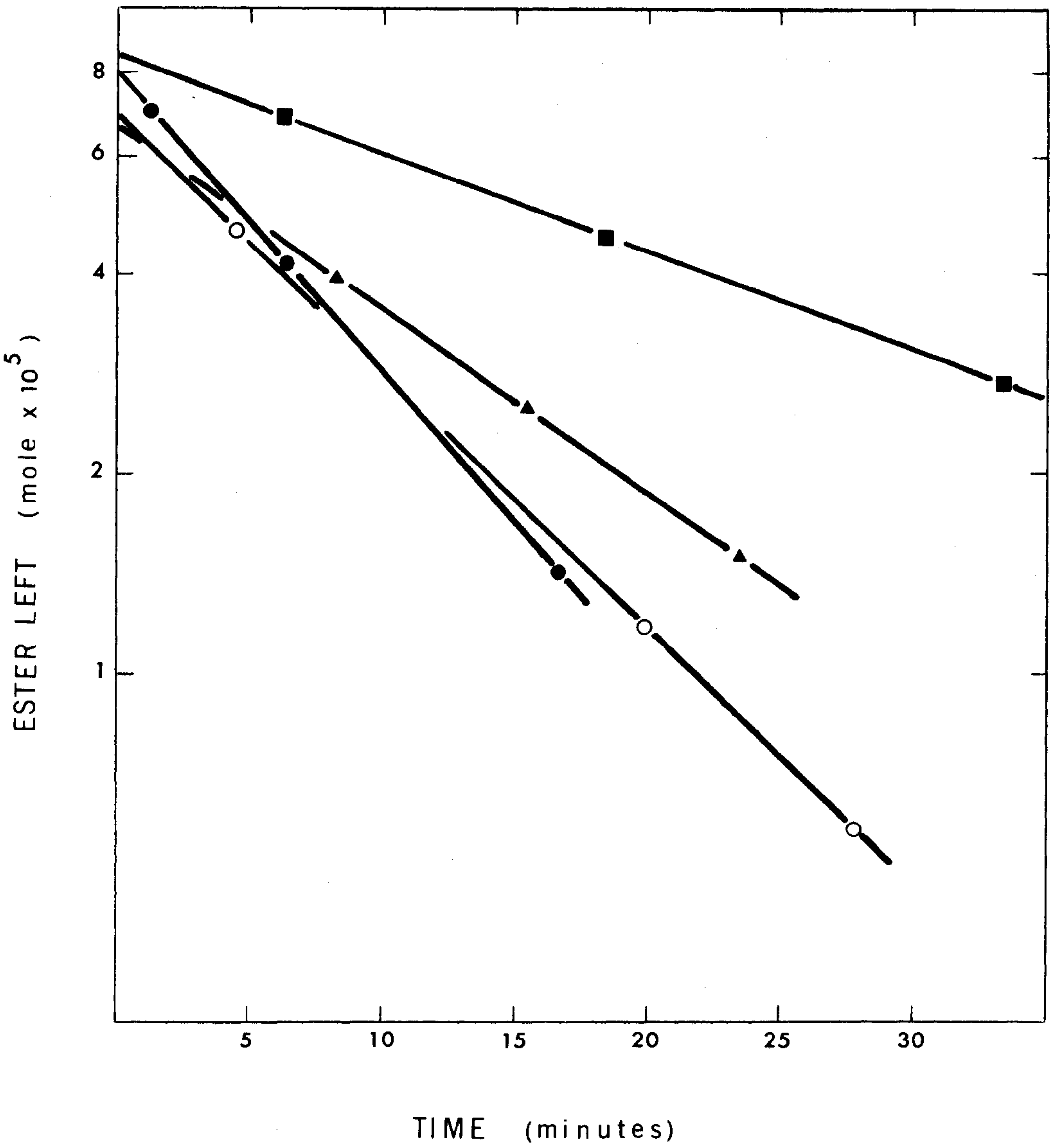


Fig. 20. The rate constants obtained for the pyrolysis of <u>trans</u>-1,2-dimethylcyclohexyl hydrogen phthalate ester have been plotted against the reciprocal of the absolute temperature on semi-logarithmic paper. The correlation coefficient was found to be, -0.9955.

Figure 20

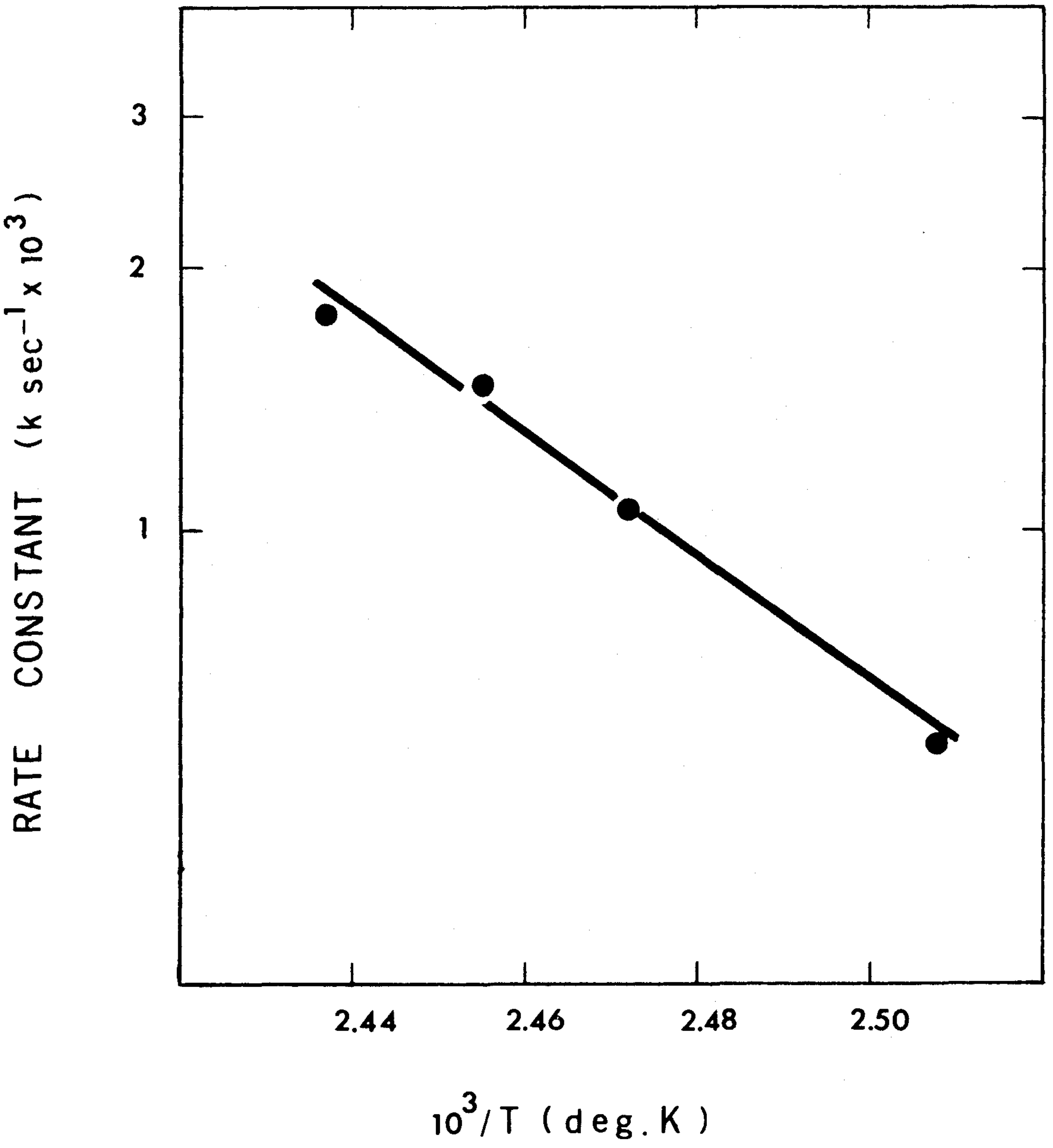


Fig. 21. A plot of moles of *cis*-1,2-dimethylcyclohexyl hydrogen phthalate ester remaining against time at different temperatures has been constructed on semi-logarithmic paper. The points on the line are only representative and the total number of points and correlation coefficient are given in Table XIII. The symbols correspond to the following temperatures in centigrade degrees: □ , 120.0; ■ , 123.6; ▲ , 125.8; ● , 130.0.

Figure 21

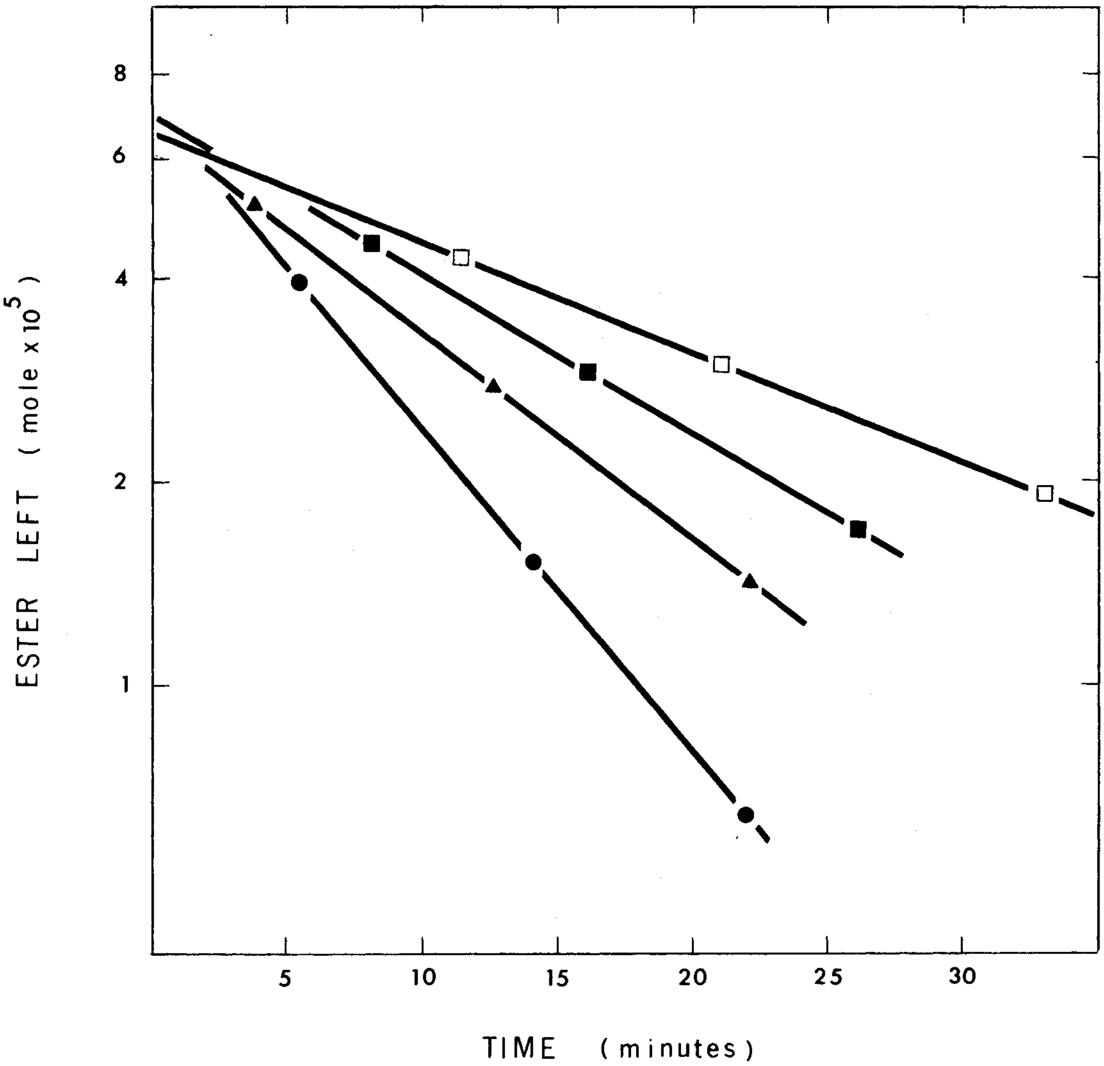
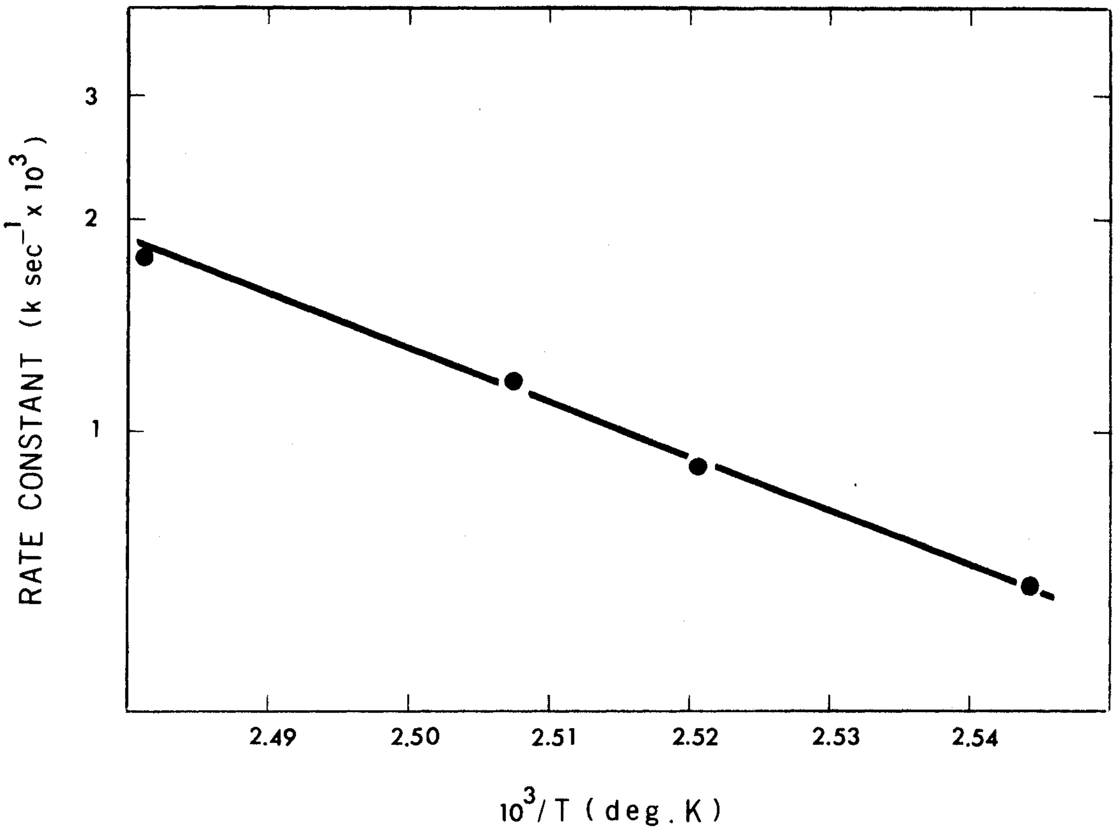


Fig. 22. The rate constants obtained for the pyrolysis of cis-1,2-dimethylcyclohexyl hydrogen phthalate ester were plotted against the reciprocal of the absolute temperature on semi-logarithmic paper. The correlation coefficient was determined to be, -0.9995.

Figure 22


RATE CONSTANT (k sec^{-1} x 10^3)
3
2
1
2.49
2.50
2.51
2.52
2.53
2.54
10^3/T (deg. K)

The *cis*- and *trans*-1-phenyl-2-methylcyclohexyl hydrogen phthalate esters were pyrolyzed in solution as previously described. Kinetic and thermodynamic data is listed in Table XIV along with the data obtained for *trans*-1-phenyl-2-methylcyclohexyl-2,6,6-d_3 hydrogen phthalate.

TABLE XIV

Pyrolysis of *cis*- and *trans*-1-Phenyl-2-methylcyclohexyl Hydrogen Phthalate Ester

Compound	Temp. ^{o}C	Rate Constant k, sec.$^{-1}$x10^{+5}	Stand. Dev. of k, sec.$^{-1}$x10^{+5}	Energy of Activation E$_{exp.}$ Kcal./mole	Arrhenius A, sec.$^{-1}$	Entropy of Activation $\Delta S^{\ddagger}$ e.u.	Number of Points	% Completion	Correlation Coefficient
trans	127.6	39.54	0.46	26.2 ± 1.6[a]	79.06×10^{11}	-11 ± 4[a]	27	58	-0.9983
	130.1	52.35	1.19				15	50	-0.9965
	132.5	61.40	0.50				24	60	-0.9993
	135.1	73.15	0.92				20	63	-0.9984
trans-2,6,6-d_3	135.1	71.34	0.78				28	71	-0.9984
cis	112.6	24.66	0.41	32.7 ± 1.4[a]	92.04×10^{13}	7 ± 4[a]	28	48	-0.9962
	115.1	34.33	0.51				29	59	-0.9969
	120.1	56.57	0.72				29	62	-0.9978

[a] This is the probable error. See Appendix 1.

Fig. 23. The concentration of _trans_-1-phenyl-2-methylcyclohexyl hydrogen phthalate ester remaining was plotted against time on semi-logarithmic paper. The number of points for each run and the correlation coefficient are listed in Table XIV. The different symbols correspond to different pyrolysis temperatures in centigrade degrees as follows: ▲ , 127.6; ■ , 130.1; ● , 132.5; ○ , 135.1.

Figure 23

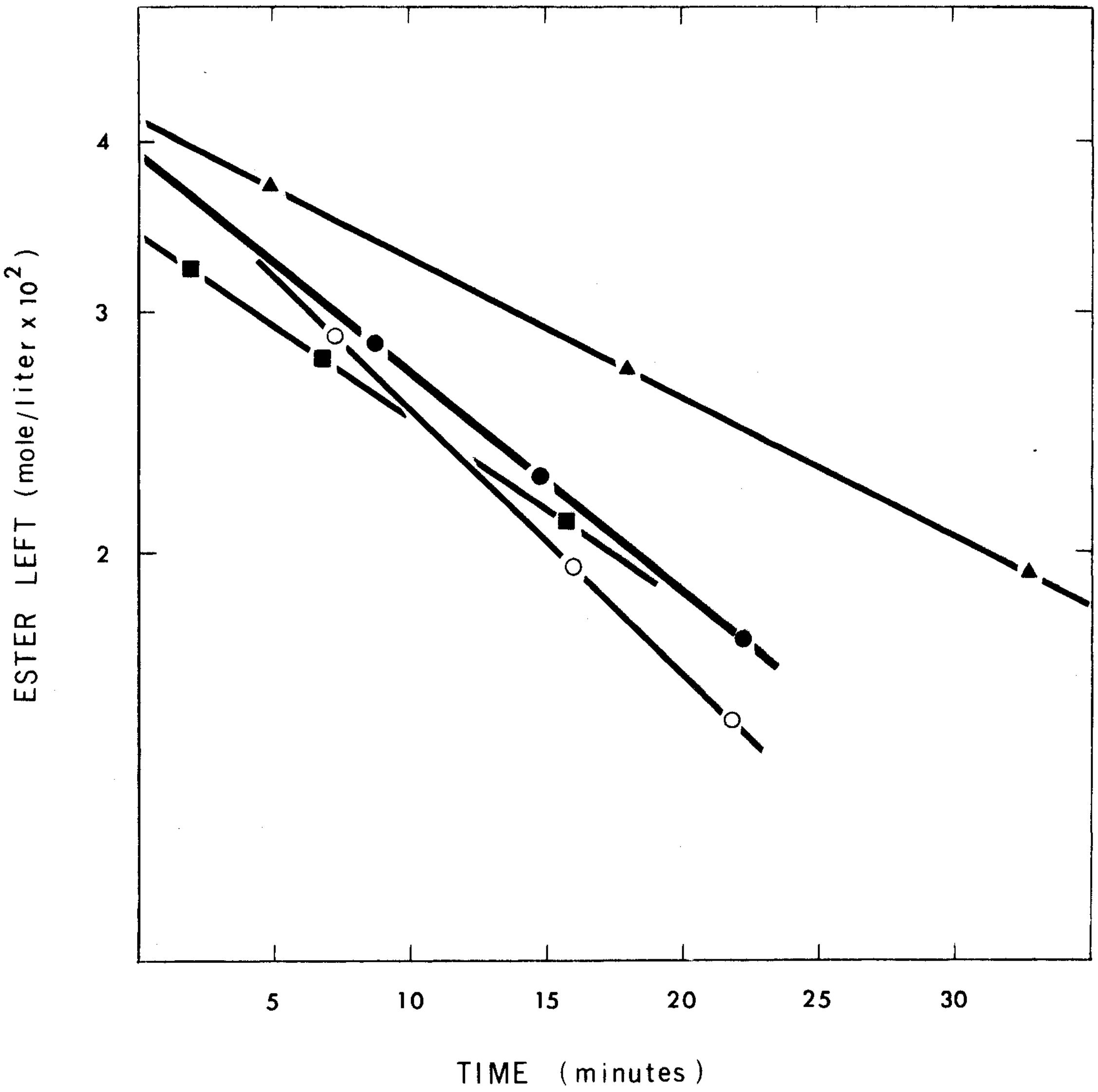


Fig. 24. The rate constants for the pyrolysis of _trans_-1-phenyl-2-methylcyclohexyl hydrogen phthalate were plotted against the reciprocal of the absolute temperature. The correlation coefficient was calculated to be, -0.9899.

Figure 24

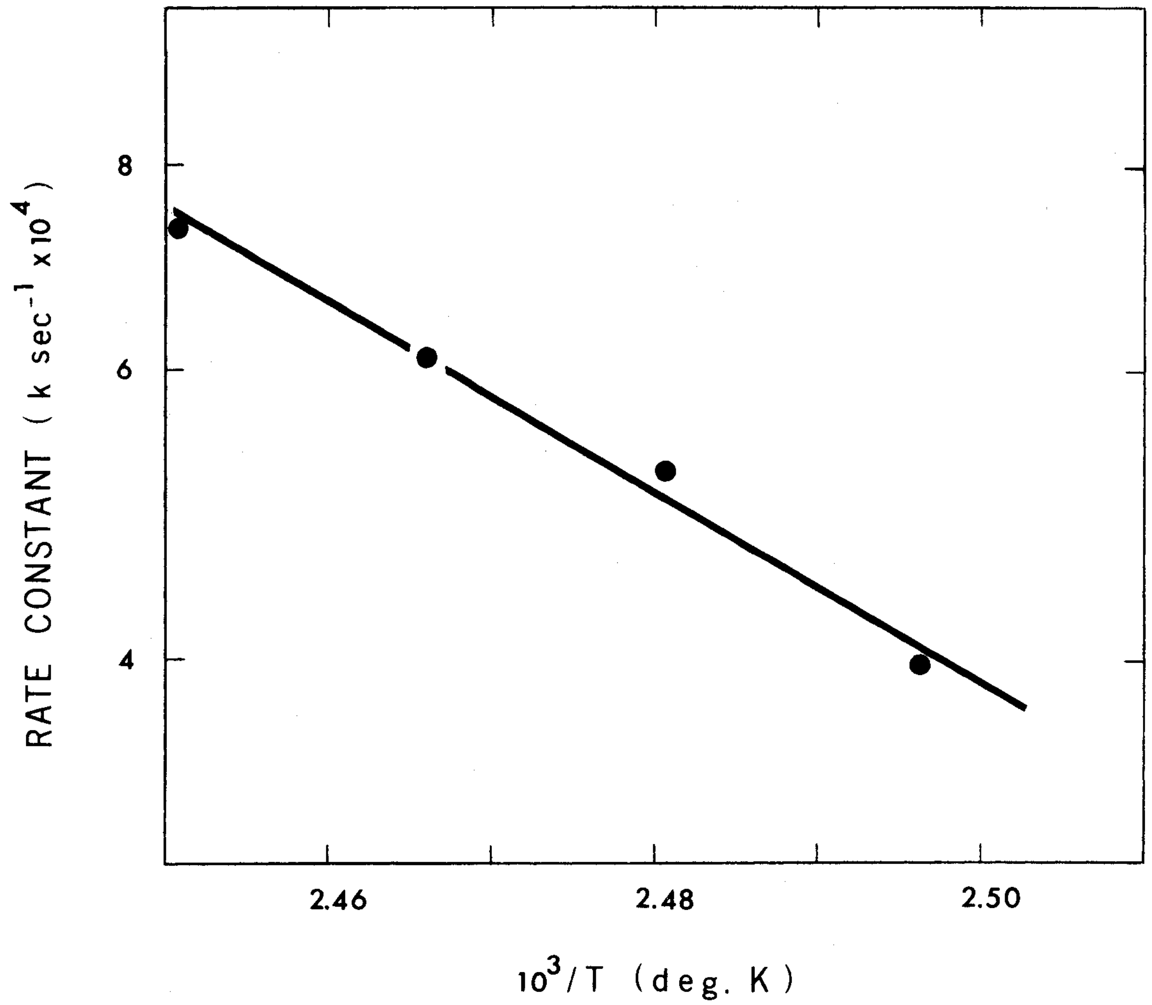


Fig. 25. The concentration of cis-1-phenyl-2-methylcyclohexyl hydrogen phthalate ester remaining was plotted against time on semi-logarithmic paper. The points on the line are only representative. The number of points for each pyrolysis run along with the correlation coefficient are listed in Table XIV. The symbols correspond to the following temperatures in centigrade degrees: ■ , 112.6; ▲ , 115.1; ● , 120.1.

Figure 25

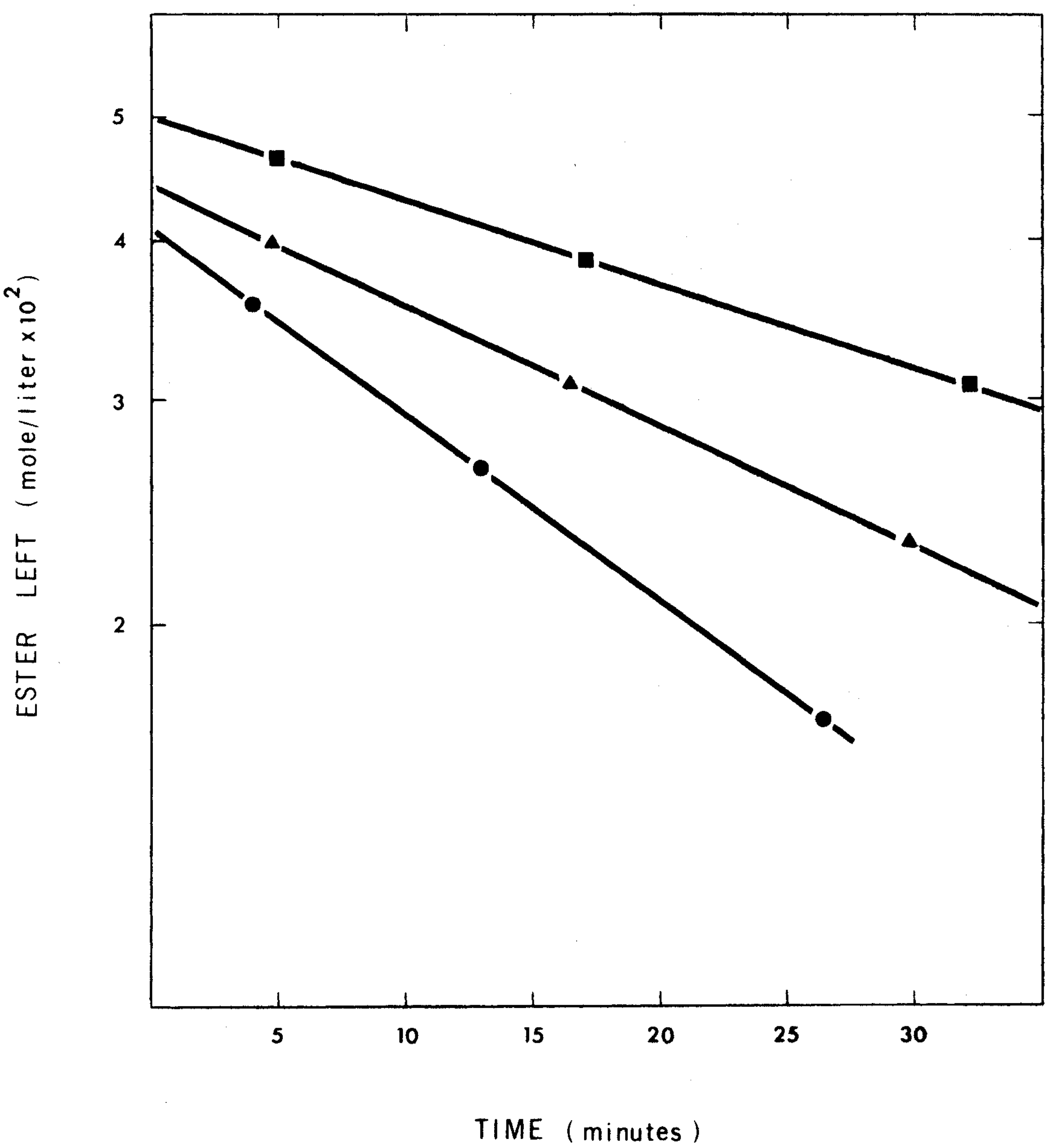
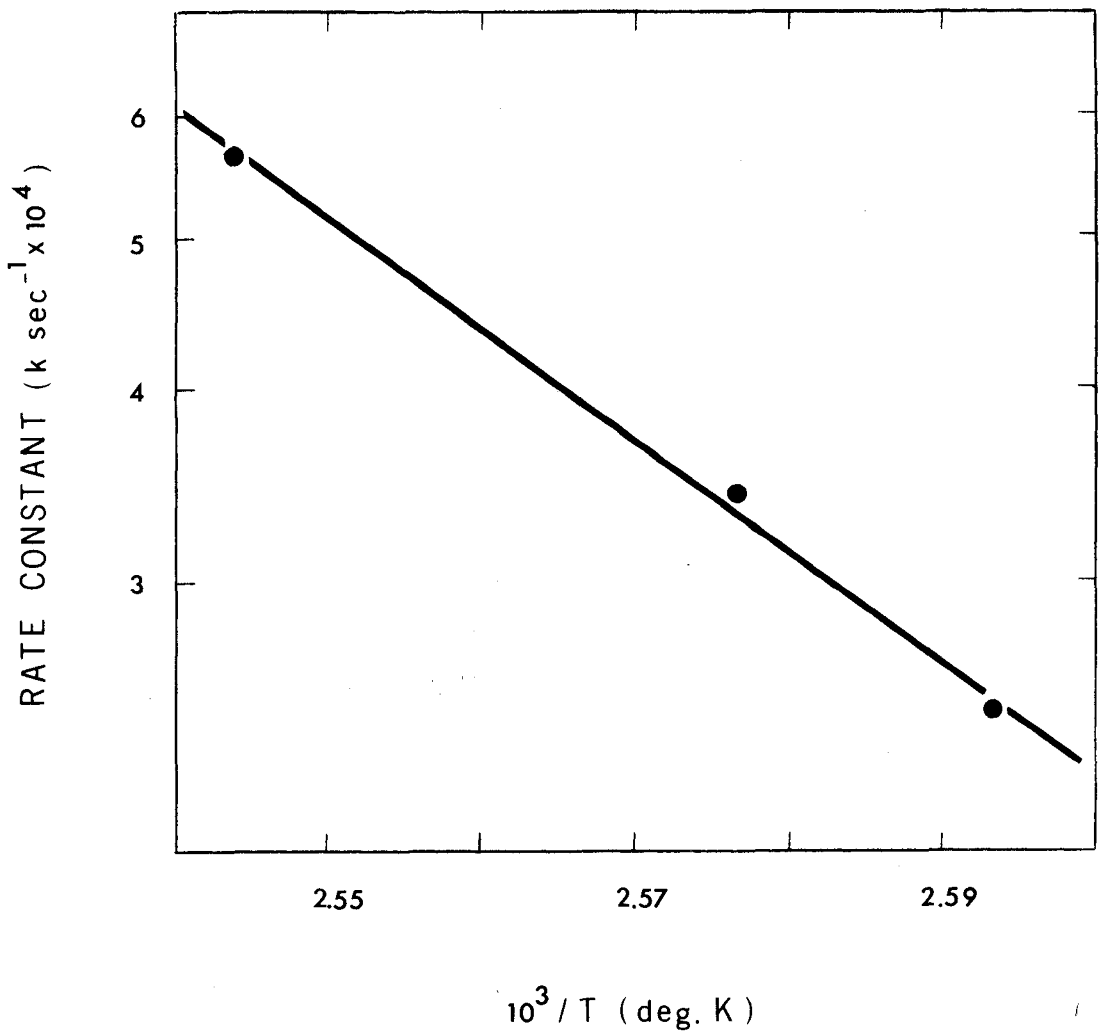


Fig. 26. The rate constants for the pyrolysis of cis-1-phenyl-2-methylcyclohexyl hydrogen phthalate ester were plotted against the reciprocal of the absolute temperature. The correlation coefficient was found to be, -0.9974.

Figure 26



Saponification of Hydrogen Phthalate Esters

To 30.0 g. (8.91×10^{-2} mole) of 1-phenyl-2-methylcyclohexyl hydrogen phthalate prepared from an isomeric mixture of the parent alcohol was added 200 ml. of a sodium hydroxide solution (3.83 g.-9.55×10^{-2} mole). The solution was refluxed overnight and allowed to cool. Chloroform (100 ml.) was then added through the condenser. The organic layer was separated, dried with anhydrous magnesium sulphate and the solvent was removed *in vacuo* (yield, 85%). Vacuum distillation of the crude product yielded three fractions. The first fraction (b.p. 23-76°/ 0.5 mm.) was shown to be olefin by ir spectroscopy and represented 16.8% of the product. The second fraction, a liquid, (b.p. 94-98°/ 0.5 mm.) indicated the presence of alcohol on ir analysis and accounted for 41.6% of the product. The remainder (b.p. 70-71°/ 0.05 mm.) solidified in the receiver and represented 41.6% of the product. Recrystallization of the solid from hot petroleum ether (b.p. 30-60°) yielded a pure white solid (m.p. 59-61°) and ir analysis indicated this compound to be an alcohol. The retention times of the second and third fraction were identical to the retention times of the isomeric alcohols as synthesized by the Grignard reaction.

Synthesis of the Acetate of 1-Phenyl-2-methylcyclohexanol

To a solution of phenyl magnesium bromide prepared from magnesium turnings (6.08 g.-0.25 mole), bromobenzene (39.3 g.-0.25 mole) and 200 ml. of anhydrous ether, was added a solution of 2-methylcyclohexanone (28.3 g.-0.25 mole). The resulting Grignard reagent was decomposed by the dropwise addition of freshly distilled acetic anhydride (51.0 g.-0.5 mole) while the stirred reaction mixture was cooled in an ice bath. The reaction mixture was stirred at room temperature for an additional three hr. and then water was added cautiously. The ethereal layer was separated, washed with a 5% sodium bicarbonate solution followed by washing with water. The organic layer was separated, dried with anhydrous magnesium sulphate and the solvent was removed *in vacuo*. The yield of crude acetate was 86%. Vacuum distillation yielded an isomeric mixture of pure 1-phenyl-2-methylcyclohexyl acetate, b.p. 75-76.5°/ 0.07 mm., d_D^{25} 1.5172.

Anal. Calcd. for $C_{15}H_{20}O_2$: C, 77.60; H, 8.69.

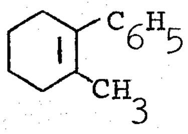
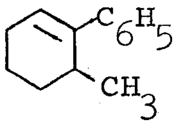
Found : C, 77.55; H, 8.89.

Pyrolysis of 1-Phenyl-2-methylcyclohexyl Acetate

The acetate was pyrolyzed by direct injection into the gas chromatograph (Se-30 column) at varying injector port temperatures. The olefins were identified by comparison with the retention times of the known dehydration products of an isomeric mixture of the parent alcohol. In Table XV, the injector port temperature and olefin distribution are listed.

TABLE XV

Pyrolysis of 1-Phenyl-2-methylcyclohexyl Acetate

Injector Port Temperature °C	Olefin Distribution	
		
290	17	83
220	17	83
170	17	83

When 1 g. of the olefinic mixture from the alcohol dehydration, was refluxed for 0.5 hr. with an equimolar amount of freshly distilled acetic acid, no change in the isomer distribution was observed on glc analysis.

APPENDIX I

Formulae Used in the Calculations[1,2]

The first order rate equation $\ln E_L = - kt + \ln E_o$ and the Arrhenius equation $\ln k = - E_{exp.}/RT + \ln A$, are equations of straight lines of the form $y = mx + b$.

E_L = ester left at any time t.

E_o = initial amount of ester at t_o.

t = time in seconds.

k = rate constant (sec.^{-1}).

$E_{exp.}$ = experimental activation energy (cal. mole^{-1}).

T = absolute temperature (deg.).

The slope m, may be found from:

$$m = \frac{N \sum xy - \sum x \sum y}{N \sum x^2 - (\sum x)^2}$$

and the intercept on the y axis, b, from:

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1 M. J. Moroney, <u>Facts from Figures</u>, 3rd. ed., Penguin Books Ltd., Harmondsworth, Middlesex, England, 1964, pp. 284-295.

2 H. Margenau and G. M. Murphy, <u>The Mathematics of Physics and Chemistry</u>, 2nd. ed., D. Van Nostrand Co., Inc., Princeton, New Jersey, 1961, p. 519.

$$b = \frac{\sum x \sum xy - \sum y \sum x^2}{(\sum x)^2 - N(\sum x^2)}$$

The correlation coefficient, r, between x and y is given by:

$$r = \frac{{}^1/N \sum xy - \bar{x}\,\bar{y}}{\sigma_x \times \sigma_y}$$

where σ_x and σ_y are the standard deviations of x and y.

The probable error in the intercept A, is calculated from:

$$P_A = r_e \sqrt{\frac{\sum x_i^2}{D}}$$

where $r_e = 0.6745 \sqrt{\frac{\sum d_i^2}{(n-2)}}$

$$D = n \sum x_i^2 - (\sum x_i)^2$$

and d_i is the deviation in ln k as obtained by the use of the least squares determination, n is the number of points.

The probable error in the entropy of activation is simply R times the error in the y intercept.

The probable error in the energy of activation $E_{exp.}$ is determined from the formula:

$$P_{E_{exp.}} = r_e \sqrt{\frac{n}{D}}\,.$$

where r_e, n and D are as previously defined.

APPENDIX II

Programme Used for the Calculations

The following programme is written in Kingstran (free format) and is for use with the IBM 1620^{II}.

Programme Instructions

First card: Number of different compounds used (integer).

Second card: Number of temperatures used for the first compound (integer).

Third card: Data for a particular run at a certain temperature. All numbers on this card must be decimal numbers.

first entry: temperature for the run in degrees centigrade.

second entry: normality of the base used in equivalents per liter.

third entry: concentration of the ester (monoacidic) in equivalents per liter.

fourth entry: aliquot used in the titration, the same aliquot must be used throughout a run, for neat work set this at 0.0.

fifth entry: number of moles of ester used for neat work, for solution work set this at 0.0.

sixth entry: 0.0 for solution, 1.0 for neat.

The third card is arranged for free format, the variables must be in the above stated order but are not restricted to any particular field.

Fourth card: The actual data for a run is placed on this and subsequent cards and free format is used.

first entry: ml. of base used.

second entry: time elapsed in minutes.

Fifth and succeeding cards: rest of data for a run, at the end of each run insert a card with two zeros (0.0 0.0). For the next run at a different temperature, start again at the third card. After all the data for one compound is punched, start at the second card for the next compound.

This programme contains a plotter sub-routine and if a graph is to be plotted, instruct the operator to turn sensory switch 1 on.

```
ZZJOB 5
ZZXEQ KF2                          L
*      JOB             S WASSENAAR     *
      DIMENSION TEMP(20)
         DIMENSION FRRENT(20)
      DIMENSION SRATE(20),SSIGRT(20)
      DIMENSION A(100), B(100), X(100), Y(100), RR(20),TT(20),RRR(20),
     1DIFF1(40),DIFF2(40)
      DO 995 J=1,3
      PUNCH 997
  997 FORMAT(50H**************************************************)
  995 CONTINUE
      PUNCH 996
  996 FORMAT(///)
      PUNCH 998
  998 FORMAT(32H  SIEK WASSENAAR****************////)
      READ, KLOP
      KK5=0
  100 CONTINUE
      KK5=KK5+1
      READ,KKK
      K=0
   35 CONTINUE
      K=K+1
      READ,YY55    ,FNORMB,CESTOR,ALIQ,FMSTOR,VAR
      J=0
    3 CONTINUE
      J=J+1
        READ,A(J),B(J)
      X(J)=B(J)*60.
      IF(A(J)) 2,2,3
    2 N=J-1
      FN=N
      TEMP(K)=YY55
      TT(K)=YY55+273.
      DO 4  J=1,N
      Y(J)=(A(J)/1000.)*FNORMB
      IF(VAR) 5,5,6
    5 DIFF1(J)=Y(J)-(ALIQ/1000.)*CESTOR
       DIFF2(J)=(ALIQ/1000.*CESTOR-DIFF1(J))
      GO TO 7
    6 DIFF1(J)=Y(J)-FMSTOR
      DIFF2(J)=FMSTOR-DIFF1(J)
    7 CONTINUE
    4 Y(J)=LOGF(DIFF2(J))
      AVGY=0.0
      AVGX=0.0
      DO 8  J=1,N
      AVGY=AVGY+Y(J)/FN
    8 AVGX=AVGX+X(J)/FN
      VAR1=0.0
      VAR2=0.0
      DO 9  J=1,N
      VAR1=VAR1+X(J)*Y(J)
    9 VAR2=VAR2+ X(J)*X(J)
      SLOPE1=(VAR1-FN*AVGX*AVGY)/(VAR2-FN*AVGX**2)
       YINTER=AVGY-SLOPE1*AVGX
      RR(K)=-SLOPE1
      F11=0.0
      F12=0.0
      F13=0.0
```

```
      F14=0.0
      F15=0.0
      F16=0.0
      F17=0.0
      DO 786 J=1,N
      F11=F11+FN*X(J)*Y(J)
       F12=F12+X(J)
      F13=F13+Y(J)
      F14=F14+X(J)*X(J)
      F15=F15+Y(J)*Y(J)
      F16=F16+(Y(J)-AVGY)*(Y(J)-AVGY)/(FN-1.)
      F17=F17+(X(J)-AVGX)*(X(J)-AVGX)/(FN-1.)
 786  CONTINUE
       RSQN=(F11-F12*F13)*(F11-F12*F13)
      RSQD=(FN*F14-F12*F12)*(FN*F15-F13*F13)
      RSQ=RSQN/RSQD
      SIG2=((FN-1.)/(FN-2.))*F16*(1.-RSQ)
      SIGRT=SIG2/((FN-1.)*F17)
        SIGRT=ABSF(SIGRT)
      SIGRT=SQRTF(SIGRT)
      RRR(K)=SIGRT
      IF(SENSE SWITCH 1) 528,829
 528  CONTINUE
      FMAX=Y(1)
       DO 109 J=2,N
      SS=Y(J)-FMAX
      IF(SS) 10,10,12
  10  FMAX=FMAX
      GO TO 109
  12  FMAX=Y(J)
 109  CONTINUE
      IF(YINTER-FMAX) 300,302,302
 300  FMAX=FMAX
      GO TO 309
 302  FMAX=YINTER
 309  CONTINUE
      FMIN=Y(1)
      DO 409 J=2,N
      SS=FMIN-Y(J)
       IF(SS) 400,400,402
 400  FMIN=FMIN
       GO TO 409
 402  FMIN=Y(J)
 409  CONTINUE
       YEXTER=SLOPE1*(X(N)+300.)+YINTER
      IF(FMIN-YEXTER) 500,500,502
 500  FMIN=FMIN
      GO TO 509
 502  FMIN=YEXTER
 509  CONTINUE
      FSEP=FMAX-FMIN
      FSEP=(1./18.)*FSEP
      YMAX=FMAX+FSEP
      YMIN=FMIN-FSEP
      XMAX=X(N)+300.
      XMIN=0.0
      XD=XMAX
      YD=YMAX-YMIN
      YL=9.0
      XL=11.0
      IF(K+KK5-3)  767,768,768
```

```
  767 CONTINUE
      TYPE 841
  841 FORMAT(35HTHERE IS GRAPH OUTPUT AT THIS STAGE)
      TYPE 842
  842 FORMAT(25HPLEASE SET UP THE PLOTTER)
      PAUSE
  768 CONTINUE
      CALL PLOT(101,XMIN,XMAX,XL,XD,YMIN,YMAX,YL,YD)
      CALL PLOT(99)
      BB=YINTER
      XX=-300.0
   13 CONTINUE
      XX=XX+300.0
      YY=SLOPE1*XX+BB
      CALL PLOT(0,XX,YY)
      IF(XX-XMAX) 13,14,14
   14 CONTINUE
      CALL PLOT(99)
      DIMX=(XMAX-XMIN)/88.
      DIMY=(YMAX-YMIN)/88.
      DO 15 J=1,N
      RHO1=X(J)-DIMX
      RHO2=Y(J)
      CALL PLOT(90,RHO1,RHO2)
      RHO1=RHO1+2.*DIMX
      CALL PLOT(90,RHO1,RHO2)
      CALL PLOT(99)
      RHO1=X(J)
      RHO2=Y(J)-DIMY
      CALL PLOT(90,RHO1,RHO2)
      RHO2=RHO2+2.*DIMY
      CALL PLOT(90,RHO1,RHO2)
   15 CALL PLOT(99)
      OROX=0.4*(XMAX-XMIN)
      OROY=0.8*(YMAX-YMIN)
      CALL PLOT(90,OROX,OROY)
      CALL CHAR(2,0.1,0,K,KK5)
   16 FORMAT(11HRUN NUMBER ,I4,2X,4HSEQ ,I4)
      CALL PLOT(7)
  829 CONTINUE
      PUNCH 17,K,KK5
   17 FORMAT(35X,11HRUN NUMBER ,I4,2X,4HSEQ ,I4/)
      PUNCH 18
   18 FORMAT(2X,8HTIME MIN,5X11HNO.MLS BASE,5X14HMOL. EST. LEFT/)
      J=0
  199 CONTINUE
      J=J+1
      PUNCH 19,B(J),A(J),DIFF2(J)
   19 FORMAT(2X,F8.3,5X,F10.6,5X,E12.6)
       IF(J-N) 199,119,119
  119 CONTINUE
      PUNCH 20,TEMP(K),FNORMB
   20 FORMAT(/6HTEMP =,F6.1,1X,4HCENT,5X,16HNORMALITY BASE =,F9.6,
     11X,12HEQUIVS/LITRE/)
      IF(VAR) 21,21,22
   21 PUNCH 24,CESTOR,ALIQ
   24 FORMAT(12HESTER CONC =,F8.4,1X,12HEQUIVS/LITRE,2X,
     115HALIQUOTS USED =,F5.2,1X,4HMLS.)
      PUNCH 25
   25 FORMAT(7HAQUEOUS/)
      GO TO 30
```

```
  22 PUNCH 26, FMSTOR
  26 FORMAT(21HNO MOLES ESTER USED =,F10.8)
     PUNCH 27
  27 FORMAT(5HSOLID/)
  30 CONTINUE
     SRATE(K)=RR(K)*100000.
     SSIGRT(K)=RRR(K)*100000.
      PUNCH 31,SRATE(K)
  31 FORMAT(15HRATE CONSTANT =, F10.4,1X,1HX,1X,6H10**-5, 5HSEC-1/)
     PUNCH 32,SSIGRT(K)
  32 FORMAT(22HSTANDARD DEV OF RATE =,F10.6,1X,1HX,6H10**-5,5HSEC-1/)
     PUNCH 33
  33 FORMAT(///)
     IF(K-KKK) 35,36,36
  36 CONTINUE
     R=1.9872
     FKKK=KKK
     VAR2=0.0
      VAR3=0.0
     VAR4=0.0
     VAR5=0.0
       DO 549 K=1,KKK
     QX=1./(R*TT(K))
     QY=LOGF(RR(K))
     QXY=(1./(R*TT(K)))*LOGF(RR(K))
      QXX=(1./(R*TT(K)))**2
     VAR2=VAR2+QX
     VAR3=VAR3+QY
     VAR4=VAR4+QX**2
 549 VAR5=VAR5+QXY
     SLOPE=(FKKK*VAR5-VAR2*VAR3)/(FKKK*VAR4-VAR2**2)
     YINTER=(VAR2*VAR5-VAR3*VAR4)/(VAR2**2-FKKK*VAR4)
     ARRH=EXPF(YINTER)
     PUNCH 601,ARRH
 601 FORMAT(15HINTERCEPT ARRH=,E12.5)
     BNIP=SLOPE
     SLOPE=-SLOPE/1000.
     DELT=0.1
     SIGRT=0.0
     SDI2=0.
     DO 330 K=1,KKK
     CALC=YINTER+BNIP/(R*TT(K))
 330 SDI2=SDI2+(LOGF(RR(K))-CALC)**2
     RE=0.6745*SQRTF(SDI2/(FKKK-2.))
     DE=FKKK*VAR4-(VAR2)**2
     DYINT=RE*SQRTF(VAR4/DE)
     SIGRT=RE*SQRTF(FKKK/DE)
     DYINT=ABSF(DYINT)
     SIGRT=ABSF(SIGRT)
     BOLTZ=1.38*1.E-16
      BTZ=1./BOLTZ
     PLANK=6.62*1.E-27
     PUNCH 90,KK5
  90 FORMAT(20X,8HSEQUENCE,I3/)
     PUNCH 51,SLOPE
  51 FORMAT(12HENERGY ACT =,F10.4,1X,11HKCALS /MOLE/)
     PUNCH 52,SIGRT
  52 FORMAT(27HPROBABLE ERROR ENERGY ACT.=,E12.4,1X,10HCALS /MOLE/)
     DO 331 K=1,KKK
      ENTROP=R*LOGF(1/2.71828*PLANK*BTZ/TT(K))+R*YINTER
     PUNCH 53,K,ENTROP
```

```
  331 CONTINUE
   53 FORMAT(17HENTROPY OF ACT.T(,I1,2H)=,F10.5,1X,13HCALS/MOLE/DEG/)
      ERRENT=R*ABSF(DYINT)
      PUNCH 54,ERRENT
   54 FORMAT(25HPROBABLE ERROR IN ENTROP=,E12.4,1X,14HCALS/MOLE/DEG.)
      IF(KK5-KLOP) 100,101,101
  101 CONTINUE
      PUNCH 539
  539 FORMAT(///)
      PUNCH 894
  894 FORMAT(32HEND OF OUTPUT FOR SIEK WASSENAAR//)
      DO 895 J=1,3
      PUNCH 896
  896 FORMAT(50H**************************************************)
  895 CONTINUE
      PUNCH 897
  897 FORMAT(/////)
      CALL EXIT
      END
*     EOJ
ZZXEQ RUN
    4
   4
  125.7  0.01425  0.0  0.0  0.00008888  1.0
  6.237  0.0
  6.637  1.5
  7.108  3.0
  0.0  0.0
  131.5  0.01632  0.0  0.0  0.00007018  1.0
  4.300  0.0
  4.538  1.0
ZZZZ
```

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