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ESTER PYROLYSIS STUDY OF SOME STERICALLY HINDERED ALCOHOLS

BY

RAPHAEL MARTIN OTTENBRITE

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

1966

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## ABSTRACT

An isotope study of the thermal decomposition of the hydrogen phthalate ester of trans-1,2-dimethylcyclohexanol in which  $O^{18}$  was incorporated into the carbonyl function of the ester was carried out. The presence of  $O^{18}$  in the alcohol portion of the undecomposed ester supports an earlier postulate that an ion pair is involved in the thermal decomposition of this sterically hindered ester. The hydrogen phthalate ester of 2-methyl-1-phenylcyclohexanol was prepared. Although the stereochemistry of the alcohol was not proved it is believed that the phenyl and methyl groups bear a trans relationship to each other by virtue of the method of preparation which was analogous to that used to prepare trans-1,2-dimethylcyclohexanol. The pyrolysis of the 2-methyl-1-phenylcyclohexyl hydrogen phthalate ester yielded 1-phenyl-2-methylcyclohexene (8%) and 2-phenyl-3-methylcyclohexene (92%). The appearance of only 8% of the former isomer supports an earlier postulate that a "cis effect" is operative in the thermal decomposition of 1,2-disubstituted cyclohexyl hydrogen phthalate esters.

Evidence of carbonium ion character in the transition state of the decomposition of the S-methyl xanthate ester of trans-1,2-dimethylcyclohexanol is strongly supported by the appearance of 1,2-dimethylcyclohexene (17%) on pyrolysis.

The S-methyl xanthate esters of 1-methylcyclopentanol, 1-methylcycloheptanol and tert-amyl alcohol were also prepared, subjected to thermal decomposition and the olefinic products determined. The potassium xanthate salts of the above alcohols as well as 1-methylcyclohexanol, 1-ethylcyclohexanol, 1-isopropylcyclohexanol and dimethylcyclohexylcarbinol were prepared and thermally decomposed. Comparisons, where possible, of the yields of the olefins obtained with this technique indicated a decided improvement as regards synthetic value over the classical Chugaev reaction.

## ACKNOWLEDGEMENTS

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## CHAPTER I

### INTRODUCTION

Thermal decomposition reactions have been employed by organic chemists for many years for the production of unsaturated compounds.<sup>1</sup> These reactions encompass, for the greater part, the pyrolysis of carboxylic acid esters (usually acetates), xanthate esters, and amine oxides although vinyl ethers and amine oxides have been the subject of limited study.

The literature is voluminous as regards studies both from the standpoint of yields and direction of elimination of the pyrolysis of acetate esters, xanthate esters and amine oxides. In the few systems where direct comparisons have been reported, acetate and xanthate esters furnish on pyrolysis, olefinic mixtures nearly identical in composition.<sup>2,3</sup> This might seem surprising since the decomposition reactions proceed at much lower temperatures for the xanthate esters (ca. 200°) than for the acetate

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1 C.H. DePuy and R.W. King, Chem. Revs., 60, 431 (1960). An excellent review of the literature can be found in this article.

2 C.H. DePuy, C.A. Bishop, and C.N. Goeders, J. Am. Chem. Soc., 83, 2151 (1961).

3 C.H. DePuy and R.W. King, loc. cit.

esters (ca. 500°).

In general, olefin-producing reactions can be classified into two types; one which yields predominantly the most alkylated isomer (Saytzeff product) and the other which yields predominantly the least alkylated isomer (Hofmann product). Primary alcohol esters (acetate, xanthate, etc.) have been pyrolyzed and found by several workers in the field to yield exclusively the Hofmann product while esters of secondary and tertiary alcohols yield a mixture of Hofmann and Saytzeff products. DePuy and King<sup>4</sup> consider three factors as being important in determining the ratios of Saytzeff product to Hofmann product obtained in the pyrolysis of aliphatic esters. These factors include: steric effects, statistical effects and thermodynamic considerations.

Statistically the elimination should occur in the direction in which there is a greater number of hydrogen atoms. That is, the hydrogen atom which is abstracted during the pyrolysis should be abstracted preferentially from adjacent CH<sub>3</sub>, CH<sub>2</sub>, and CH groups in the ratio of 3:2:1. This effect leads to the production of the least alkylated olefin as the predominating isomer according to the Hofmann rule. The high temperature pyrolysis of sec-

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<sup>4</sup> C.H. DePuy and R.W. King, loc. cit.

butyl acetate exemplifies this quite well. The formation of 1-butene is favoured statistically over 2-butene by a factor of 3:2. This is in good agreement with the experimental data obtained (57% 1-butene and 43% 2-butene). Similar agreement between statistical and experimental results was obtained in the pyrolysis of tert-amyl acetate.<sup>5</sup>

Steric effects appear to govern the proportion of the cis- and trans-2-butene obtained in the pyrolysis of sec-butyl acetate. Statistically the isomers should be obtained in equal amounts. However, the trans olefin predominates over the cis isomer by a factor of 2:1. DePuy and coworkers<sup>6</sup> suggest that the methyl-methyl repulsion in the transition state of elimination leads to the formation of the trans isomer. Therefore, as a general rule, steric effects will favour the formation of primary (exo) and trans olefins and hinder the formation of internal (endo) and cis olefins.

Thermodynamic considerations should favour the formation of the more stable olefinic isomer in thermal decomposition reactions. Voge and May<sup>7</sup> reported that the butenes,

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<sup>5</sup> W.J. Bailey and W.F.Hale, J. Am. Chem. Soc., 81, 647 (1959).

<sup>6</sup> D.H. Froemsdorf, C.H. Collins, G.S. Hammond, and C.H. DePuy, J. Am. Chem. Soc., 81, 643 (1959).

<sup>7</sup> H.H.Voge and N.C. May, J. Am. Chem. Soc., 68, 550 (1946).

in equilibrium at 500°, exist in the ratio of 28% 1-butene, 41% trans-2-butene, and 31% cis-2-butene. It has been suggested by Rutherford<sup>8</sup> that the contact time in the vapour-phase pyrolysis is usually so small that thermodynamic effects should be insignificant. In low temperature pyrolysis in which the contact time is in the order of only a few seconds, the thermodynamic effects should also be negligible.

#### Thermal Decomposition Studies of Acetate Esters

The most extensively studied olefin-producing thermal decomposition reaction involves the pyrolysis of acetate esters. Generally, the acetate esters are decomposed by adding the ester dropwise through a glass tube packed with glass beads and preheated to the desired cracking temperature, usually from 300-600°. The products obtained are olefin(s) and acetic acid. The acetic acid does not cause rearrangement of the double bond even at high temperatures. The main advantage of acetates as precursors to the desired alkene lies in the ease of separation of the acetic acid from the olefinic products.

On the bases of stereochemistry, Hurd and Blunck<sup>9</sup> proposed a cyclic, concerted mechanism for the pyrolytic

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<sup>8</sup> K.G. Rutherford and D.P.C. Fung, Can. J. Chem., **42**, 2657 (1964).

<sup>9</sup> C.D. Hurd and F.H. Blunck, J. Am. Chem. Soc., **60**, 2419 (1939).

decomposition of acetate esters. These authors observed that ethylene and phenylacetic acid were the only products obtained on pyrolysis of ethyl phenylacetate at 435°. The proposed mechanism involves a six-membered transition state represented by structure II in Fig. 1.

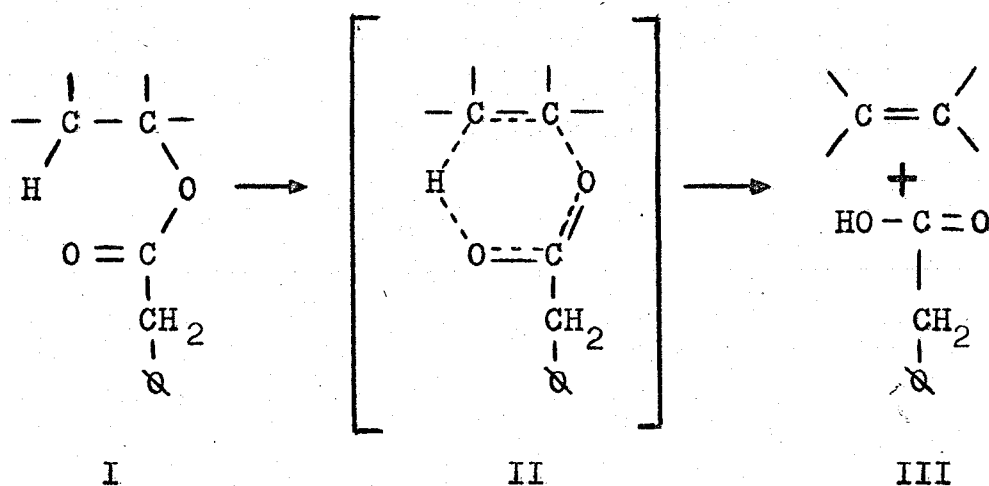


Fig. 1. - Concerted Mechanism Proposed for Acetate Pyrolysis.

This mechanism has been accepted, since it demonstrates that the reaction is homogeneous and unimolecular,<sup>10</sup> and that it preferably proceeds via removal of a cis-β-hydrogen atom.<sup>11</sup> The facts that the activation entropy is negative<sup>12</sup> and that β-deuterated acetates show an isotope

<sup>10</sup> A.T. Blades, Can. J. Chem., 31, 418 (1953).

<sup>11</sup> C.D. Hurd and F.H. Blunck, loc. cit.

<sup>12</sup> D.Y. Curtin and D.B. Kellom, J. Am. Chem. Soc., 75, 6011 (1953).



effect<sup>13</sup> also concur with this mechanism.

Several examples of the apparent cis nature of the acetate ester pyrolysis elimination reaction have been reported in the literature.<sup>14</sup> The most elegant demonstration has been provided by Curtin and Kellom.<sup>15</sup> These authors prepared threo- and erythro-2-deutero-1,2-diphenylethanol by the reduction with lithium aluminium deuteride of cis- and trans-stilbene oxide, respectively. The pyrolysis of the acetate ester of both of these alcohols yielded trans-stilbene (Fig. 2).

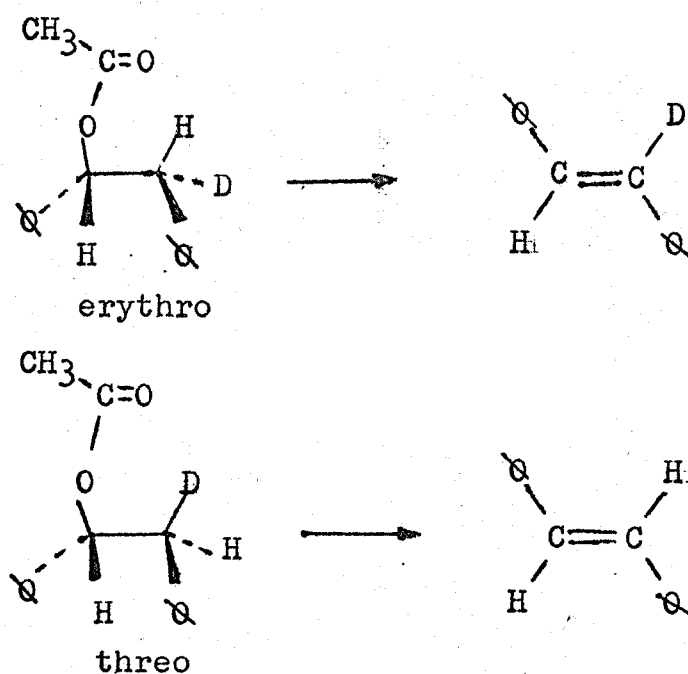


Fig. 2. - Pyrolysis of the Acetate Esters of threo- and erythro-2-Deutero-1,2-diphenylethanol.

13 A.T. Blades, Can. J. Chem., 32, 366 (1954).

14 C.H. DePuy and R.W. King, loc. cit.

15 D.Y. Curtin and D.B. Kellom, loc. cit.

The stilbene obtained from the erythro compound retained all of its deuterium and that obtained from the threo isomer lost most of its deuterium. These results are consistent with the cis-elimination of a  $\beta$ -hydrogen and the acetoxy group.

Sixma and coworkers,<sup>16</sup> however, contend that the cyclic homolytic elimination mechanism for the acetate pyrolysis does not provide a satisfactory explanation for several observations. A significant fact involves the influence of the acid residue which increases the reaction rate, but does not affect the composition of the olefin produced. Nor can the small effects which alkyl substituents on the B-carbon atom exert on the reaction rate be accounted for by means of the concerted mechanism; electron-releasing groups increase the rate whereas electron-attracting groups decrease it.

Sixma maintains that the normal acetate pyrolytic elimination reaction occurs via an ionic mechanism similar to that proposed by Maccoll<sup>17</sup> (Fig.3). In this mechanism the C - O bond is broken heterolytically, forming an ion pair in the transition state. Although a heterolytic

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<sup>16</sup> J.C. Scheer, E.C. Kooyman, and F.L.J. Sixma, Rec. Trav. Chim., 85, 1123 (1963).

<sup>17</sup> A. Maccoll in "Theoretical Organic Chemistry", (Kekule symposium London 1958), Butterworths Sc. Publ. London, 1959, p. 29.

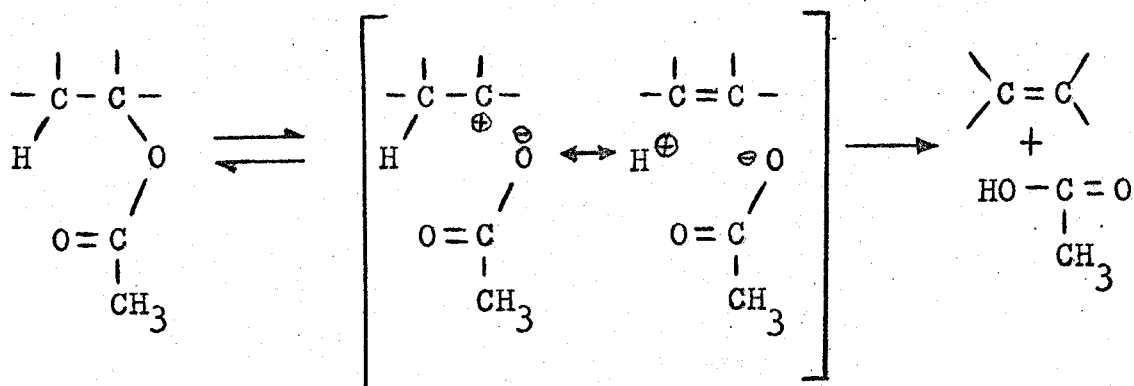


Fig. 3. - Proposed Ionic Mechanism for Acetate Pyrolysis

cleavage in vacuo requires more energy than a homolytic fission, heterolytic formation of an ion pair is not theoretically improbable, since Coulombic energy can be gained back. If the distance between the ions is of the order of  $2 \text{ \AA}$ , the Coulombic energy can amount to 170 kcal/mole.

Sixma contends that an electron-donating group on the  $\beta$ -carbon atom would facilitate the formation of an ion pair by an inductive effect and would thus increase the rate of decomposition. On the other hand an electron-withdrawing group on the  $\beta$ -carbon atom would withdraw some of the negative charge from the  $\alpha$ -carbon atom and hence counteract the formation of an ion pair and so reduce the rate of reaction. These effects can not be explained by a concerted mechanism.

The objections raised by DePuy<sup>18-19</sup> against an ionic mechanism are based on the premise that such a mechanism would be of an E<sub>1</sub> type. This would mean that the breaking of the C-H bond must be preceded by a heterolytic fission of the C-O bond. If such were the case, the fission would be rate-determining and the isotope effect observed could not be accounted for. Sixma<sup>20</sup> counters that the isotope effect is not necessarily in conflict with the heterolytic fission to an ion pair, since if the reversal of the ion pair to the initial state proceeded faster than the transition to olefin and acetic acid, then a larger isotope effect is possible.

#### Thermal Decomposition Studies of Xanthate Esters

The Chugaev<sup>21</sup> reaction is another pyrolytic, olefin-producing reaction which has been widely used for the formation of olefins. This reaction involves the thermal decomposition of xanthate esters of corresponding alcohols.

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18 C.H. DePuy and R.E. Leary, J. Am. Chem. Soc., **79**, 2705 (1959).

19 C.H. DePuy, R.W. King, and D.H. Froemsdorf, Tetrahedron **7**, 123 (1959).

20 J.C. Scheer, E.C. Kooyman, and F.L.J. Sixma, loc. cit.

21 L. Chugaev, Ber. **32**, 3332 (1899).

The products obtained on pyrolysis of these xanthate esters are: olefin(s), carbon oxysulphide and mercaptan (Fig. 4). This reaction, which is analogous to the pyrolytic decomposition of acetate esters, appears to proceed by the preferential removal of a hydrogen atom from an adjacent carbon atom as well. The olefinic products are found to be formed free from rearrangement products.<sup>22</sup> The most commonly used xanthate ester is the S-methyl derivative ( $-O-\overset{\text{S}}{\text{C}}-\text{SCH}_3$ ), to which the term xanthate ester will hereafter refer.

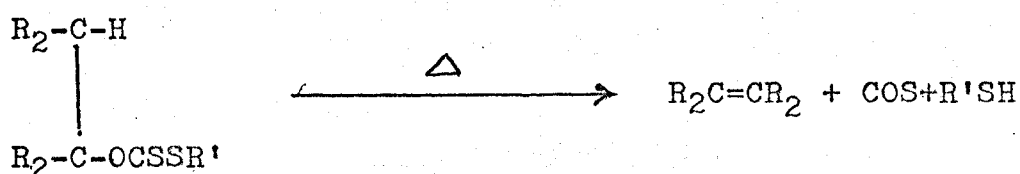


Fig. 4. - Decomposition Products on Pyrolysis of Xanthate Ester.

The direction of elimination in the Chugaev reaction has not been as extensively studied as the acetate ester pyrolysis. Although normal xanthates have been proposed to undergo elimination via the same type of cyclic transition as their acetate counterparts, higher temperatures (300-600°) are required for the acetate pyrolysis while most xanthates decompose below 200°. Since

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<sup>22</sup> H.R. Nace in "Organic Reactions:", Vol. XII, ed. A.C. Cope, John Wiley and Sons, Inc., New York, 1962, p. 58.

primary and secondary acetates are generally easier to prepare than the corresponding xanthates, acetate pyrolysis is preferred to xanthate pyrolysis. Nevertheless, the low temperature decomposition of xanthate esters has advantages with regards to avoiding rearrangements which could conceivably occur at the higher decomposition temperatures required for acetate pyrolysis. Again, it is interesting to note that despite the differences in reaction conditions and the atoms involved in the transition state the product distributions have been found to be nearly identical.

The predominant cis-character of xanthate pyrolysis was first indicated by the pyrolysis products of the isomeric decalyl xanthates reported by Hückel and coworkers.<sup>23</sup> Elimination occurred mainly toward the ring junction when a cis-β-hydrogen was available, and mainly away from the ring junction when no cis-hydrogen was available. (Fig. 5)

It has been generally conceded by many researchers that the reaction path involves a concerted intramolecular cyclic elimination of a cis-β-hydrogen, similar to that of the acetate mechanism proposed by Hurd,<sup>24</sup> as shown in Fig. 6.

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<sup>23</sup> W. Hückel, W. Tappe, and G. Legutke, Ann., 543, 191 (1940).

<sup>24</sup> C.D. Hurd and F.H. Blunck, J. Am. Chem. Soc., 60, 2419 (1939).

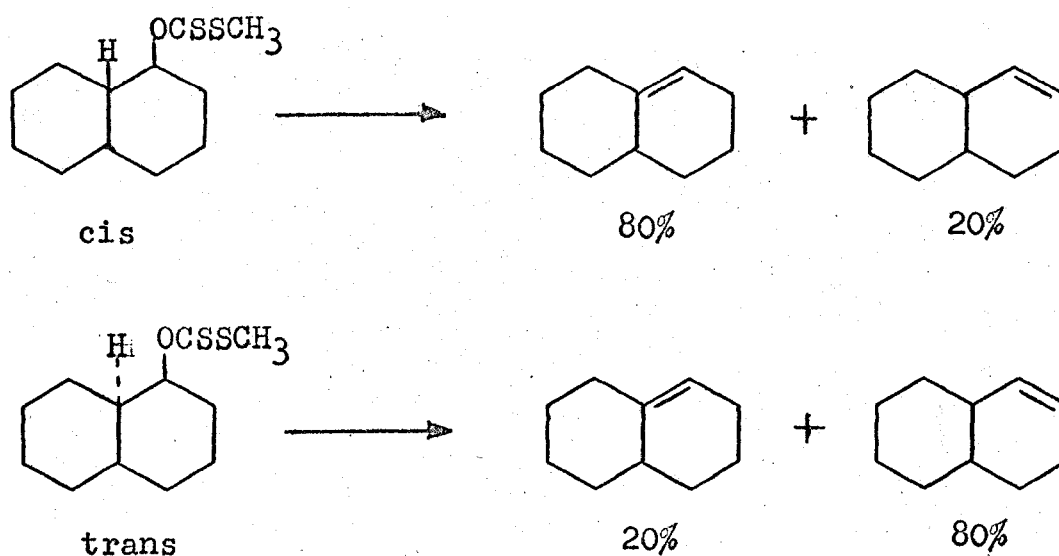


Fig. 5. - Predominant cis-Elimination of Isomeric Decalyl Xanthates.

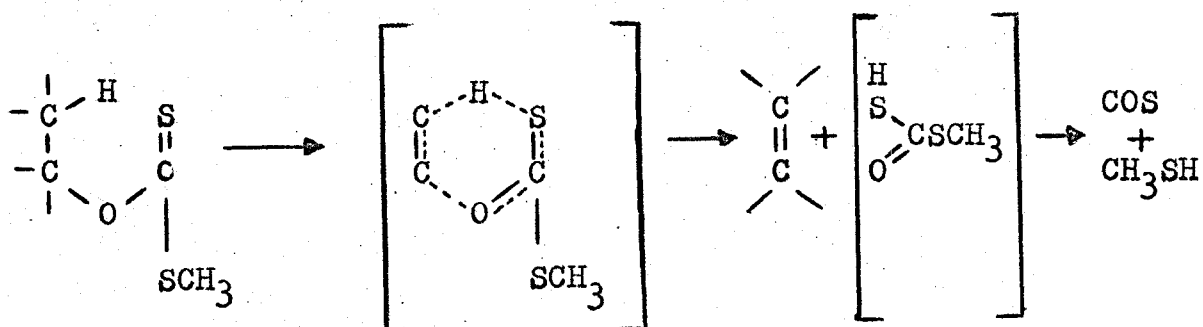


Fig. 6. - Cyclic Concerted Chugaev Elimination Mechanism.

This observation has been substantiated by the demonstration of first order kinetics for the decomposition reaction.<sup>2</sup>

<sup>2</sup> 25 G.L. O'Connor and H.R. Nace, J. Am. Chem. Soc., **74**, 5454 (1952); ibid **75**, 2118 (1953).

The stereochemistry was confirmed by Cram<sup>26</sup> by showing that threo- and erythro-3-phenyl xanthate esters decompose stereospecifically with the formation of cis- and trans-2-phenyl-2-butene, respectively (Fig. 7):

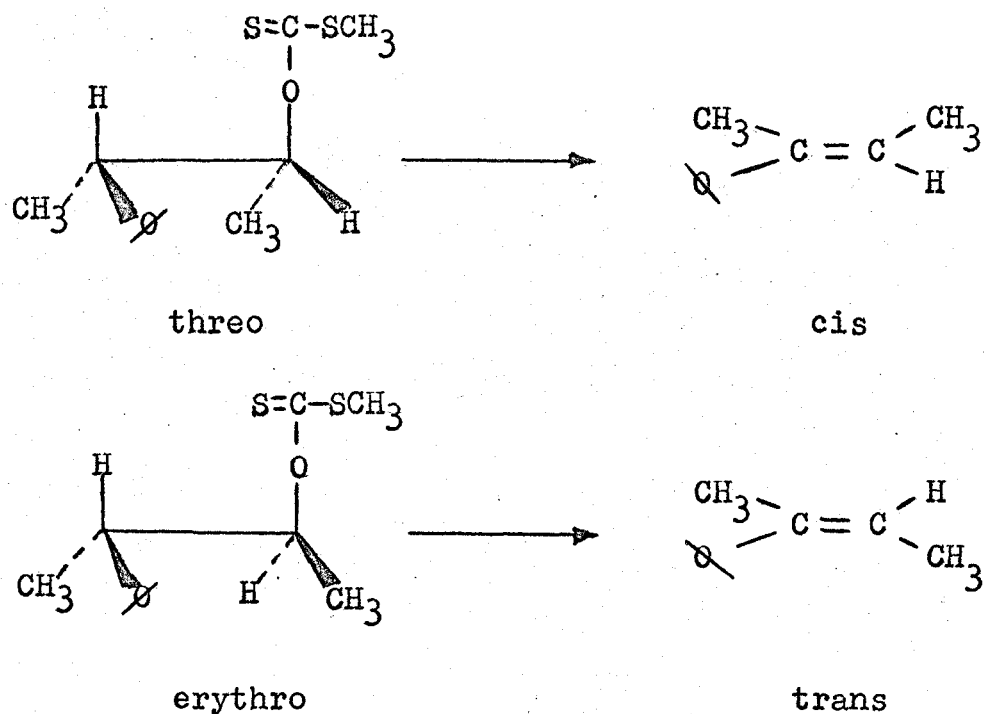


Fig. 7. - Decomposition of threo- and erythro-3-Phenyl Xanthates.

Evidence that the thion sulphur atom ( $-C=S$ ), rather than the thiol sulphur atom ( $-SCH_3$ ), attacked the  $\beta$ -hydrogen

26 D.J. Cram, J. Am. Chem. Soc., 71, 3883 (1949).



atom was obtained by Bader and Bourns.<sup>27</sup> These workers made a study of sulphur and carbon isotope effects for the pyrolysis of trans-2-methyl-1-indanyl xanthate of natural isotopic abundance. Predicted isotope effects for the thion sulphur, thiol sulphur and the carbon atom were obtained by the use of Bigeleisen equation. The observed isotope effect agreed with the predicted one for the abstraction of the hydrogen by the thion sulphur atom.

There is, however, evidence in the literature that the Chugaev reaction yields significant amounts of trans-elimination products. This indicates that either the reaction in certain cases is not mechanistically homogeneous or that the reaction path proceeds by another mechanism. Huckel's study of elimination reactions of cis- and trans-1-decalyl xanthate esters<sup>28</sup> indicated that the trans isomer yielded on pyrolysis 20% of the olefinic product with the double bond at the ring junction (Fig. 6). This isomer represents trans-elimination product. Again, Alexander and Mudrack<sup>29</sup> found that on pyrolysis of cis-1-hydroxy-2-methylindanyl xanthate ester that 20% of the 2-methylindene was obtained (Fig. 8):

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<sup>27</sup> R.F.W. Bader and A.N. Bourns, Can. J. Chem., **39**, 348 (1961).

<sup>28</sup> W. Huckel, W. Tappe, and G. Legutke, loc. cit.

<sup>29</sup> L.R. Alexander and A. Mudrack, J. Am. Chem. Soc., **73**, 59 (1951).

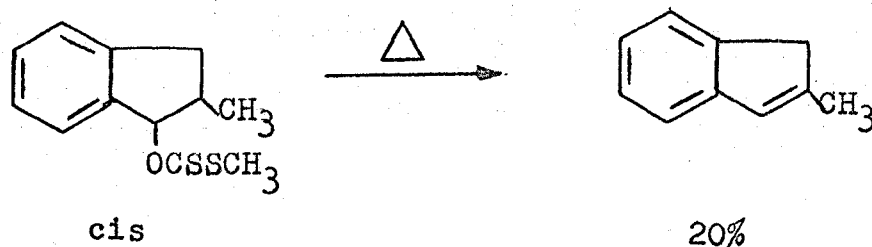


Fig. 8. - Pyrolysis of cis-1-Hydroxy-2-Methylindanyl Xanthate.

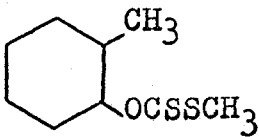
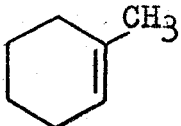
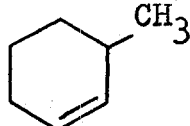
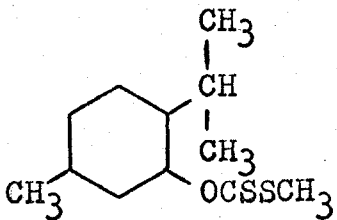
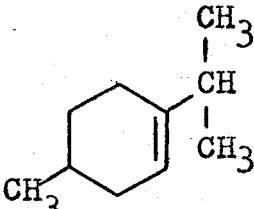
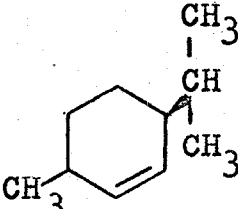
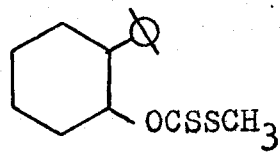
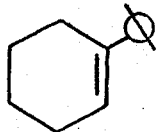
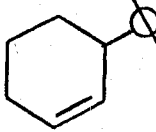
These observations would appear to indicate that a substantial amount of the elimination reaction is occurring in a trans manner. Other examples of this anomalous type of elimination for the Chugaev reaction are shown in Table I.

Bordwell and Landis<sup>30</sup> have demonstrated exclusive trans-elimination on pyrolysis of a xanthate ester by the incorporation of a hydrogen-acidifying agent in the  $\beta$ -position. These authors reported that cis-2-p-tolylsulfonylcyclohexyl xanthate (structure IV, Fig. 9) decomposed on heating to yield almost entirely 1-p-tolylsulfonylcyclohexene (V) rather than the predicted 3-p-tolylsulfonylcyclohexene isomer. The mechanism was interpreted as a stepwise trans-elimination which proceeds by initial ionization of the  $\beta$ -hydrogen atom, rendered more labile by the tosylate group on the same atom. These same authors

<sup>30</sup> F.G. Bordwell and P.S. Landis, J. Am. Chem. Soc., **80**, 2450 (1958).

TABLE I

Pyrolysis of Xanthates Showing trans-Elimination

Xanthate	Olefin Products	
 <p>cis</p>	 <p>49%</p>	 <p>51% (31)</p>
 <p>cis</p>	 <p>20%</p>	 <p>80% (32)</p>
 <p>cis</p>	 <p>0-7%</p>	 <p>100-93% (33)</p>

31 D.G. Botteron and G.P. Schulman, *J. Org. Chem.*, **27**, 2007 (1962).

32 W. Hüchel, W. Tappe, and G. Legutke, *Ann.*, **543**, 191 (1940).

33 E.R. Alexander and A. Mudrack, *J. Am. Chem. Soc.*, **72**, 1810 (1950).

reported that the pyrolysis of erythro-2-p-tolylsulfonyl-2-butyl xanthate ester gave cis-2-p-tolylsulfonyl-2-butene (the trans elimination product) in 38% yield. The effect of other labilizing groups on the B-hydrogen has not been investigated.

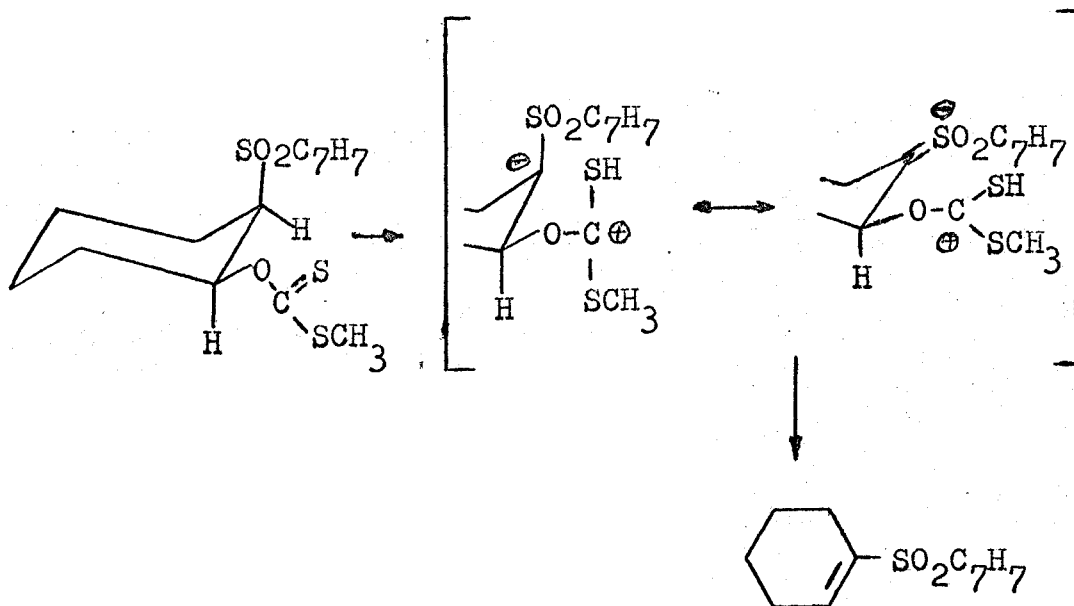


Fig. 9. - Pyrolysis of cis-2-p-Tolylsulfonylcyclohexyl Xanthate.

The Chugaev reaction then can be visualized as occurring by several routes. The above authors rule out intermolecular  $\text{E}_2$  type elimination in light of the first order kinetics observed. A concerted intramolecular trans-elimination has also been discredited as this would involve considerable strain in the transition state.

Thermal Decomposition Studies of Hydrogen Phthalate Esters

More recently, Rutherford and Fung<sup>34</sup> have reported olefin formation on the pyrolysis of tertiary phthalate esters. It had been reported previously by Botteron<sup>35,36</sup> that hydrogen phthalate esters of primary and secondary alcohols were found to decompose to yield phthalic anhydride and the corresponding alcohol. Conversely, Rutherford demonstrated that hydrogen phthalate esters of tertiary alcohols decompose at relatively low temperatures to yield olefin(s) and phthalic acid. The olefinic product distribution compared favourably in some cases with those attained by the pyrolysis of the corresponding acetate esters.

Of particular interest in this investigation were the products obtained on the pyrolysis of the phthalate ester of trans-1,2-dimethylcyclohexanol: 46% 2,3-dimethylcyclohexene, 35% 2-methylmethylenecyclohexane and 19% 1,2-dimethylcyclohexene. These are in contrast to the products obtained by DePuy<sup>37</sup> on the pyrolysis of the corresponding

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<sup>34</sup> K.G. Rutherford and D.P.C. Fung, Can. J. Chem., 42, 2657 (1964)..

<sup>35</sup> G.P. Shulman, J.H. Bennett, and D.G. Botteron, J. Org. Chem., 27, 3923 (1962)..

<sup>36</sup> D.G. Botteron and G.P. Shulman, J. Org. Chem., 27, 785 (1962).

<sup>37</sup> D.H. Froemsdorf, C.H. Collins, G.S. Hammond, and C.H. DePuy, J. Am. Chem. Soc., 81, 643 (1959)..

acetate at 450° which yielded 26% 2,3-dimethylcyclohexene and 46% 2-methylmethylenecyclohexane. None of the 1,2-dimethylcyclohexene isomer was observed.

Rutherford suggested that carbonium ion character was evident (at least in part) in the transition state during the pyrolysis of this hydrogen phthalate ester. It was proposed that the olefin formation involved initial ionization of the ester. The possible transition states for the 1,2-dimethylcyclohexyl carbonium ion are illustrated in Fig. 10. The amount of Saytzeff products obtained was believed to be controlled by steric effects as well as statistical considerations. The steric effect of the methyl-methyl repulsion in the transition state "A" would hinder the formation of 1,2-dimethylcyclohexene, the most stable isomer from hyperconjugation considerations. There is much less of this "cis effect" in the transition states "B" and "C".

It was reported<sup>38</sup> that on pyrolysis of the hydrogen phthalate esters of 1-methylcyclopentanol, 1-methylcyclohexanol, and 1-methylcycloheptanol that the amount of Hofmann product (exo isomer) increased markedly with increasing ring size (3%, 12%, and 28%, respectively). It was concluded that the larger ring size could favour an

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<sup>38</sup> K.G. Rutherford and D.C.P. Fung, Can. J. Chem., 42, 2657, (1964).

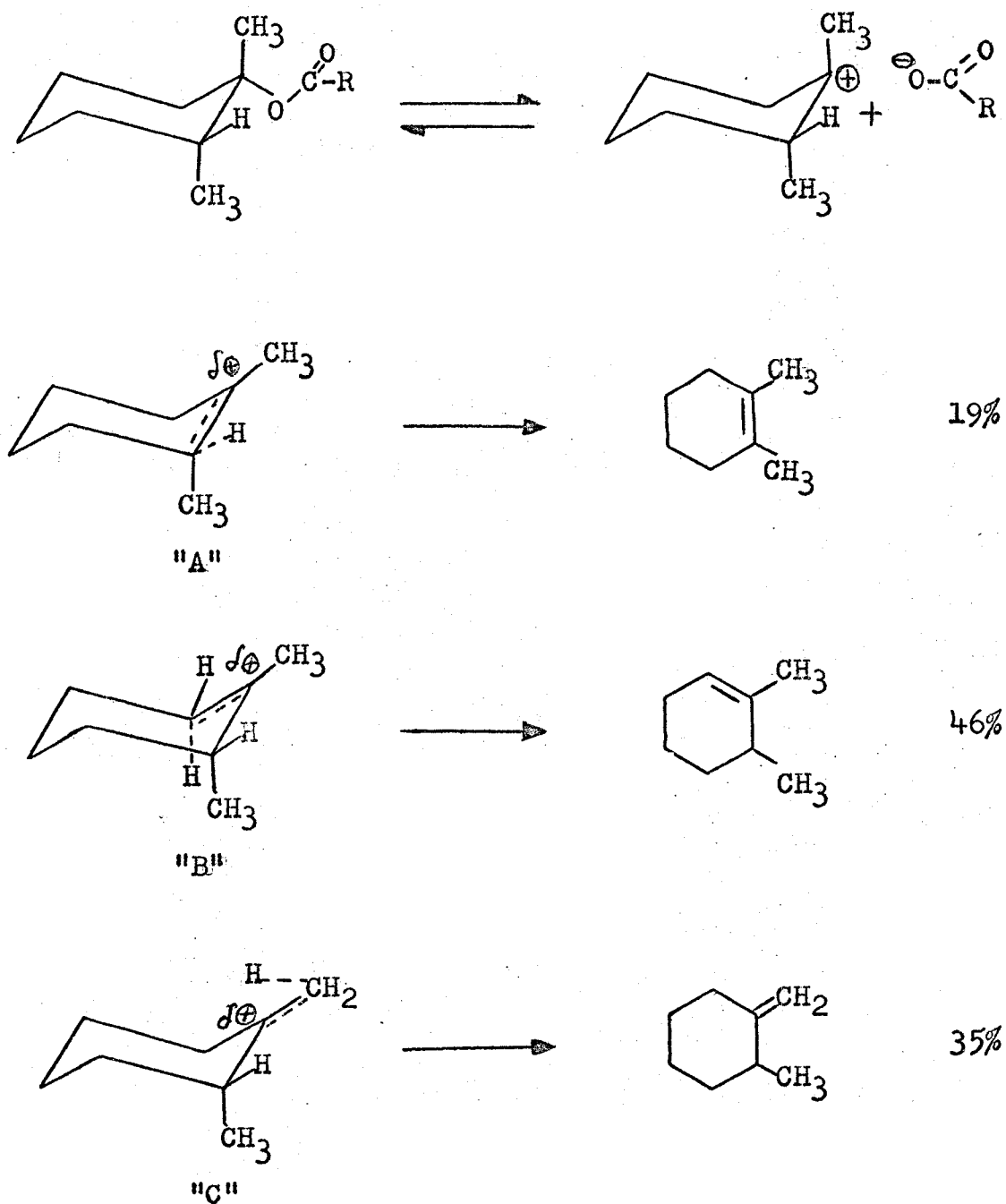


Fig. 10. - Possible Elimination Transition States for 1,2-Dimethylcyclohexyl Carbonium Ion.

ionic transition state as the ring bond angle can be expanded towards  $120^\circ$ ; thus the observed increase of Hofmann product with increasing ring size.

It was deemed of interest to investigate further the "cis effect" and to establish, if possible, more concrete evidence for the ionic character postulated in the thermal decomposition of sterically hindered hydrogen phthalate esters. It was also decided to investigate the pyrolysis of xanthate esters of sterically hindered alcohols to determine whether there is any evidence of ionic character in the transition state during the thermal decomposition as well.



## CHAPTER II

## RESULTS AND DISCUSSION

Thermal Decomposition Studies of Hydrogen Phthalate Esters

The further investigation of the "cis effect" and possible ionic character as postulated by Rutherford and Fung<sup>1</sup> in the decomposition of sterically hindered hydrogen phthalate esters involved the preparation and thermal decomposition of trans-2-methyl-1-phenylcyclohexyl hydrogen phthalate ester.

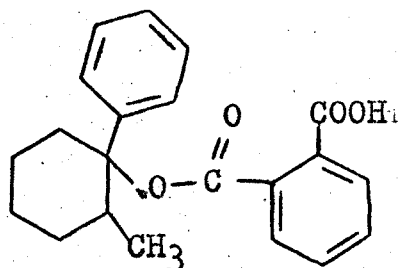


Fig. 11. - trans-2-Methyl-1-phenylcyclohexyl Hydrogen Phthalate.

The presence of the phenyl group in the 1-position should

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<sup>1</sup> K.G. Rutherford and D.P.C. Fung, Can. J. Chem., 42, 2657 (1964).

impart more stability to the ion pair relative to that of the methyl analogue in the decomposition of the 1,2-dimethylcyclohexyl hydrogen phthalate. This increased stability of the ion pair could lead to enrichment in Saytzeff product (1-phenyl-2-methylcyclohexene). At the same time, however, the phenyl group, which is bulkier than the methyl group, would enhance the steric effect in the transition state of the elimination. This would be expected to result in enrichment of the Hofmann product (2-phenyl-3-methylcyclohexene) due to the "bis effect". The possible transition states for the elimination reaction involving the 2-methyl-1-phenylcyclohexyl carbonium ion are illustrated in Fig. 12. The steric effect of the cis methyl and phenyl groups in transition state "A" would hinder the formation of 1-phenyl-2-methylcyclohexene. Relevant to this, the acid-catalyzed dehydration (an equilibrium process) of 2-methyl-1-phenylcyclohexanol has been shown to yield only 20% 1-phenyl-2-methylcyclohexene and 77% 2-phenyl-3-methylcyclohexene.<sup>2</sup>

The synthesis of trans-2-methyl-1-phenylcyclohexyl hydrogen phthalate was accomplished by treating 2-methylcyclohexanone with phenylmagnesium bromide. The alcohol was isolated by fractional distillation. It was found

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2 E.W. Garbisch Jr., J. Org. Chem., 27, 4243 (1962).

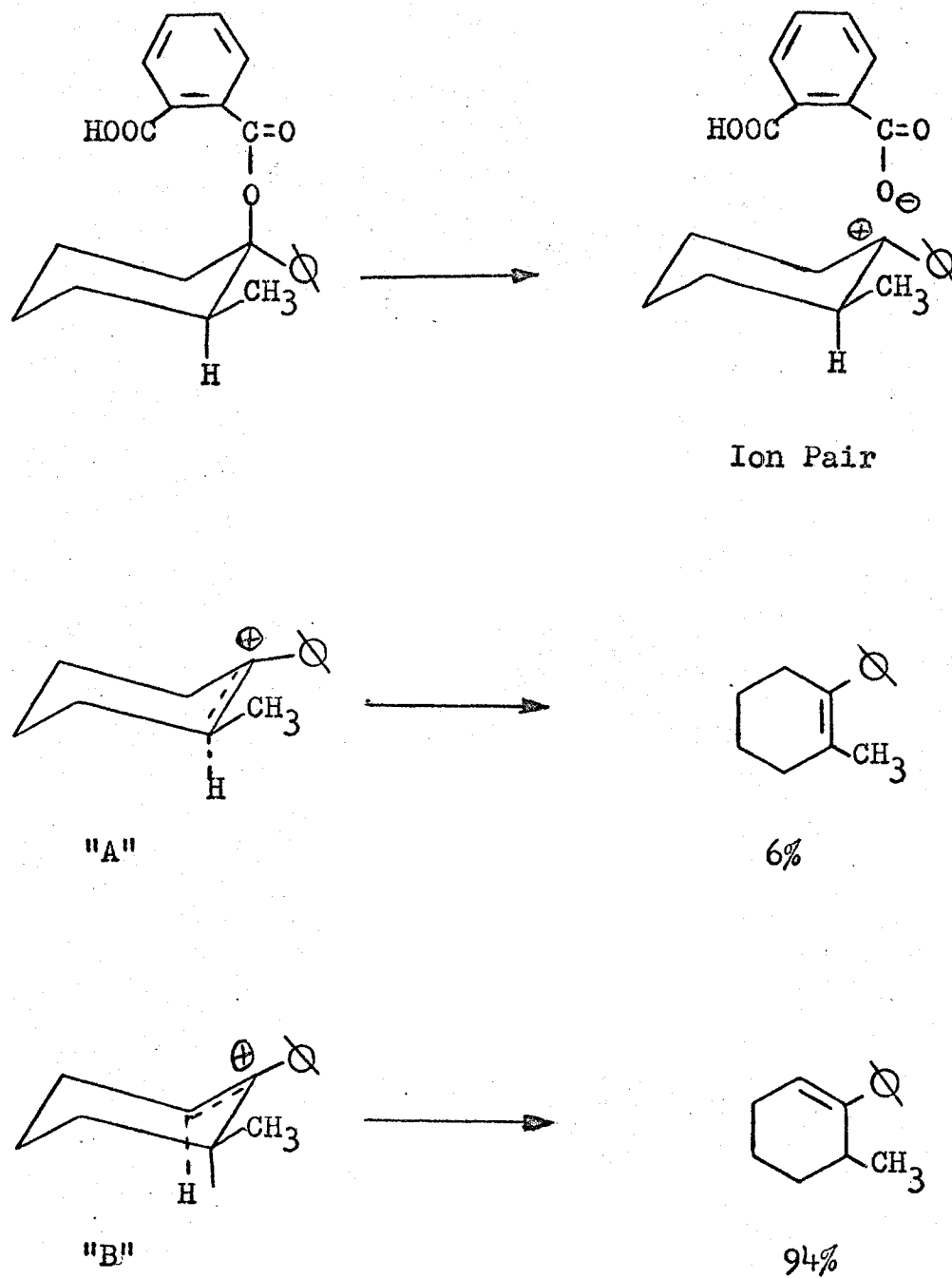


Fig. 12. - Possible Elimination Transition States For 2-Methyl-1-Phenylcyclohexyl Hydrogen Phthalat

that in the synthesis of 1,2-dimethylcyclohexanol, more than 95% of the alcohol obtained in this reaction was the trans isomer.<sup>3</sup> This was undoubtedly due to the steric effect of the equatorial methyl group of the 2-methylcyclohexanone which is in accordance with Cram's rule of "steric control of asymmetric induction". This steric effect should be greater in the case of the reaction with phenylmagnesium bromide; thus giving a greater proportion of the trans isomer.

The NMR spectrum was used in an attempt to establish the structure and the conformation of this alcohol. It has been reported in the literature<sup>4,5</sup> that the resonance peak due to the ring protons is fairly broad when 1,2-disubstituents are trans to each other and narrow when they are cis. This is apparently a result of interaction of the tertiary protons and the other ring protons. In the trans derivative the substituents exist predominantly in the diequatorial conformation and hence the tertiary ring protons are in the axial position and interact more strongly with the other ring protons. The cis compound has an axial and equatorial conformation; only one tertiary proton is in the axial position, and this causes less interaction and a narrower peak. The values for 2-methylcyclohexanol are: cis, 0.21 ppm and trans,

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<sup>3</sup> T.D. Nevitt and G.S. Hammond, J. Am. Chem. Soc., 76, 4124 (1954).

<sup>4</sup> S. Brownstein and R. Miller, J. Org. Chem., 24, 1886 (1959).

<sup>5</sup> R.U. Lemieux, R.K. Kullnig, H.J. Bernstein, and W.G. Schneider, J. Am. Chem. Soc., 80, 6098 (1958).

0.55 ppm measured at half peak height. The 2-methyl-1-phenylcyclohexanol has a half-width of 0.24 ppm for the ring proton which would indicate that the tertiary proton spends most of its time in the axial position.

Garbisch<sup>6</sup> has reported that the resonance peak of the hydroxyl proton of trans-4-tert-butyl-1-phenylcyclohexanol (I) is at  $\delta$  1.65 and for the cis isomer (II) at  $\delta$  1.91. The higher chemical shift for the hydroxyl proton of I as compared with that of II is due to slightly more hydrogen bonding than in I. The peak at  $\delta$  1.44 for the hydroxyl proton of 2-methyl-1-phenylcyclohexanol suggests that the hydroxyl group is in the axial position similar to that of structure I (Fig. 13).

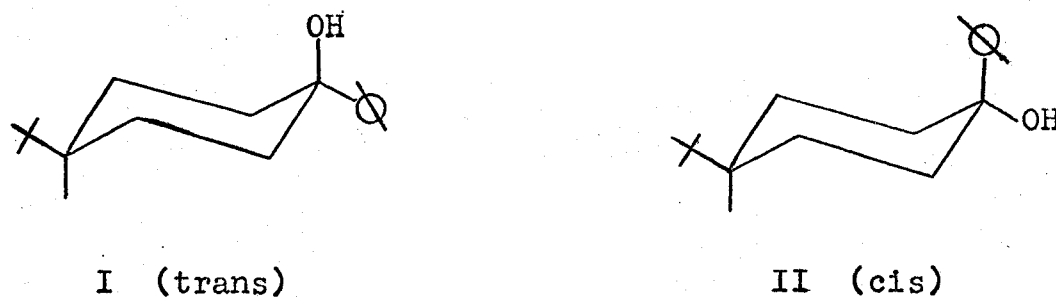


Fig. 13. - Isomer Conformations of 4-tert-Butyl-1-Phenylcyclohexanol.

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<sup>6</sup> E.W. Garbisch Jr. and D.B. Patterson, J. Am. Chem. Soc., 85, 3228 (1963).

This evidence suggests then that the tertiary proton and the hydroxyl group are trans (a,a) to each other; hence the methyl and the phenyl would also be trans (e,e) to each other. It must be noted that the above deductions from the NMR spectrum cannot be construed as elucidating the structure of the 2-methyl-1-phenylcyclohexanol as having the trans geometry without a direct comparison to the NMR spectrum of the other isomer (work in this area is presently being conducted in this laboratory). However by analogy with the reaction of methylmagnesium iodide with 2-methylcyclohexanone one would expect the phenylmagnesium Grignard reagent to react with the same ketone with similar stereochemical consequences and give predominantly the trans isomer. Furthermore the trans cyclohexanols are known to have lower boiling points than the cis isomers and so only the lower boiling fraction was isolated.

The trans-2-methyl-1-phenylcyclohexanol was treated with an ethereal solution of triphenylmethyl sodium whereupon the hydrogen phthalate ester was obtained (m.p. 150°) on addition of phthalic anhydride. The thermal decomposition of the ester was carried out in a micro-distillation apparatus at 155°. The olefinic product distribution, as determined by vapour phase chromatography, indicated the presence of 8% 1-phenyl-2-methylcyclohexene (Saytzeff product) and 92% 2-phenyl-3-methylcyclohexene (Hofmann

product).

Each olefin was identified by comparison with authentic samples obtained by acid-dehydration of the alcohol.<sup>7</sup> Any rearrangement of the olefinic mixture during pyrolysis is considered to be improbable since no observable change in product composition was found when the pyrolysate was heated with and redistilled from phthalic acid at 155°.

The decrease in Saytzeff product (8%) as compared with that obtained on decomposition of trans-1,2-dimethylcyclohexyl hydrogen phthalate (19%) is considered to be a manifestation of "cis effect" in the transition state of decomposition. Here again, the presence of 1-phenyl-2-methylcyclohexene would indicate ion formation prior to decomposition. Although the ion in this case would be expected to be more stable than the methyl-stabilized counterpart, the presence of adjacent phenyl and methyl groups in the transition state would provide a greater barrier to the formation of the Saytzeff product.

Experimental data has been presented that on pyrolyses of trans-1,2-dimethylcyclohexyl and trans-2-methyl-1-phenylcyclohexyl hydrogen phthalate esters, carbonium ion character seems apparent in the transition state of the decomposition. If this is fact then an internal ion pair could be involved in the decomposition reaction mechanism

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





Goering<sup>9</sup> who demonstrated ion pair phenomena in the solvolysis of trans- $\alpha, \gamma$ -dimethylallyl p-nitrobenzoate.

The relationship between the locations of the oxygen atoms when the ion pair returns to the ester is dependent upon the structure and the bonding in the intermediate IV. On one hand, the O<sup>16</sup> could return as the alkyl oxygen to give the original ester as illustrated in structure III. On the other hand, the O<sup>18</sup> (the carbonyl oxygen in the original compound) could become the oxygen in the alkyl ester position as illustrated in structure IV. If O<sup>18</sup> were incorporated in the alkyl oxygen position of the undecomposed hydrogen phthalate ester then, this should demonstrate that carbonium ion character is present in the thermal decomposition of these esters.

The isotope study involved the preparation of trans-1,2-dimethylcyclohexyl hydrogen phthalate with an excess of O<sup>18</sup> incorporated in the ester carbonyl position. Phthalic acid with approximately 5 atom % excess of O<sup>18</sup> present in each oxygen position was prepared from commercial phthalic anhydride and water with 20 atom % O<sup>18</sup> enrichment. The resultant phthalic acid was dehydrated to obtain the phthalic anhydride-O<sup>18</sup>. The trans-1,2-dimethylcyclohexyl hydrogen phthalate with 5 atom % O<sup>18</sup> in the carbonyl

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<sup>9</sup> H.L. Goering and M.M. Pombo, J. Am. Chem. Soc., **82**, 2515 (1960).

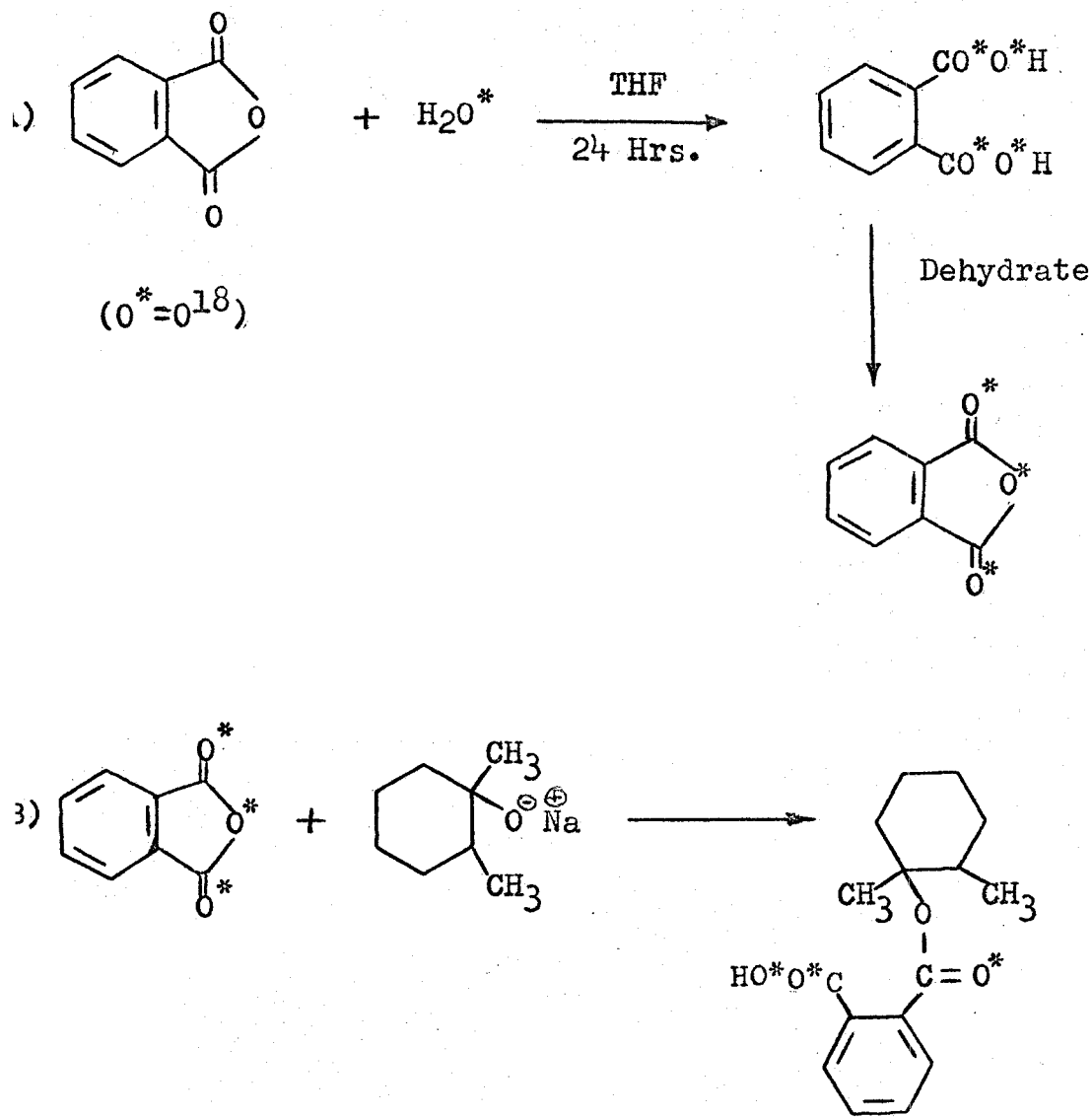


Fig. 15. - Reactions Involved in Preparing trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate with  $O^{18}$  in the Ester Carbonyl Position.

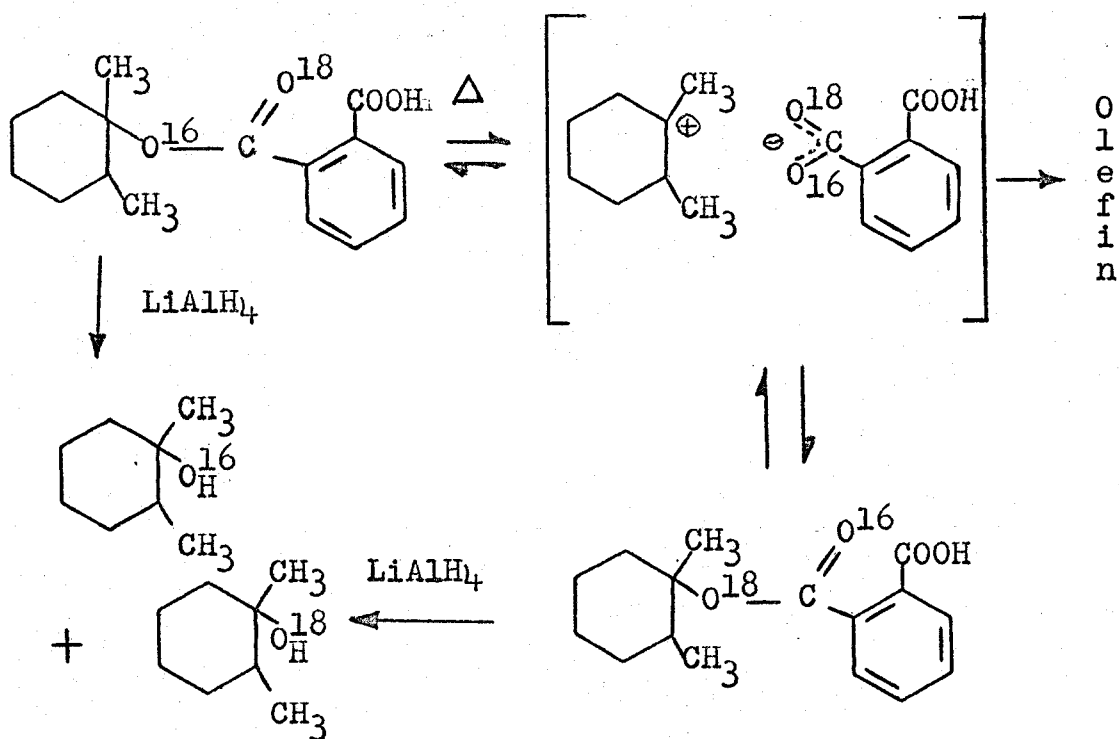
position was then prepared from the sodium derivative of trans-1,2-dimethylcyclohexanol and the  $O^{18}$  enriched phthalic anhydride (Fig. 15).

To achieve the equilibrium illustrated in Fig. 14 the carbonyl- $O^{18}$  enriched trans-1,2-dimethylcyclohexyl hydrogen phthalate was heated to the melting point  $124^{\circ}$  (decomposition point  $128^{\circ}$ ) and held for ten minutes. The temperature was then slowly raised to  $128^{\circ}$  until approximately 10% decomposition had occurred. The ester was then reduced with lithium aluminium hydride to the trans-2,-dimethylcyclohexanol and  $\omega, \omega'$ -dihydroxy-o-xylene (Fig. 16). The trans-1,2-dimethylcyclohexanol was analyzed by mass spectrometry for  $O^{18}$  incorporation.

The theoretical  $p + 2$  peak of this alcohol is 0.55% based on  $p + 2 / p$ . The mass spectrum of an authentic sample of this alcohol indicated a  $p + 2$  peak of 0.57%. The alcohol obtained from the isotope experiment had a  $p + 2$  peak of 1.09% indicating the presence of approximately 0.5% excess  $O^{18}$  in the sample.<sup>10</sup> This 0.5% excess  $O^{18}$  indicates that approximately 20% exchange between the alkyl oxygen and the carbonyl oxygen of the ester had occurred. It may be concluded from the above data that ionic character is in fact present in the transition state of decomposition of tertiary hydrogen phthalate esters.

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<sup>10</sup> This value is based on the average of three independent experiments and analyses.



† w,w'-Dihydroxy-o-xylene

Fig. 16. - Scheme for  $O^{18}$  Incorporation in 1,2-Dimethylcyclohexanol Through Internal Return of the Ion Pair.

#### Thermal Decomposition Studies of Xanthate Esters

As discussed earlier in the introduction, the pyrolysis of the acetate ester and of the hydrogen phthalate ester of trans-1,2-dimethylcyclohexanol yielded quite different olefin product distributions. The acetate ester on pyrolysis at  $450^\circ$  yielded 45% 2,3-dimethylcyclohexene and 55% 2-methylmethylenecyclohexane.<sup>11</sup> In contrast, the pyrolysis

<sup>11</sup> D.H. Froemsdorf, C.H. Collins, G.S. Hammond, C.H. DePuy, *J. Am. Chem. Soc.*, **81**, 643 (1959).

of the hydrogen phthalate ester at 150° yielded 46% 1,2-dimethylcyclohexene, 35% 2-methylmethylenecyclohexane, and 19% 1,2-dimethylcyclohexene.<sup>12</sup> It was deemed of interest to investigate the pyrolysis of the xanthate ester of this alcohol and other sterically hindered alcohols to determine whether there is any evidence of ionic character in the transition state of the decomposition; particularly in view of the xanthate esters cited in Table I which did not decompose in a stereospecific manner.

Many researchers have encountered difficulty in the purification of xanthate esters.<sup>13</sup> It appears that unless the xanthate ester can be distilled or crystallized then purification is impracticable. McAlpine<sup>14</sup> has observed two forms of xanthate esters, "stable" xanthates and "unstable" xanthates. The stable xanthates are readily distilled in vacuo, whereas the unstable xanthates decompose. This same author found that the "stable" xanthate ester could sometimes be obtained by distillation under reduced pressure which was usually accompanied with over 50% decomposition.<sup>15</sup> McAlpine was unable to detect any difference in

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<sup>12</sup> K.G. Rutherford and D.P.C. Fung, Can. J. Chem., 42, 2657 (1964).

<sup>13</sup> H.R. Nace, "Organic Reactions", Vol. XII, editor-in-chief A.C. Cope, John Wiley and Sons, London, 1962, p. 58.

<sup>14</sup> I.M. McAlpine, J. Chem. Soc., 1114 (1931).

<sup>15</sup> I.M. McAlpine, J. Chem. Soc., 906 (1932).

the physical properties of the two "forms". It was also demonstrated that the two forms gave identical decomposition products.<sup>16</sup> Nace's<sup>17</sup> investigations indicated that the instability was caused by some impurity, probably a peroxide, in very small quantities.

The trans-1,2-dimethylcyclohexyl xanthate ester was synthesized according to the procedure of Chugaev.<sup>18</sup> The potassium salt of the alcohol was prepared in solution and an excess of carbon disulfide was added. After stirring for twelve hours, an excess of methyl iodide was added. The resultant xanthate ester was a heavy deep-yellow liquid.

The xanthate ester could not be purified. The crude product was too unstable to permit distillation even under reduced pressure with the employment of the mercury diffusion pump. All efforts to crystallize the oil were also unsuccessful. Several attempts were made to purify the compound by column chromatographic methods. Decomposition occurred on various alumina and silica gel columns and charcoal and cellulose columns failed to yield a stable xanthate.

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<sup>16</sup> D.H. Barton, A.J. Head, and R.J. Williams, J. Chem. Soc., 453 (1952).

<sup>17</sup> H.R. Nace, D.G. Manly, and S. Fusco, J. Org. Chem., 23, 687 (1958).

<sup>18</sup> L.A. Chugaev, Ber., 32, 3332 (1899).

Attempts were also made to prepare this xanthate ester by the use of thiophosgene to convert the alcohol to the corresponding chlorothioncarbonate, followed by treatment

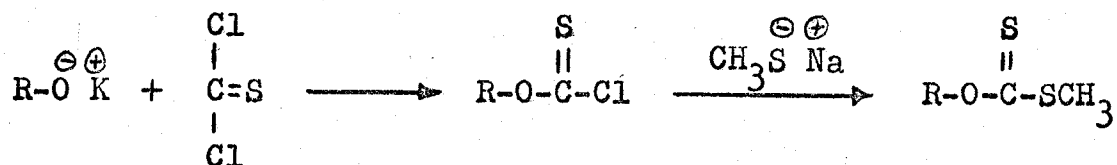


Fig. 17. - Proposed Xanthate Synthesis with Thiophosgene

with methyl mercaptan. A tarry material was obtained which eluded purification. Nace<sup>19</sup> observed that this reaction yielded the disubstituted thioncarbonate. He was unable to prepare the xanthate even in the presence of a large excess of thiophosgene.

Other researchers have decomposed the crude xanthate esters as obtained from the reaction mixture when isolation of the pure xanthate ester was impracticable. These crude mixtures have been reported to contain at least 5% of the unreacted alcohol.<sup>20</sup> It would seem that the presence of this amount of alcohol could affect the olefin distri-

<sup>19</sup> G.L. Nace and H.R. O'Connor, J. Am. Chem. Soc., 74, 5454 (1952).

<sup>20</sup> R.A. Benkeser and J.J. Hazdra, J. Am. Chem. Soc., 81, 228 (1959).

bution obtained on pyrolysis through dehydration of the alcohol. To avoid the presence of any alcohol in the crude xanthates pyrolyzed in this laboratory, it was found that the potassium salt of the xanthate could be isolated and washed free of any unreacted alcohol. The S-methyl ester was then obtained by suspending the dried xanthate salt in hexane and adding the required amount of methyl iodide. Purification of the unstable xanthate was then limited to filtration through a column of successive layers of charcoal and filter aid.

The thermal decomposition of the trans-1,2-dimethylcyclohexyl S-methyl xanthate ester was carried out at 100°. The olefinic product distribution, as determined by vapour phase chromatographic analysis, indicated the presence of 38% 2,3-dimethylcyclohexene, 45% 2-methylmethylenecyclohexane and 17% 1,2-dimethylcyclohexene. This product distribution is comparable with that obtained on the pyrolysis of the corresponding hydrogen phthalate ester. Of particular interest is the formation of 17% 1,2-dimethylcyclohexene which represents trans-elimination product. It is doubtful that this isomer could have resulted from a rearrangement process particularly when the Chugaev reaction is noted for yielding unrearranged products.

The conformations of this xanthate ester (Fig. 18) indicate that in order to obtain the 1,2-dimethylcyclohexene isomer from the pyrolysis reaction the tertiary



$\beta$ -hydrogen trans to the xanthate group would have to be eliminated.

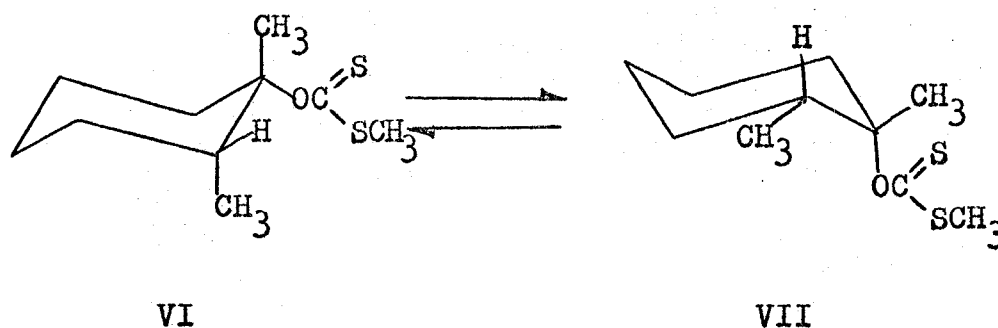


Fig. 18.. - Conformations of trans-1,2-Dimethylcyclohexyl Xanthate.

The concerted mechanism for the decomposition of xanthate esters supported by much of the literature does not provide a satisfactory explanation for the trans-elimination product observed in this pyrolysis. The termination state for the concerted cyclic mechanism would have to contain three partial double bonds as shown in Fig. 19 (two about to be formed and one about to be broken).

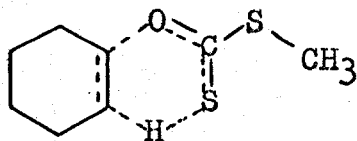


Fig. 19. - Transition State For Concerted Cyclic Elimination.

Therefore the six atoms involved in the cycle would have to be almost coplanar. It is theoretically possible to force a cis axial-equatorial (a,e) bond of a cyclohexyl ring into a plane but an equatorial-equatorial (e,e) bond would be much more difficult.<sup>21</sup> Therefore to obtain the necessary conditions for a concerted cyclic mechanism during the pyrolysis of a cyclohexyl xanthate, the xanthate group and the  $\beta$ -hydrogen which is undergoing elimination must bear a cis axial-equatorial (a,e) relationship to each other.

In both conformations of the trans-1,2-dimethylcyclohexyl xanthate ester the tertiary  $\beta$ -hydrogen is always trans to the xanthate group (Fig. 18). In structure VI these two groups are trans equatorial-equatorial (e,e) and in structure VII they are trans axial-axial (a,a). Therefore a cyclic concerted mechanism is unlikely in the formation of the 1,2-dimethylcyclohexene. It would appear then that to obtain this isomer ionic formation would of necessity occur in the transition state of the thermal decomposition of this xanthate ester similar to that experienced for the decomposition of the corresponding hydrogen phthalate ester. The fact that more of the 1,2-dimethylcyclohexene was not obtained may again be attributed to the "cis effect" which would

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21 E.L. Eliel, et al., "Conformational Analysis", Interscience Publ.; New York, 1965, p. 231.

be exhibited in the transition state of the elimination (Fig. 20).

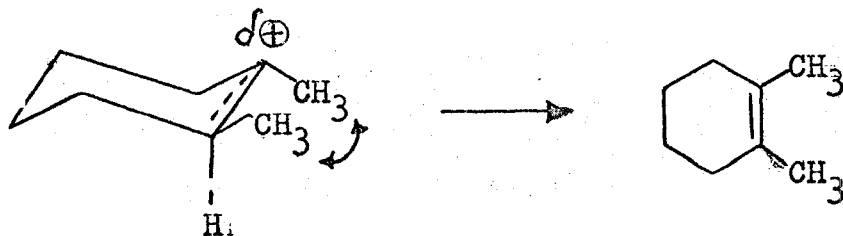


Fig. 20. - "cis Effect" in the Formation of 1,2-Dimethylcyclohexene.

The further investigation of the "cis effect" and of the possible ionic character in the transition state of the decomposition of sterically hindered xanthate esters involved the preparation of the xanthate ester of trans-2-methyl-1-phenylcyclohexanol. As outlined in the case of the hydrogen phthalate ester of this alcohol, the presence of the phenyl group in the 1-position should impart on decomposition more stability to the ion pair relative to that obtained in the decomposition of the trans-1,2,-dimethylcyclohexyl xanthate ester, which could lead to an increase in Saytzeff product (1-phenyl-2-methylcyclohexene). However, the phenyl group is much bulkier than the methyl group, which would enhance the steric effect in the transi-

tion state of the Hofmann product (2-phenyl-3-methylcyclohexene).

The synthesis of trans-2-methyl-1-phenylcyclohexyl xanthate ester was carried out similarly to the procedure used in preparing the trans-1,2-dimethylcyclohexyl xanthate ester. The potassium salt was isolated and then treated with methyl iodide in hexane. This xanthate was purified by crystallization (m.p. 56°).

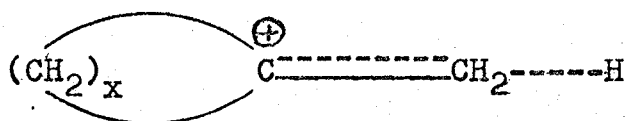
The pyrolysis of trans-2-methyl-1-phenylcyclohexyl ester was carried out at 150°. The olefinic products consisted of 6% 1-phenyl-2-methylcyclohexene (Saytzeff product) and 94% 2-phenyl-3-methylcyclohexene (Hofmann product). This product distribution is again very similar to that obtained on pyrolysis of the corresponding hydrogen phthalate ester. The appearance of 6% 1-phenyl-2-methylcyclohexene indicates that trans-elimination has occurred and, here again, ionic character appears evident in the transition state of the decomposition. The phenyl group probably does impart more stability to the carbonium ion intermediate, as discussed in the case of the thermal decomposition of the corresponding hydrogen phthalate ester, however, again the steric effect in the transition state is more predominant here than in the case of the 1,2-dimethylcyclohexyl carbonium ion. Consequently, only 6% of the Saytzeff product was realized.

In light of the experimental data presented supporting apparent carbonium ion character in the transition state of decomposition, it was considered of interest to study the effect of ring size on the decomposition products on pyrolysis of 1-methyl alicyclic xanthate esters. Pyrolysis of the xanthate ester of 1-methylcyclopentanol yielded almost entirely Saytzeff product (99-100%). This is in close agreement with the products obtained on pyrolysis of the corresponding acetate ester and the hydrogen phthalate ester. Similarly the pyrolysis of 1-methylcycloheptyl xanthate afforded 70% 1-methylcycloheptene (Saytzeff product) and 30% 1-methylenecycloheptane (Hofmann product). This is in agreement with the pyrolysis products of the corresponding hydrogen phthalate ester which were 72% and 28%, respectively.

It is interesting to note that there is an increase in Hofmann product with increase in ring size. The xanthate esters of 1-methylcyclopentanol, 1-methylcyclohexanol,<sup>22</sup> and 1-methylcycloheptanol yielded on pyrolysis 0-1%, 22%, and 30% Hofmann product, respectively. One may conclude, as in the case the hydrogen phthalate ester pyrolysis of these alcohols, that the ionic transition state is more favorable with the larger ring size since the ring bond angle can expand to  $120^{\circ}$ .

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<sup>22</sup> R.A. Benkeser and J.J. Hazdra, J. Am. Chem. Soc., 81, 228 (1959).



Since the evidence presented demonstrates that certain xanthate esters decompose in a manner other than the accepted concerted cyclic mechanism, it was deemed worthwhile to investigate some of the nonstereospecific decompositions reported in the literature. For example, Botteron<sup>23</sup> reported that pyrolysis of cis-2-methylcyclohexyl xanthate ester yielded 49% 1-methylcyclohexene and 51% 3-methylcyclohexene. Since this product distribution seems to be contrary to both the concerted mechanism and the carbonium ion intermediate proposal, the former because it would involve a trans-elimination and the latter because of the absence of a group to promote the stability of the carbonium ion intermediate, it was felt necessary to repeat the experiment.

The cis-2-methylcyclohexanol was isolated from an (commercial) isomeric mixture by fractional distillation from a glass-bead packed distillation column. The xanthate ester was prepared in the usual manner and decomposed at 200°. The product ratio was in good agreement with that reported by Botteron, 46% 1-methylcyclohexene and 54% 3-methylcyclohexene.

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<sup>23</sup> D.G. Botteron and G.P. Schulman, J. Org. Chem., 27, 2007 (1962).

It is interesting to note that Alexander and Mudrack<sup>24</sup> reported, on pyrolysis of cis-2-phenylcyclohexyl xanthate ester, that 93-100% 3-phenylcyclohexene and 7-0% 1-phenylcyclohexene was observed. The latter represents trans-elimination product. Here again, a concerted mechanism is unlikely and stability of a carbonium ion intermediate does not seem probable. Berti<sup>25</sup> repeated this experiment and concurred with the above results.

Contrary to the results of the forementioned cis-2-substituted cyclohexyl xanthate esters, Bordwell and Landis<sup>26</sup> reported 100% 3-t-butylcyclohexene on pyrolysis of cis-2-t-butylcyclohexyl xanthate ester. These authors, however, used a mixture of 85% cis- and 15% trans-2-t-butylcyclohexanol to prepare the xanthate ester. The reported 100% of the 3-isomer was based only on infrared spectra and index of refraction. In view of the two previous cis-2-substituted cyclohexyl xanthate esters whereby some trans-elimination product was obtained in each case, it was deemed necessary to repeat this work.

The pure cis-2-t-butylcyclohexanol was isolated by preparing the p-nitrobenzoate ester from an isomeric mixture of the alcohol and p-nitrobenzoate. The p-nitro-

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<sup>24</sup> E.R. Alexander and A. Mudrak, J. Am. Chem. Soc., 72, 1810 (1950).

<sup>25</sup> G. Berti, J. Am. Chem. Soc., 76, 1216 (1954).

<sup>26</sup> F.G. Bordwell and P.S. Landis, J. Am. Chem. Soc., 80, 6379 (1958).

benzoate ester obtained was recrystallized until a fraction of pure cis-2-*t*-butylcyclohexyl *p*-nitrobenzoate was isolated (m.p. 78-9°).<sup>27</sup> The ester was saponified with alcoholic sodium hydroxide and the cis-2-*t*-butylcyclohexanol recovered by steam distillation.

The xanthate ester was prepared by the usual method and purified by crystallization (m.p. 36°). Pyrolysis of the xanthate ester yielded only one olefin product as indicated by vapour phase chromatographic analysis. This product was identified by infrared spectra and NMR spectra as the 3-*t*-butylcyclohexene isomer. Thus it may be concluded that this xanthate pyrolyzed stereospecifically according to a concerted cyclic mechanism.

The xanthate ester of tert-amyl alcohol was pyrolyzed at 100°. The olefinic products were composed of 46% 2-methyl-2-butene and 54% 2-methyl-1-butene. This product ratio was in contrast with the 53% 2-methyl-2-butene and 47% 2-methyl-1-butene obtained on pyrolysis of the corresponding hydrogen phthalate ester.<sup>28</sup> It is also in contrast to the low temperature pyrolysis at 225° of the tert-amyl acetate ester which yield 58% 2-methyl-2-butene and 42% 2-methyl-1-butene.<sup>29</sup> It is not too clear as to why the

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<sup>27</sup> H.L. Goering and R.L. Reeves, J. Am. Chem. Soc., **78**, 4926 (1956).

<sup>28</sup> K.G. Rutherford and D.P.C. Fung, Can. J. Chem., **42**, 2657 (1964).

<sup>29</sup> W.J. Bailey and W.F. Hale, J. Am. Chem. Soc., **81**, 647 (1959).



olefin ratio should change so much in the case of this xanthate ester.

A summary of the xanthate esters prepared and pyrolyzed is given in Table II. From the experimental evidence presented in this dissertation and the literature cited, one must conclude that the mechanism involved in the thermal decomposition of xanthate esters is not necessarily homogeneous. It has been shown that a concerted cyclic type elimination seems prevalent in some of the decomposition reactions discussed. It also has been shown that carbonium ion character seems evident at least to a certain degree in the decomposition transition state of some sterically hindered xanthate esters.

It is probable then that an ionic mechanism similar to that proposed by Sixma<sup>30</sup> for the pyrolysis of acetate esters, which has been confirmed in this laboratory for the decomposition of sterically hindered hydrogen phthalate esters, is operative in the thermal decomposition of xanthate esters as well. In this mechanism the carbon-oxygen bond is broken heterolytically to form an ion pair in the transition state as shown in Fig. 21. If the distance between the ions of the pair is small then internal return of the ion pair to the initial state could proceed more

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<sup>30</sup> J.C. Scheer, E.C. Kooyman, and F.S.J. Sixma, loc. cit.

TABLE II  
 PYROLYSIS OF XANTHATE ESTERS OF SOME ALCOHOLS

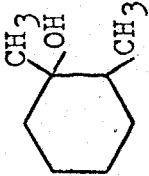
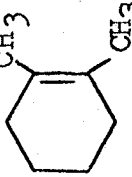
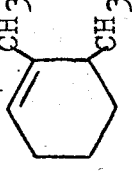
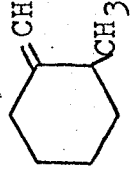
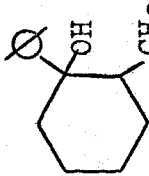
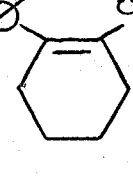
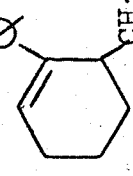
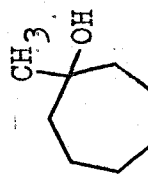
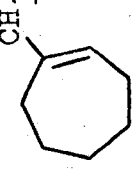
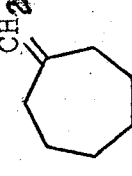
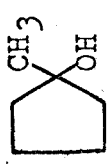
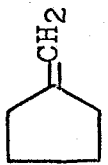
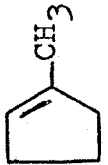
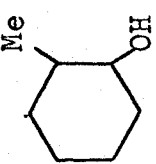
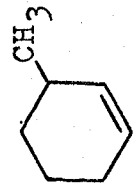
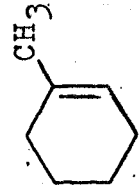
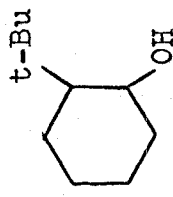
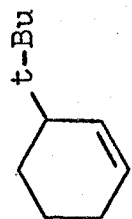
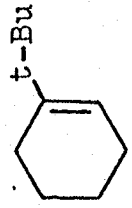
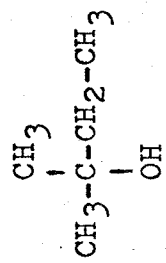
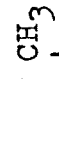
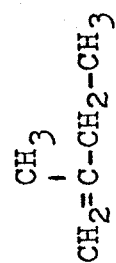
ALCOHOL	XANTHATE YIELD	PYROLYSIS TEMP., °C	OLEFIN YIELD	PRODUCT DISTRIBUTION
 trans	72%	100°	68%	 17%  38%  45%
 trans	51%	150°	78%	 45%  94.5%
	34%	100°	42%	 70%  30%

TABLE II (CONTD)  
 PYROLYSIS OF XANTHATE ESTERS OF SOME ALCOHOLS

ALCOHOL	XANTHATE YIELD	PYROLYSIS TEMP., °C	OLEFIN YIELD	PRODUCT DISTRIBUTION
	66%	Distilled 100°	61%	 0-1%  100-99%
 cis	82%	230°	60%	 54%  46%
 cis	70%	200°	69%	 100%  0%
	82%	100°	84%	 46%  54%

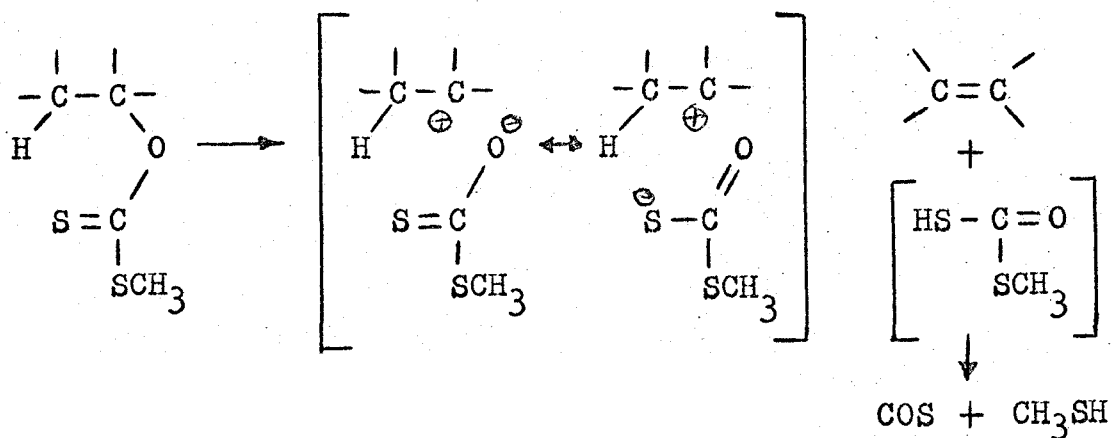


Fig. 21. - Proposed Ion Pair Mechanism for Xanthate Decomposition.

rapidly than the transition to decomposition products. This mechanism does not involve a concerted ring; therefore coplanarity is not necessary. In which case the thion sulphur can easily reach a trans equatorial  $\beta$ -hydrogen when the xanthate group is in the equatorial position as well. This could account for the near equal amounts of each isomer obtained on pyrolysis of cis-2-methylcyclohexyl xanthate. It may be possible to explain other cases of nonsterospecific pyrolysis with this possible mechanism of decomposition, however, more experimental evidence is necessary before any further speculation can be made.

#### Thermal Decomposition Studies of Potassium Xanthate Salts

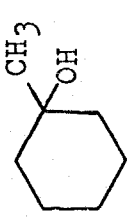
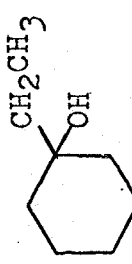
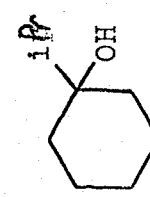
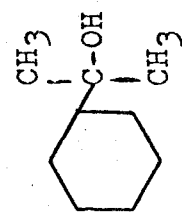
Since the potassium xanthate salts were isolated to form xanthate esters free of starting alcohol, the possibility that these salts could undergo thermal decomposition

was considered. Potassium trans-1,2-dimethylcyclohexyl xanthate was heated in a micro-distillation apparatus at 200° for thirty minutes. The infrared spectrum indicated that the distilled decomposition products were olefinic. Vapour phase chromatographic analysis showed that the olefinic mixture consisted of 9% 1,2-dimethylcyclohexene, 34% 2,3-dimethylcyclohexene, and 57% methylenemethylcyclohexane. This product distribution compares reasonably with that obtained on pyrolysis of the corresponding xanthate ester, (19%, 46% and 35%, respectively). The interesting fact is that the overall yield of olefin from the xanthate salt pyrolysis was 75% whereas the overall yield of olefin from the pyrolysis of the xanthate ester was 45%.

The pyrolysis of the potassium xanthate salt of trans-2-methyl-1-phenylcyclohexanol yielded 7% 1-phenyl-2-methylcyclohexene and 93% 2-phenyl-3-methylcyclohexene. This product distribution is almost identical with that obtained from pyrolysis of the corresponding xanthate ester. The overall yield from the salt pyrolysis was 63% as compared to 36% overall yield obtained from the xanthate ester.

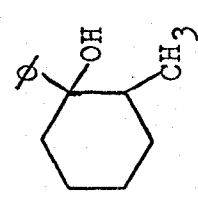
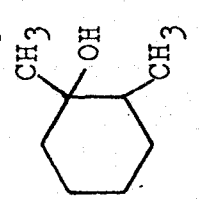
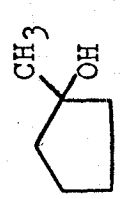
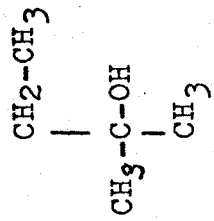
The pyrolyses of several other xanthate salts of tertiary alcohols were conducted (Table III). In each case the product distribution was very similar to that obtained on pyrolysis of the corresponding xanthate esters. It is interesting to note that the overall yields from the pyrolysis of these xanthate salts were increased in each case

TABLE III  
COMPARISON OF PYROLYSIS PRODUCTS OF XANTHATE SALTS TO ESTERS

ALCOHOL	% XANTHATE YIELD		% OLEFIN YIELD		% EXO ISOMER	
	ESTER	SALT	ESTER	SALT	ESTER	SALT
	(31)	82	49	74	21	18
	(31)	84	52	80	12	11
	(31)	83	46	81	22	18
	(31)	81	51	71	21	18

31 B.A. Benkeser and J.J. Hazdra, *J. Am. Chem. Soc.*, **81**, 229 (1959). Crude xanthate esters were pyrolyzed with up to 5% alcohol present. Yields were not reported.

TABLE III (CONTD)  
 COMPARISON OF PYROLYSIS PRODUCTS OF XANTHATE SALTS TO ESTERS

ALCOHOL	% XANTHATE YIELD		% OLEFIN YIELD		% EXO ISOMER	
	ESTER	SALT	ESTER	SALT	ESTER	SALT
	46	72	78	88		
	65	92	68	83	45	57
	48	86	62	81	1	1
	69	84	64	72	54	46

by 10-30% over that obtained from the overall yields from pyrolysis of the corresponding xanthate esters. This could prove to be of value in synthetic work as it eliminates the preparation of the S-methyl derivative which could prove to be unstable as well as more costly in time and materials.

It was also found that pyrolysis of potassium xanthate salts of primary and secondary alcohols yielded a mixture of olefin(s) and starting alcohol. On pyrolysis of potassium cyclohexyl carbinyl xanthate, 46% cyclohexylcarbinol and 29% methylenecyclohexane were recovered. Similarly the pyrolysis of potassium isoamyl xanthate yielded 44% isoamyl alcohol and 15% amylene. The pyrolysis of the secondary potassium xanthate salts of both 2-methylcyclohexanol and 3-methylcyclohexanol yielded 42-45% of the corresponding starting alcohol and 24-32% olefinic mixture respectively.

It is not too clear why starting alcohols are recovered on pyrolysis of primary and secondary potassium xanthate salts and not from the pyrolysis of the tertiary xanthate salts. It is known, however, that xanthic acids are extremely unstable and decompose to carbon disulfide and the corresponding alcohol. It is felt that perhaps the proton on the decomposition moiety potassium hydrogen dithiocarbonate ( $\text{HS}-\overset{\text{O}}{\parallel}{\text{C}}-\text{SK}$ ) is acidic enough to cause a similar breakdown of the potassium xanthate salts of primary and secondary alcohols, whereas, the steric hinderence involved in



the tertiary xanthate salts would favour the thermal decomposition of the xanthate salts to produce only the olefinic products and no alcohol.

### Conclusions

It is difficult to draw a comparison from the pyrolysis of tertiary hydrogen phthalate, xanthate, and acetate esters, of the corresponding alcohol. It has been demonstrated by the decomposition of trans-2-methyl-1-phenylcyclohexyl hydrogen phthalate ester and by an isotope study of the decomposition of trans-1,2-dimethylcyclohexyl hydrogen phthalate ester that sterically hindered hydrogen phthalate esters decompose by an ion pair mechanism. These esters have a greater internal strain and undoubtedly lend themselves more readily to this ionic-type break down, thus they decompose at lower temperatures and give a different product ratio.

It may also be concluded that tertiary xanthate esters thermally decompose, at least in part, by an ionic mechanism. This seems evident by the appearance of 17% 1,2-dimethylcyclohexene and 6% of 1-phenyl-2-methylcyclohexene on pyrolysis of the xanthate esters of trans-1,2-dimethylcyclohexanol and trans-2-methyl-1-phenylcyclohexanol, respectively. Also, the increase of exo olefin product obtained with increase of ring size would be favoured by this type of decomposition. Laasko<sup>32</sup> has demonstrated that neopentyl

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32 N. Laasko, Suomen Kemistehti, 16B, 19 (1943).

xanthate, which does not have any  $\beta$ -hydrogens for elimination, rearranges to the more stable dithiocarbonate. If

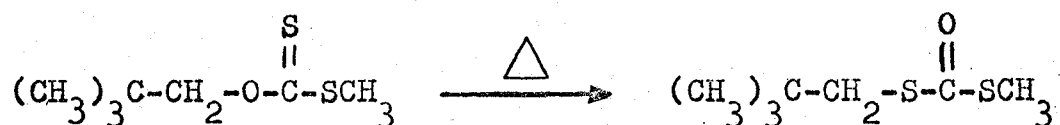


Fig. 22. - Pyrolysis of Neopentyl Xanthate.

this rearrangement takes place by an ionic mechanism then it may be concluded that the decomposition of xanthate esters to olefin products would also go by this method. It is suggested that this may be determined by pyrolyzing the optically active  $\alpha$ -deuterated neopentyl xanthate ester and see if optical activity is retained. It has also been shown that potassium xanthate salts of tertiary alcohols decompose to give good yields of olefin products.

Again it is remarkable that xanthate, hydrogen phthalate and acetate esters of corresponding alcohols furnish, on pyrolysis, olefinic products almost identical in most cases. From the limited number of low-temperature ester pyrolysis experiments carried out with tertiary alcohols, indications are that an increase in the ionic character in the elimination transition state seems evident by an increase in the steric requirement about the carbon atom.

## CHAPTER III

## EXPERIMENTAL

Analytical Determinations.- Infrared spectra were run by Mr. David Hill on the Beckman IR-10 in chloroform solutions or as potassium bromide pellets. Melting points were taken on the Fisher-Johns melting point apparatus and are uncorrected. Microanalyses were performed by Schwarzkopf Microanalytical Laboratory 56-19 37th Avenue, Woodside, New York, and by Midwest Microlab Inc., 6000 East 46th St., Indianapolis Indiana.

Vapour Phase Chromatographic Analysis.- Vapour phase chromatographic analysis was employed to quantitatively resolve the components in each olefinic mixture. The particular retention time of each olefin was identified by comparison with authentic samples. Relative concentrations of the olefins were determined by taking peak areas according to the triangulation method.<sup>1</sup>

For optimum results the vapour phase chromatographic analyses were carried out on two different instruments and columns. The Perkin-Elmer, model 800, was employed with a

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<sup>1</sup> A.I. Keulemans, "Gas Chromatography", Reinhold Publ. Corp., New York, N.Y. 1960, p. 32.

Golay "R" column (175 ft. long and 0.01 inch diameter). The F&M dual column chromatograph, model 720, was used with a 10% silicone rubber SE-30 on 60-80 mesh Chromosorb W column (8 ft. long and 0.25 inch diameter). The instrument and column employed along with the conditions used in each analysis are indicated in the individual experimental procedures described.

Thermal Decomposition Studies of Hydrogen Phthalate Esters

trans-2-Methyl-1-Phenylcyclohexanol.— Magnesium turnings (24.3 g.— 1.0 mole) and anhydrous 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 bromobenzene (173 g.— 1.1 mole) and anhydrous ether (300 ml.) was added drop-wise at a rate sufficient to maintain constant reflux. After this solution was added, the reaction mixture was stirred at room temperature for one hour; the mixture was then cooled by immersing the flask into a crushed ice bath. An ethereal solution (250 ml.) of 2-methylcyclohexanone (100 g.— 0.9 mole) was added to the cooled mixture over a period of two hours; the reaction mixture was stirred for an additional hour. The contents were then poured on a mixture of crushed ice and concentrated ammonium chloride in order to decompose the Grignard complex. The ethereal layer was separated, washed three

times with water (200 ml. portions) and dried over sodium sulphate. The ethereal solution was recovered by filtration and the ether removed in vacuo. Fractional distillation of the resultant oil yielded 115 g. (65%) of 2-methyl-1-phenylcyclohexanol b.p. 83.5-85° (0.35 mm.),  $n_D^{25}$  1.5353 (reported<sup>2</sup> b.p. 105-106° (1 mm.),  $n_D^{25}$  1.5359; reported<sup>3</sup> b.p. 105-108° (2 mm.),  $n_D^{25}$  1.5366).

The structure of this alcohol was determined to be trans-2-methyl-1-phenylcyclohexanol from the NMR spectrum<sup>4</sup>.

Data: (Varian A.60)

Solution: Approx. 10% v/v in  $CCl_4$ .

T.M.S. internal standard.

Doublet at  $\delta$  0.55 (3 H)  $J = 6.5$  cps.

Singlet at  $\delta$  1.44 (1 H)

Broad band with main peak at 1.55 (9 H)

Multiplet centred at 7.25 (5 H)

The doublet at  $\delta$  0.55 is due to the methyl protons as the integrated area was three and the splitting was of the order expected for  $CH_3-CH$  (6.3 to 7.2 cps.). The singlet at  $\delta$  1.44 was assigned to the hydroxyl proton

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<sup>2</sup> R.B. Carlin and H.P. Landerl, J. Am. Chem. Soc., **75**, 5969 (1953).

<sup>3</sup> N.G. Siderova and S.D. Nikonovich, Zh. Obshch. Khim., **30**, 1921 (1960).

<sup>4</sup> The NMR spectrum was run and interpreted by Victor Wright, Lash-Miller-Chemical Laboratories, University of Toronto.

on the basis of the integrated area of one and its down-field shift with the addition of mineral acid. The broad band centred at  $\delta = 1.55$  was due to the ring proton resonance. The multiplet centred at  $\delta 7.25$  was the benzene protons.

trans-2-Methyl-1-Phenylcyclohexyl Hydrogen Phthalate.- The hydrogen phthalate ester was prepared according to the procedure developed in this laboratory.<sup>5</sup> 2-Methyl-1-phenylcyclohexanol (15.2 g.- 0.08 mole) and 150 ml. of anhydrous ether were placed in a one-liter Erlenmeyer flask. To this rapidly stirred solution was added an ethereal solution of triphenylmethyl sodium until a persistent red colour indicated a slight excess of base. Powdered phthalic anhydride (12 g.- 0.085 mole) was added in one portion; the flask was stoppered and the reaction mixture stirred for forty-eight hours. Water (200 ml.) was added and the mixture was stirred vigorously for ten minutes. The aqueous layer was separated and poured on a mixture of crushed ice and concentrated hydrochloric acid. The precipitated hydrogen phthalate ester was recovered by filtration, dried, and recrystallized from a chloroform-petroleum ether (b.p. 30-60°) solvent pair. A white powder was obtained (110 g.- 70%) m.p. 149-150° with decomposition. The infrared spectrum showed the following significant absorption bands: 3500  $\text{cm}^{-1}$ , -OH stretch; 3030-

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<sup>5</sup> K.G. Rutherford, J.M. Prokipcak, and D.P. Fung, J. Org. Chem., 28, 582 (1963).

3050  $\text{cm}^{-1}$ , aromatic CH stretching; 2920, 2850  $\text{cm}^{-1}$ , aliphatic CH stretching; 1715  $\text{cm}^{-1}$ , ester CO stretching; 1690  $\text{cm}^{-1}$ , aromatic acid CO stretching; 1590, 1578  $\text{cm}^{-1}$ , aromatic skeletal vibrations; 1250-1300  $\text{cm}^{-1}$ , aromatic ester stretching; 1110  $\text{cm}^{-1}$  monosubstituted aromatic ring CH in-plane deformation; 1170  $\text{cm}^{-1}$  1,2-disubstituted aromatic ring CH in-plane deformation; and 990  $\text{cm}^{-1}$ , 1,2-disubstituted aromatic ring out-of-plane deformation.

Analysis:	Calcd: $\text{C}_{21}\text{H}_{22}\text{O}_4$ :	C, 74.53;	H, 6.55
	Found:	C, 74.28;	H, 6.61
	Neut. Equiv.	Calcd: 338.4	
		Found: 337.5	

Dehydration of 2-Methyl-1-Phenylcyclohexanol.- 2-Methyl-1-phenylcyclohexanol (20 g.- 0.1 mole) was dissolved in 150-ml. solution of 2.5% sulphuric acid (by volume) in acetic acid and allowed to stand at room temperature for fifty minutes with intermittent stirring. During this time the alkene had separated as an oily layer. The mixture was poured into a mixture of pentane (200 ml.) and water (200 ml.). The pentane layer was separated and washed twice with 50-ml. portions of 5% sodium carbonate, and twice with 50-ml. portions of water. The solution was dried over sodium sulphate. The mixture was filtered and the pentane evaporated under reduced pressure. Fractional distillation yielded 12.6 g. (70%) b.p. 123-124° (14 mm.),  $n_D^{25}$  1.5495

of olefinic mixture. Vapour phase chromatographic analysis (F&M, Model 720, silicone rubber column previously described at 140°) indicated that the olefin distribution was 76% 1-phenyl-6-methylcyclohexene and 24% 1-phenyl-2-methylcyclohexene (reported<sup>6-8</sup> 77% 2-phenyl-3-methylcyclohexene and 23% 1-phenyl-2-methylcyclohexene b.p. 121° (12 mm.),  $n_D^{25}$  1.5488).

Pyrolysis of trans-2-Methyl-1-Phenylcyclohexyl Hydrogen

Phthalate. - The pyrolysis was carried out according to the method of Rutherford and Fung.<sup>9</sup> 2-Methyl-1-phenylcyclohexyl hydrogen phthalate (8.46 g. - 0.025 mole) was placed in a reaction flask (25 ml.) fitted with a Claisen distillation head (thermometer attached), a condenser and an adapter with a receiving flask. The reaction flask was immersed in an oil bath which was controlled from 150-160°. The olefinic product was collected under reduced pressure (10 mm.) over a period of thirty minutes; 3.8 g. (88%) of product were obtained,  $n_D^{25}$  1.5518. Vapour phase chromatographic analysis of the olefinic mixture (F&M, model 720 as previously

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6 E.W. Garbisch, Jr., J. Org. Chem., 27, 4243 (1962).

7 E.W. Garbisch, Jr., J. Org. Chem., 26, 4156 (1961).

8 R.B. Carlin and D.A. Constantine, J. Am. Chem. Soc., 69, 50 (1947).

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



described) indicated 8% 1-phenyl-2-methylcyclohexene and 92% 2-phenyl-3-methylcyclohexene. The particular retention time of each olefin was identified by comparison with that of the olefins obtained by the acid-dehydration.

A mixture of the pyrolytic olefin product (3 g.) and phthalic acid (3 g.) was heated for twenty minutes at 150° and then the olefin was removed by distillation under reduced pressure (10 mm.). Vapour phase chromatographic analysis showed that the relative retention times and the peak areas were unaffected.

Preparation of Phthalic Anhydride- $O^{18}$ . - Commercial phthalic anhydride (8.9 g.- 0.06 mole), recrystallized from chloroform, was placed in a one-necked, round-bottomed flask (50 ml.) along with 25 ml. of dried tetrahydrofuran and water (1.00 ml.- 0.055 mole) 20 atom %  $O^{18}$  enriched. The flask was fitted with a reflux condenser and a stirring bar. The mixture was heated at reflux temperature with constant stirring for a period of 12 hours, during which time, phthalic acid was observed to precipitate from solution. The flask was cooled to room temperature and dry hydrochloric acid was bubbled through the solution to supply protons to aid the equilibration of the hydrogen between the oxygens of the carboxylate groups. The mixture was stirred at room temperature for one hour and then at reflux temperature for an additional two hours. The mixture was cooled and

transferred quantitatively to a 250-ml. Erlenmeyer flask. The phthalic acid was completely precipitated upon addition of 150 ml. of petroleum ether (b.p. 30-60°) and removed by filtration. The crude product was stirred in 100 ml. of hot chloroform to dissolve any unreacted phthalic anhydride. The phthalic acid was recovered by filtration and dried in vacuo; 9.0 g. (98%) were obtained m.p. 210°.

The phthalic acid was placed in a micro-distillation apparatus and heated with a flame. The powder melted and heating was continued until the melt was brought to reflux. The reaction vessel was held at reflux temperature for ten minutes. The flask was cooled and the phthalic anhydride was purified by recrystallization from a chloroform-petroleum ether (b.p. 30-60°) solvent pair. This procedure yielded 7.2 g. (90%) of phthalic anhydride m.p. 132° with approximately 5 atom % O<sup>18</sup> in each oxygen position.

trans-1,2-Dimethylcyclohexanol.— A solution of methylmagnesium iodide was prepared from magnesium turnings (27.6 g.— 1.1 mole), methyl iodide (170 g.— 1.2 mole) and 500 ml. anhydrous ether. To this ethereal Grignard solution was added 2-methylcyclohexanone (100 g.— 0.9 mole) diluted in 200 ml. of anhydrous ether. The resultant Grignard complex was decomposed with a solution of ammonium chloride. The ether layer was separated and dried with anhydrous sodium sulphate. The ether was removed in vacuo. Fractional

distillation of the resultant oil gave pure trans-1,2-dimethylcyclohexanol, b.p. 84-86° (50 mm.),  $n_D^{25}$  1.4590 (reported<sup>10</sup> b.p. 86.8 (52 mm.),  $n_D^{25}$  1.4588).

trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate-O<sup>18</sup>.- trans-1,2-Dimethylcyclohexanol (6.4 g.- 0.05 mole) and 100 ml. of anhydrous ether were placed in a 500-ml. Erlenmeyer flask. Added to this solution was an equivalent of triphenylmethyl sodium. The phthalic anhydride O<sup>18</sup> enriched (7.2 g.- 0.049 mole) was added in one portion; the flask was stoppered and the mixture stirred for twelve hours. Water (200 ml.) was added and the mixture stirred vigorously for ten minutes. The aqueous layer was separated and poured on a mixture of crushed ice and concentrated hydrochloric acid. The precipitated hydrogen phthalate ester was recovered by filtration, dried, and recrystallized from a chloroform-petroleum ether (b.p. 30-60°) solvent pair. A white powder 8.3 g. (67%) was obtained m.p. 124-5°; decomposition point 128° (reported<sup>11</sup> m.p. 124-5°).

Partial Thermal Decomposition of trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate-O<sup>18</sup>.- The hydrogen phthalate

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<sup>10</sup> T.D. Nevitt and G.S. Hammond, J. Am. Chem. Soc., 76, 4124 (1954).

<sup>11</sup> K.G. Rutherford and D.P.C. Fung, Can. J. Chem., 42, 2657 (1964).

ester (5 g.) was placed in a 125 ml. Erlenmeyer flask and immersed in a mineral oil bath maintained at 125°. After the phthalate ester melted and the temperature was carefully raised to 126° and held there for ten minutes. The temperature was then slowly raised to 128°. When decomposition became evident, by the appearance of phthalic acid as a precipitate in the melt, the reaction was quenched by rapidly cooling the flask in an ice bath. The unreacted hydrogen phthalate was dissolved in 60 ml. of anhydrous ether; the insoluble phthalic acid obtained from the decomposition was removed by filtration (0.32 g. indicating more than 10% decomposition had occurred).

Reduction of trans-1,2-Dimethylcyclohexyl Hydrogen Phthalate-O<sup>18</sup>.— The ethereal solution from the above procedure was placed in a two-necked, round-bottomed flask (250 ml.) which was fitted with a reflux condenser. Small pieces of lithium aluminium hydride were added as rapidly as they were being consumed until vigorous reaction ceased and the mixture became grayish in colour. The mixture was then heated to reflux temperature for one hour. The excess lithium aluminium hydride was destroyed by adding ethyl acetate dropwise to the mixture. The lithium and aluminium complexes were decomposed by the slow addition of water containing a trace of hydrochloric acid. The ethereal layer was separated, washed several times with water, and then dried over

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magnesium sulphate. The ether was removed in vacuo. Petroleum ether (b.p. 30-60°) was added to precipitate the  $\omega, \omega'$ -dihydroxy-o-xylene which was removed by filtration m.p. 64°. The ethereal solution was treated with charcoal and the ether removed in vacuo. The resultant oil was subjected to molecular distillation (0.01 mm.). The infrared spectrum of the product was identical to that of an original sample of trans-1,2-dimethylcyclohexanol. The index of refraction,  $n_D^{20}$  1.4612 was also comparable (reported<sup>12</sup>  $n_D^{25}$  1.4588). The mass spectra from three individual experiments indicated that 0.5 atom % excess  $O^{18}$  was incorporated in the alcohol.<sup>13</sup>

Data: Indirect introduction at 250°

Theoretical:  $C_8H_{16}O$ : p = 100; p + 1 = 9.84; p + 2 = 0.55

Found: Original

$C_8H_{16}O$ : p = 100; p + 1 = 8.95; p + 2 = 0.57

Isotope  $C_8H_{16}O$ : p = 100; p + 1 = 8.90; p + 2 = 1.09

#### Thermal Decomposition Studies of Xanthate Esters

trans-1,2-Dimethylcyclohexyl Xanthate. - The xanthate ester was prepared according to the method of Chugaev.<sup>14</sup> trans-1,2-Dimethylcyclohexanol (12.4 g. - 0.1 mole) was added to

<sup>12</sup> K.G. Rutherford and D.P.C.Fung, loc. cit.

<sup>13</sup> The mass spectra analyses and interpretations were done by Morgan Schaffer Corporation, 5110 Coutrai Ave., Montreal 26, Quebec.

<sup>14</sup> L.A. Chugaev, Ber., 32 3332 (1899).

a stirring suspension of metallic potassium metal (3.9 g.- 0.1 mole) in 100 ml. of dry benzene. The mixture was stirred for three hours at 50-55°. All the potassium seemed to have reacted at the end of this time. Carbon disulfide (10 g.- 0.13 mole) was added and the solution heated at reflux temperature for eight hours. Methyl iodide (16 g.- 0.11 mole) was added and the mixture was allowed to stir overnight. The inorganic material was removed by filtration and the filtrate was washed thoroughly with water, dried over sodium sulphate and the solvent removed in vacuo. The residual oil obtained 182 g. (85%) was too unstable to permit purification by distillation, even under reduced pressure with the employment of a mercury diffusion pump. All efforts to crystallize the oil were also unsuccessful. Treatment with solutions of ferrous ammonium sulphate according to Nace<sup>15</sup> proved unsuccessful with this compound. Several attempts were made to purify the compound by column chromatographic methods. Decomposition occurred on various types of alumina and silica gel columns with petroleum ether as the eluent. Charcoal and cellulose columns also proved unsuccessful as the xanthate obtained was still unstable. Purification was limited to filtration through a column of successive layers of charcoal and filter aid.

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<sup>15</sup> H.R. Nace, D.G. Manly, and S. Fusco, J. Org. Chem., 23, 687 (1958).

aid. The infrared spectra showed that approximately 5% alcohol was present in the product.

Attempted Thiophosgene Preparation of trans-1,2-Dimethylcyclohexyl Xanthate.- The trans-1,2-dimethylcyclohexanol (5 g.) was reacted with an equivalent of sodium hydride in dry tetrahydrofuran. The reaction mixture was then cooled to 0° with an ice bath. Thiophosgene was added in excess with the temperature being kept at 0°. After one hour the reaction mixture was allowed to warm to room temperature. The reaction vessel became quite warm and a tarry substance ensued which eluded attempts of purification. Other attempts by this procedure also failed.

A similar attempt was made with methyl sulphide. The methyl sulphide (5 g.) was reacted with an equivalent of sodium metal in (100 ml.) tetrahydrofuran. The reaction was cooled to 0° and thiophosgene was added in slight excess. After thirty minutes the sodium salt of 1,2-dimethylcyclohexanol was added. The reaction mixture was stirred at 0° for two hours and then allowed to warm to room temperature. The mixture was filtered and the solvent removed in vacuo. The resultant oil was fractionally distilled; one fraction was collected b.p. 35-38° (0.25 mm.),  $n_D^{22}$  1.4562; another fraction was collected b.p. 43° (0.25 mm.) which gave no observable index of refraction. The first fraction was identified by infrared spectrum as 1,2-dimethylcyclohexanol.

The second fraction was deduced to be dimethyl tricarbonate from elemental analysis and infrared spectrum.

Analysis: Calcd:  $C_3H_6S_3$ : C, 26.13 H, 4.38 S, 69.52  
 Found: C, 26.70 H, 4.30 S, 69.33

Potassium trans-1,2-Dimethylcyclohexyl Xanthate.- trans-1,2-Dimethylcyclohexanol (12.8 g.- 0.1 mole) in 50 ml. of dry toluene was reacted with metallic potassium (3.9 g.- 0.1 mole). This solution was then diluted to 200 ml. by the addition of anhydrous ether. A solution of carbon disulfide (10 g.- 0.13 mole) was added dropwise with constant stirring. This mixture was allowed to stir over night. The potassium xanthate salt was separated by filtration, washed thoroughly with anhydrous ether to remove any of the unreacted starting alcohol, and dried in vacuo. The average yield from six runs was 22 g. (91%). Recrystallization from absolute alcohol gave a light yellow salt which decomposed at  $190^{\circ}$ . The infrared spectrum and elemental analysis indicated that the compound was potassium trans-1,2-dimethylcyclohexyl xanthate. The important infrared bands observed were:  $2910\text{ cm}^{-1}$ , CH stretching;  $1450\text{ cm}^{-1}$ ,  $CH_2$  deformation vibrations;  $1365\text{ cm}^{-1}$ , CH bend on  $CH_3$ ;  $1125\text{ cm}^{-1}$ , C-O-C stretching for xanthates;  $1020-1080\text{ cm}^{-1}$ , C=S stretching;  $825\text{ cm}^{-1}$ , C-S stretching.

Analysis: Calcd:  $C_9H_{15}OS_2K$ : C, 44.58 H, 6.25  
 Found: C, 44.83 H, 6.47



S-Methyl trans-1,2-Dimethylcyclohexyl Xanthate.- Potassium trans-1,2-dimethylcyclohexyl xanthate (12.2 g.- 0.05 mole) was suspended in a solution of hexane containing methyl iodide (8.5 g.- 0.06 mole). The mixture was allowed to stir overnight at room temperature. The inorganic salts were removed by filtration and the solvent evaporated under reduced pressure. The crude oil 8.1 g. (83%) proved too unstable to be purified by the forementioned methods. Purification was again limited to filtration through a column of charcoal and superflow filter aid,  $n_D^{25}$  1.5435. The infrared spectrum indicated that the product was S-methyl trans-1,2-dimethylcyclohexyl xanthate as bands observed were identical to those of the corresponding potassium salt with an additional band at  $1325\text{ cm}^{-1}$ , indicating S-CH<sub>3</sub> stretching. No alcohol band was observable in the spectrum.

Pyrolysis of trans-1,2-Dimethylcyclohexyl Xanthate.- The xanthate ester (5.0 g.) was placed in a micro-distillation apparatus and heated over a steam bath. The pyrolysis proceeded smoothly while the reaction flask was heated for one hour. The olefinic product 1.82 g. (72%) was collected under reduced pressure (120 mm.) b.p.  $95^\circ$ . Vapour phase chromatographic analysis (Perkin-Elmer, model 800, Golay "R" column at  $40^\circ$ ) indicated that the olefin distribution was 17% 1,2-dimethylcyclohexene, 38% 2,3-dimethylcyclohexene, and 45% 2-methylmethylenecyclohexane. The retention

time of each olefin was identical to that of a synthetic mixture obtained as described below.

Dehydration of trans-1,2-Dimethylcyclohexanol.- Following the procedure of Cardew and Burwell,<sup>16</sup> trans-1,2-dimethylcyclohexanol (6.4 g.) was dehydrated in the presence of a few crystals of iodine under reflux conditions for two hours. The resultant olefinic mixture was collected by distillation b.p. 136-138°,  $n_D^{25}$  1.4579. Vapour phase chromatographic analysis (Perkin-Elmer, model 800, Golay "R" column at 40°) showed that the mixture contained 72% 1,2-dimethylcyclohexene, 26% 2,3-dimethylcyclohexene and 2% methylene-2-methylcyclohexane.

Potassium trans-2-Methyl-1-Phenylcyclohexyl Xanthate.- trans-2-Methyl-1-phenylcyclohexanol (9.5 g.- 0.05 mole) was added to an equivalent amount of potassium metal suspended in dry toluene (60 ml.). The mixture was stirred at 65° until all the potassium had been consumed (approx. 24 hours). The reaction mixture was then diluted to 300 ml. with anhydrous ether. Carbon disulfide (5.7 g.- 0.075 mole) in anhydrous ether was added dropwise over a period of thirty minutes. The mixture was stirred at room temperature for twelve hours. The potassium xanthate salt was recovered by filtration, washed thoroughly with anhydrous ether and dried

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<sup>16</sup> M. Cardew and R.L. Burwell Jr., J. Am. Chem. Soc., 75, 6289 (1960).

in vacuo. The average yield from three runs was 10.8 g. (72%). Recrystallization from tetrahydrofuran gave a light yellow salt decomposition point 150°. The infrared spectrum and elemental analysis indicated that the compound was potassium 2-methyl-1-phenylcyclohexyl xanthate. The important infrared bands observed were: 2910, 2850  $\text{cm}^{-1}$ , CH stretching; 1595  $\text{cm}^{-1}$ , aromatic skeletal vibrations; 1455  $\text{cm}^{-1}$ ,  $\text{CH}_2$  scissor; 1110  $\text{cm}^{-1}$ , C-O-C stretching; 1020  $\text{cm}^{-1}$ , C=S stretching; 750, 700  $\text{cm}^{-1}$ , aromatic in plane bending.

Analysis: Calcd:	$\text{C}_{14}\text{H}_{16}\text{OS}_2\text{K}$ :	C, 55.21;	H, 5.58
Found:		C, 55.40;	H, 5.77

S-Methyl trans-2-Methyl-1-Phenylcyclohexyl Xanthate.- The xanthate ester was prepared in the same manner as described previously. Potassium trans-2-methyl-1-phenylcyclohexyl xanthate (10 g.- 0.033 mole) was added to an Erlenmeyer flask (250 ml.) containing a solution of methyl iodide (7.1 g.- 0.05 mole) and hexane (150 ml.). The suspension was stirred over night at room temperature, filtered and the solvent removed in vacuo. The residual oil crystallized from petroleum ether (b.p. 30-60°). White needle-shaped crystals were obtained 5.6 g. (61%) m.p. 54-55°. The infrared spectrum was identical to that of the corresponding xanthate salt with an additional band at 1325  $\text{cm}^{-1}$ , indicating S- $\text{CH}_3$  stretching.

Analysis: Calcd:  $C_{15}H_{20}OS_2$ : C, 64.22; H, 7.14; S, 22.87  
Found: C, 64.08; H, 7.24; S, 22.71

Pyrolysis of S-Methyl trans-2-Methyl-1-Phenylcyclohexyl

Xanthate.— The xanthate ester (2.28 g.) was decomposed in a micro-distillation apparatus by immersing the reaction flask into an oil bath maintained at  $150^{\circ}$  for one hour. The pyrolysis proceeded smoothly and the olefinic product was collected as the distillate under reduced pressures (0.1 mm.) yielding 1.10 g. (78%),  $n_D^{25}$  1.5518. Vapour phase chromatographic analysis indicated that the product ratio was 4.5% 1-phenyl-2-methylcyclohexene and 94.5% 2-phenyl-3-methylcyclohexene. The retention time of each olefin was compared to authentic samples as previously described employing the F&M, model 720, silicone rubber column at  $140^{\circ}$ .

1-Methylcyclopentanol.— This compound was prepared according to the method of Bailey and Hale.<sup>17</sup> Methyl iodide (212.4 g.— 1.5 mole) was added to magnesium turnings (36.0 g.— 1.5 mole) in 250 ml. of anhydrous ether to give the methylmagnesium iodide. To this ethereal Grignard reagent was added redistilled cyclopentanone (84.0 g.— 1.0 mole) which was diluted in 200 ml. of anhydrous ether. The reaction mixture

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<sup>17</sup> W.J. Bailey and W.F. Hale, J. Am. Chem. Soc., **81**, 651 (1959).

was allowed to stir overnight. The Grignard complex was decomposed in the usual manner with a saturated solution of ammonium chloride. The ethereal layer was separated, washed with water, dried over anhydrous magnesium sulphate and the ether removed in vacuo. Fractional distillation of the resultant oil yielded 61 g. (61%) of 1-methylcyclopentanol, b.p. 48-49° (16 mm.), m.p. 35-36° (reported b.p. 43° (9 mm.), m.p. 36-37°).

Potassium 1-Methylcyclopentyl Xanthate.- The alcohol (10 g.- 0.1 mole) was reacted with potassium metal in 50 ml. of dry toluene (3.9 g.- 0.1 mole). The mixture was diluted with 300 ml. of anhydrous ether. Carbon disulfide (10.0 g.- 1.3 mole) in 100 ml. of anhydrous ether was slowly added. The mixture was stirred overnight. The potassium salt was removed by filtration, washed with anhydrous ether, and dried in vacuo. The average yield from three runs was 20.4 g. (92%).

S-Methyl 1-Methylcyclopentyl Xanthate.- The potassium salt (6.75 g.- 0.0315 mole) was suspended in 100 ml. of hexane and an equivalent of methyl iodide was added. The mixture was stirred overnight. The precipitated salts were removed by filtration and the hexane was removed in vacuo. The resultant yellow oil 6.0 g. (66%) was too unstable to be purified by distillation or column chromatography.

Pyrolysis of 1-Methylcyclopentyl Xanthate.- The 1-methylcyclopentyl xanthate (5.0 g.) was decomposed in the usual manner by heating in a micro-distillation apparatus over a steam bath. The xanthate ester decomposed smoothly and the olefin was collected at atmosphere pressure as the distillate, 1.32 g. (61%) b.p. 70-75°,  $n_D^{25}$  1.4288 (reported<sup>18</sup> b.p. 74°,  $n_D^{25}$  1.4281). Vapour phase chromatographic analysis indicated that the olefinic products were composed of 0-1% methylenecyclopentane and 100-99% 1-methylcyclopentene (Perkin-Elmer, Golay "R" column at 30°). The retention time of each olefin was identical to that obtained for the olefins produced on pyrolysis of 1-methylcyclopentyl hydrogen phthalate ester.<sup>19</sup>

1-Methylcycloheptanol.- Methylmagnesium iodide was prepared from the reaction of methyl iodide (156.2 g.- 1.1 mole) and magnesium turnings (26.7 g.- 1.1 mole) in 300 ml. of anhydrous ether. A solution of cycloheptanone (106 g.- 0.95 mole) in 200 ml. of anhydrous ether was added slowly. The reaction mixture was allowed to stir for thirty hours. The Grignard complex was decomposed in the usual manner with a saturated aqueous ammonium chloride solution. The ethereal layer was separated, dried, and the ether removed in

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18 W.J. Bailey and W.F. Hale, loc. cit.

19 Sample of this hydrogen phthalate was obtained from D. Fung. (K.G. Rutherford and D.P.C. Fung, loc. cit.).

vacuo. The resultant oil was fractionally distilled to yield 80 g. (73%) of 1-methylcycloheptanol b.p. 85-86°  $n_D^{24}$  1.4698 (reported<sup>20</sup> b.p. 45° (2 mm.)  $n_D^{25}$  1.4697).

Potassium 1-Methylcycloheptyl Xanthate.— The above alcohol (12.8 g.) was reacted with an equivalent of potassium metal in 50 ml. of dry toluene. The mixture was diluted with 300 ml. of anhydrous ether and carbon disulfide (10 g.— 0.13 mole) in 100 ml. anhydrous ether was added slowly. The mixture was stirred overnight. The potassium salt was removed by filtration, washed and dried in vacuo. The average yield from three runs was 8.2 g. (34%).

S-Methyl 1-Methylcycloheptyl Xanthate.— The xanthate ester was prepared in the usual manner. The above xanthate salt (8.3 g.) was suspended in a solution of hexane and methyl iodide. After stirring overnight the inorganic salts were removed by filtration and the solvent evaporated in vacuo. The resultant oil 2.4 g. (34%) proved too unstable for further purification.

Pyrolysis of S-Methyl 1-Methylcycloheptyl Xanthate.— The above xanthate ester was heated at 100° for one hour in a

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20 W.J. Bailey and W.F. Hale, J. Am. Chem. Soc., 81, 651 (1959).

micro-distillation apparatus. The olefin was collected as the distillate b.p. 68-70° (100 mm.). Vapour phase chromatographic analysis (Perkin-Elmer, Golay "R" column at 35°) indicated that the olefin distribution was 30% methylene-cycloheptane and 70% 1-methylcycloheptene. The retention time of each olefin was identical to that of the olefins obtained on pyrolysis of the corresponding hydrogen phthalate ester.<sup>21</sup>

S-Methyl t-Amyl Xanthate.- The xanthate salt was prepared from commercial t-amyl alcohol (8.8 g.- 0.1 mole) in the usual manner. The average yield from two runs was 16.9 g. (84%). The powdered salt was suspended in a solution of hexane containing an equivalent amount of methyl iodide. The mixture was filtered and the solvent removed in vacuo. The residual oil decomposed during attempted purifications by distillation and column chromatography. The xanthate ester did distill, 11.6 g. (82%), b.p. 66° (0.1 mm.),  $n_D^{25}$  1.5326, however, the product was very unstable. The infrared spectrum indicated that the product was the desired t-amyl xanthate ester; no alcohol band was observed.

Pyrolysis of S-Methyl t-Amyl Xanthate.- This xanthate ester

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<sup>21</sup> A sample of the hydrogen phthalate and the data was obtained from D. Fung (Thesis 1964).



(5.0 g.) was pyrolyzed by the general procedure. The olefin was collected as the distillate in an ice-cooled receiver flask 1.49 g. (84%). Vapour phase chromatographic analysis (Golay "R" column at 25°) indicated the presence of 54% 2-methyl-1-butene and 46% 2-methyl-2-butene. These retention times were compared to those obtained from the olefin product on pyrolysis of the corresponding hydrogen phthalate.

Separation of cis-2-Methylcyclohexanol.- A commercial sample of 2-methylcyclohexanol was fractionally distilled on a glass bead-packed distillation column. Samples of cis-2-methylcyclohexanol were collected b.p. 162-163°,  $n_D^{22}$  1.4633 (reported<sup>22</sup> b.p. 165°,  $n_D^{20}$  1.4640).

Potassium cis-2-Methylcyclohexyl Xanthate.- The cis-alcohol (11.4 g.- 0.1 mole) was reacted with an equivalent of potassium metal in anhydrous toluene (50 ml.). The mixture was then treated with carbon disulfide (10 g.- 0.13 mole). The salt was recovered by filtration, washed with anhydrous ether, and dried. The average yield of three reaction was 21.6 g. (95%).

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22 L.M. Jackman et. al., J. Chem. Soc., 1717 (1949).

S-Methyl cis-2-Methylcyclohexyl Xanthate.- The S-methyl xanthate was prepared in the usual manner. The potassium salt was suspended in hexane which contained an equivalent of methyl iodide. After stirring overnight, the mixture was filtered, and the solvent removed in vacuo. The resultant oil was distilled yielding S-methylcyclohexyl xanthate 6.95 g. (82%) b.p.  $71^{\circ}$  (0.1 mm.)  $n_D^{25}$  1.5463 (reported<sup>23</sup> b.p.  $110-112^{\circ}$  (5 mm.),  $n_D^{20}$  1.5490).

Pyrolysis of S-Methyl cis-2-Methylcyclohexyl Xanthate.-

The above xanthate ester (6.0 g.) was heated in a micro-distillation flask at  $240^{\circ}$  by means of a Wood's metal bath for three hours. The product obtained as the distillate 1.8 g. (60%) was identified by infrared spectrum and vapour phase chromatographic analysis to be 45% 1-methylcyclohexene and 55% 2-methylcyclohexene.

Separation of cis-2-t-Butylcyclohexanol.- The 2-t-butylcyclohexanol was obtained from Dow Chemical Co. as a mixture of the cis and trans isomers. The cis isomer was separated by the method described by Goering<sup>24</sup> as the p-nitrobenzoate derivative. The alcohol (20 g.- 0.13 mole) dissolved in

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<sup>23</sup> D.G. Botteron and G.P. Shulman, J. Org. Chem., 27, 2007 (1962).

<sup>24</sup> H.L. Goering, R.L. Reeves, and H.H. Espy, J. Am. Chem. Soc., 78, 4926 (1956).

pyridine (75 ml.) and cooled to 0°. p-Nitrobenzoyl chloride (26 g.- 0.14 mole) was added slowly with stirring. The mixture was allowed to warm to room temperature over a period of thirty minutes. The excess benzoyl chloride was destroyed by carefully adding 10 ml. of water. The mixture was then diluted with water (200 ml.), filtered and the filtrate washed with cold water. The compound was dried in vacuo. The p-nitrobenzoate ester was extracted with boiling petroleum ether (b.p. 90-100°). The extracts were filtered while hot to remove the insoluble p-nitrobenzoic acid. Crystals formed on cooling. Several recrystallizations from chloroform yielded 19 g. of cis-2-t-butylcyclohexyl benzoate m.p. 89-90° (reported m.p. 88.8-89.3°).

The ester was saponified with a 1.3N sodium hydroxide in 90% ethanol solution. The product was steam distilled from the alkaline medium and extracted with ether from the distillate. The extracts were dried and the ether and ethanol were removed. The residue was fractionally distilled to yield 9.2 g. of cis-2-t-butylcyclohexanol b.p. 97° (18 mm.) m.p. 56° ( reported b.p. 99-103° (23 mm.) m.p. 56.8-57.7°).

Potassium cis-2-t-Butylcyclohexyl Xanthate.- The cis- alcohol (9.2 g.- 0.059 mole) was reacted with potassium metal (2.34 g.- 0.059 mole) in anhydrous toluene. The mixture was diluted with anhydrous ether and an equivalent amount

of methyl iodide was added. The mixture was stirred overnight, then filtered and the hexane removed in vacuo. The xanthate ester crystallized in the refrigerator overnight. The yield obtained was 9 g. (70%). The ester was recrystallized from petroleum ether (b.p. 30-60°) m.p. 33.5-34°. Infrared spectra and elemental analysis indicated that it was the desired compound.

Analysis: Calcd: C, 58.49 H, 9.00 S, 26.02

Found: C, 58.45 H, 8.90 S, 26.13

Pyrolysis of S-Methyl cis-2-t-Butylcyclohexyl Xanthate.-

The S-methyl xanthate (3.5 g.) was heated in a 50-ml. one-necked, round-bottom flask fitted with a condenser at 200-205° for three hours. The residue was distilled at atmospheric pressure b.p. 165-170°,  $n_D^{24}$  1.4582. The yield of olefin obtained was 1.22 g. (69%). The 11.90 peak, which is characteristic of 1-t-butylcyclohexene, was absent from the infrared spectra. Gas chromatographic analysis (F&M, model 720, silicone rubber column at 100°) showed only one peak. The NMR spectrum<sup>25</sup> indicated that the compound was not 1-t-butylcyclohexene.

Data: JEOL JNM-C-60

Solution: 10% by volume in  $CDCl_3$

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<sup>25</sup> The author wishes to thank Dr. G. Wood of the University of Windsor for running this spectrum.

TMS internal standard

Singlet at  $\delta = 0.85$  (9 H)

Broad band with centre at  $\delta = 1.85$  (7 H)

Wide band at  $\delta = 5.66$  (2 H)

The singlet at  $\delta = 0.85$ , because of the integration area and  $\delta$ -position, was assigned to the protons of the t-butyl group. The wide band at  $\delta = 5.66$  was assigned to the olefin protons. The broad band at  $\delta = 1.85$  was assigned to the protons on the ring due to the integration area and the position of the band.

#### Thermal Decomposition Studies of Potassium Xanthate Salts

Pyrolysis Studies.- The general procedure for the pyrolysis of the potassium xanthate salts consisted of immersing the flask containing the xanthate into a Wood's metal bath which was maintained in the temperature range of 200-250° during the pyrolysis. The reaction flask (25-ml. Erlenmeyer) was equipped with a Claisen head, a condenser and an adapter with a receiving flask. The olefin formed, as the decomposition took place, distilled out of the reaction flask and was collected in the receiving flask. It was sometimes advantageous to conduct the decomposition under reduced pressure; this ensured that the olefin products were removed as fast as they were formed. This method reduced the contamination of the olefin by sulphur-containing impurities since it is known that mercaptans will add to olefins at

elevated temperatures.<sup>26</sup>

The crude olefinic products were subjected immediately to vapour phase chromatographic analysis. The mixtures were then filtered through a charcoal column or distilled from sodium to remove sulphur-containing contaminants. Vapour phase chromatographic analysis showed that these procedures did not alter the product distribution. It was also found that none of the olefinic mixtures under investigation rearranged on standing over long periods of time.

The pyrolysis procedure described above proved quite satisfactory for the decomposition of small amounts (3-4 g.) of xanthate salt with heating periods from thirty minutes to one hour. Larger runs (10-20 g.) were made by decomposing the potassium xanthate salt in a mineral oil bath. The xanthate was added by means of a powder addition flask to the mineral oil contained in a two-necked, round-bottomed flask (150-ml.) equipped with a Claisen head, a condenser and an adapter with a receiving flask. The mineral oil was preheated and maintained at 200° by means of a Wood's metal bath. The decomposition proceeded smoothly with slow addition of the salt. After the pyrolysis was completed the reaction flask was cooled to 100° and the olefinic product recovered by steam distillation. In general, this procedure

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<sup>26</sup> H. Hickinbottom, "Reactions of Organic Compounds", 2nd edition, Longmans Green and Co., London, 1948, p. 30.

gave smaller yields than the previous method but the products were purer.

Pyrolysis of Potassium trans-1,2-Dimethylcyclohexyl Xanthate.

The xanthate salt was pyrolyzed as previously described; an accurate weight (4.25 g.) of salt was heated for one hour under reduced pressure. The olefin was collected as it was formed. The average yield from four runs was 1.58 g. (83%). Vapour phase chromatographic analysis, as previously described, indicated that the isomer ratio was 9% 1,2-dimethylcyclohexene, 24% 2,3-dimethylcyclohexene and 57% methylene-2-methylcyclohexane.

This xanthate salt was also pyrolyzed in a heated mineral oil bath according to the procedure explained earlier. Potassium 1,2-dimethylcyclohexyl xanthate (10 g.- 0.044 mole) was added to a mineral oil bath maintained at 200°. The decomposition proceeded smoothly with the slow addition of the salt. When the addition had been completed the bath was maintained at 200° for an additional fifteen minutes and then cooled to 100°. The olefinic product was recovered by steam distillation and subsequent extraction of the distillate with ether. The ethereal layer was dried over sodium sulphate and then separated by filtration. The ether was then removed in vacuo. The resultant material was distilled b.p. 137-139°  $n_D^{25}$  1.4578 and 3.48 g.. (73%) were obtained.

The infrared spectra was identical to that obtained

in the previous pyrolysis. Vapour phase chromatographic analysis showed that the olefin ratios were also in agreement.

Pyrolysis of Potassium trans-2-Methyl-1-phenylcyclohexyl

Xanthate.- Potassium 2-methyl-1-phenylcyclohexyl xanthate (4.70 g.- 0.015 mole) was added to an Erlenmeyer flask (25 ml.) which was outfitted according to the procedure previously described. The flask was heated by means of a Wood's metal bath from 200-230° for a period of thirty minutes. Decomposition proceeded smoothly and the olefinic mixture distilled under reduced pressure (60 mm.). The crude product 2.4 g. (90%) was redistilled from metallic sodium to remove the sulphur odour b.p. 120-122° (12 mm.)  $n_D^{20}$  1.5506. The olefinic mixture was analyzed, by vapour phase chromatography as previously described, indicating the presence of 6.5% 1-phenyl-2-methylcyclohexene and 93.5% 2-phenyl-3-methylcyclohexene.

Pyrolysis of Potassium 1-Methylcyclopentyl Xanthate.- The potassium salt was pyrolyzed in the usual manner, by heating in a flask as a dry powder. The salt (4.20 g.) was decomposed in a micro-distillation apparatus heated by means of a Wood's metal bath at 220-230° for thirty minutes. The distilled product 1.6 g. (81%) was obtained; b.p. 75-76°,  $n_D^{23}$  1.4320. The product did not show any absorption in the



alcohol region of the infrared spectrum. Vapour phase chromatographic analysis (Golay "R" column at 30°) indicated that the products ratio was 0-1% methylenecyclopentane and 100-99% 1-methylcyclopentene.

Pyrolysis of Potassium t-Amyl Xanthate.- The xanthate salt (4.2 g.) was pyrolyzed in the usual manner at 200-220°. The olefin product 1.4 g. (72%) was collected as the distillate. Vapour phase chromatographic analysis indicated the presence of 54% 2-methyl-2-butene and 46% 2-methyl-1-butene. The retention time of each olefin was identical to that of xanthate ester decomposition products.

1-Methylcyclohexanol.- A solution of methylmagnesium iodide was prepared by adding methyl iodide (156.2 g.- 1.1 mole) to magnesium turnings (27.6 g.- 1.1 mole) in 500 ml. of anhydrous ether. To this ethereal Grignard solution was added cyclohexanone (84.0 g.- 1.0 mole) dissolved in 200 ml. of anhydrous ether. The Grignard complex was decomposed in the usual manner and the ether layer separated and dried. The ether was then removed in vacuo. Fractional distillation of the resultant oil gave 1-methylcyclohexanol, b.p. 63-64°;  $n_D^{25}$  1.4626 (reported<sup>27</sup> b.p. 56.5°;  $n_D^{25}$  1.4610).

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27 W.A. Mosher, J. Am. Chem. Soc., 62, 552 (1940).

Potassium 1-Methylcyclohexyl Xanthate.- 1-Methylcyclohexanol (11.4 g.- 0.1 mole), diluted with 50 ml. of anhydrous toluene, was reacted with potassium metal (3.9 g.- 0.1 mole). The solution was then diluted with 200 ml. of anhydrous ether. A solution of carbon disulfide (10 g.- 1.3 mole) in 100 ml. of anhydrous ether was added slowly with constant stirring; a precipitate was obtained immediately. The mixture was stirred overnight. The xanthate salt was removed by filtration and washed thoroughly with anhydrous ether. After drying in vacuo, the product weighed 18.8 g. (82.5%).

Pyrolysis of Potassium 1-Methylcyclohexyl Xanthate.- The pyrolysis was carried out in a heated oil bath as previously outlined. The xanthate salt (16.1 g.- 0.075 mole) was added to the preheated oil bath which was maintained at 200-220°. After the addition was completed the temperature was held for another fifteen minutes to ensure complete decomposition. The olefinic product was steam distilled, extracted with ether and dried over anhydrous sodium sulphate. The ether was removed in vacuo. The residue was then distilled b.p. 101-110°;  $n_D^{23}$  1.4492. The yield was 4.99 g. (74%). The infrared spectrum showed absorption at 6.15 and 11.25  $\text{cm}^{-1}$  indicating the presence of methylenecyclohexane. Vapour chromatographic analysis (Perkin-Elmer 700, Golay "R" column at 60°) gave two peaks the larger of which had the same retention time as an authentic sample of 1-methylcyclohexene.

It was calculated that the olefin ratio was 18% methylene-cyclohexane and 82% 1-methylcyclohexene.

This compound was also pyrolyzed by heating in a flask as a dry powder. The salt (3.76 g.) was heated at 200-220° for thirty minutes. The product collected (1.23 g.- 78%;  $n_D^{24}$  1.4488) was analyzed by gas chromatography which gave the same retention times as above and the peaks were in the same ratio.

1-Ethylcyclohexanol.- An ethereal solution of ethylmagnesium bromide was prepared from ethyl bromide (119.9 g.- 1.1 mole) and magnesium turnings (26.7 g.- 1.1 mole). Cyclohexanone (98 g.- 1.0 mole) in 250 ml. anhydrous ether was added slowly. The decomposition of the Grignard complex was carried out in the usual manner. The ethereal layer was separated, dried, and the ether removed in vacuo. The resultant oil yielded on fractional distillation 77 g. (61%) of 1-ethylcyclohexanol (b.p. 80° (20 mm.),  $n_D^{25}$  1.4621). The constants reported were b.p. 78° (20 mm.),  $n_D^{20}$  1.4640.<sup>28</sup>

Potassium 1-Ethylcyclohexyl Xanthate.- 1-Ethylcyclohexanol (12.8 g.- 0.1 mole) in 50 ml. of anhydrous ether were reacted with metallic potassium (3.91 g.- 0.1 mole). The mixture was diluted with anhydrous ether and a solution of

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28 W.A. Mosher, J. Am. Chem. Soc., 62, 552 (1940).

carbon disulfide added dropwise with constant stirring. The xanthate salt was separated by filtration, washed with anhydrous ether, and dried in vacuo. The product obtained weighed 22.1 g. (84%).

Pyrolysis of Potassium 1-Ethylcyclohexyl Xanthate.- This compound was pyrolyzed in the usual manner by heating in a flask as a dry powder. The salt (4.12 g.) was heated at 200-220° for thirty minutes. The yield of olefin was 1.5 g. (80%) b.p. 134°,  $n_D^{23}$  1.4557. Gas phase chromatographic analysis indicated that the product ratio was 89% 1-ethylcyclohexene and 11% ethylidenecyclohexane.

1-Isopropylcyclohexanol.- An ethereal solution of isopropyl magnesium bromide was prepared from 2-bromopropane (135.3 g.- 1.1 mole) and magnesium turnings (26.7 g.- 1.1 mole). Cyclohexanone (98 g.- 1.0 mole) which was dissolved in 250 ml. anhydrous ether was added slowly. Decomposition of the Grignard complex was carried out in the usual manner. The ether layer was separated, dried and the ether removed in vacuo. The resultant liquid on fractional distillation yielded 1-isopropylcyclohexanol b.p. 76-78° (10 mm.);  $n_D^{23}$  1.4671 (reported<sup>29</sup> b.p. 76-78° (10 mm.);  $n_D^{20}$  1.4683).

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29 K. Auwers and P. Ellinger, Ann., 387, 200 (1912).

Potassium 1-Isopropylcyclohexyl Xanthate.- 1-Isopropylcyclohexane (9.6 g.- 0.068 mole) in 50 ml. of anhydrous toluene was reacted with metallic potassium (2.68 g.- 0.068 mole). This mixture was then diluted with 200 ml. of anhydrous ether. A solution of carbon disulfide (10 g.- 0.13 mole) in 150 ml. of anhydrous ether was added dropwise with constant stirring. The xanthate salt was separated by filtration, washed thoroughly with anhydrous ether and dried in vacuo. The product obtained weighed 15.7 g. (83%). The infrared spectrum indicated that the compound was potassium 1-isopropylcyclohexyl xanthate.

Pyrolysis of Potassium 1-Isopropylcyclohexyl Xanthate.- The xanthate salt (12.8 g.- 0.05 mole) was pyrolyzed in an oil bath in the usual manner. The temperature of the bath was maintained at 180-200° during the addition of the salt. After the addition was complete the bath was held at 200° for an additional fifteen minutes. The olefinic product was recovered from the oil by steam distillation and by extraction with ether from the distillate. The ether layer was dried and the ether removed in vacuo. Fractional distillation of the residue yielded 4.97 g. (80.8%) b.p. 150-165°;  $n_D^{23}$  1.4608. The infrared spectrum and vapour phase chromatographic analysis indicated the olefinic product was 18% isopropylidene-cyclohexane and 82% isopropylcyclohexene.

Pyrolysis of Potassium cis-2-Methylcyclohexyl Xanthate.-

The xanthate salt (4.21 g.) was pyrolyzed as the dry powder in the usual manner at 220-240°. The product obtained by distillation (1.72 g.) proved to be a mixture of 66% 2-methylcyclohexanol and 34% olefin. Gas chromatographic analysis of the olefin indicated that the olefin ratio was 49% 1-methylcyclohexene and 51% 2-methylcyclohexene.

Dimethylcyclohexylcarbinol.- An ethereal solution of cyclohexylmagnesium bromide was prepared from cyclohexyl bromide (90 g.- 0.55 mole) and magnesium turnings (13.4 g.- 0.55 mole). Acetone (29 g.- 0.5 mole) in anhydrous ether (200 ml.) was added slowly. The decomposition of the Grignard complex with ammonium chloride solution was carried out in the usual manner. The ethereal layer was separated, dried over magnesium sulphate, and the ether removed in vacuo. The resultant oil yielded on fractional distillation 28.4 g. (40%) of dimethylcyclohexylcarbinol b.p. 86° (14 mm.)  $n_D^{23}$  1.4682 (reported<sup>30</sup> b.p. 85-86° (14 mm.)  $n_D^{12}$  1.4720).

Potassium Dimethylcyclohexylcarbinyl Xanthate.- The alcohol (7.1 g.- 0.05 mole) was reacted with an equivalent of potassium metal in dry toluene. The mixture was diluted with

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<sup>30</sup> R.A. Benkeser and J.J. Hazdra, J. Am. Chem. Soc., 81, 228 (1959).

anhydrous ether and carbon disulfide (5 g.- 0.6 mole) was added. After stirring overnight the salt was recovered by filtration, washed with dry ether, and dried in vacuo. The resultant yellow powder weighed 10.2 g. (81%).

Pyrolysis of Potassium Dimethylcyclohexylcarbinyl Xanthate.-

The salt was pyrolyzed in the usual manner. The powdered xanthate (4.12 g.) was heated at 230° for thirty minutes in a micro-distillation apparatus. The product obtained was redistilled yielding 1.42 g. (71%) of olefin b.p. 150-165°. Vapour phase chromatographic analysis indicated that the product distribution was 19% isopropylidenecyclohexane and 81% 2-cyclohexylpropylene.

Potassium Cyclohexylcarbinyl Xanthate.- Cyclohexylcarbinol

(11.4 g.- 0.1 mole) was reacted with an equivalent of potassium metal in 50 ml. of dry toluene. After dilution of this mixture to 300 ml. with anhydrous ether, carbon disulfide (10 g.- 0.13 mole) was added slowly. The mixture was allowed to stir overnight. The potassium salt was recovered by filtration, washed, and dried in vacuo. The potassium cyclohexylcarbinyl xanthate obtained weighed 20.4 g. (89%).

Pyrolysis of Potassium Cyclohexylcarbinyl Xanthate.- The

potassium salt (4.62) was pyrolyzed in a micro-distillation apparatus in the usual manner. The reaction flask was

immersed in a Wood's metal bath held at 230-240° for thirty minutes. The infrared spectrum indicated that the distillate was composed of cyclohexylcarbinol and methylene-cyclohexane. Fractional distillation of this mixture yielded 60% of alcohol and 40% of the olefinic product.

Potassium Isoamyl Xanthate.- Isoamyl alcohol (8.8 g.- 0.1 mole) was reacted with an equivalent of potassium metal in 50 ml. of dry toluene. The mixture was diluted with 300 ml. of anhydrous ether. Carbon disulfide (10 g.- 0.13 mole) in 100 ml. of anhydrous ether was added slowly. The mixture was allowed to stir for twelve hours. The potassium salt was recovered by filtration, washed, and dried in vacuo. The potassium isoamyl xanthate obtained weighed 18.4 g. (91%).

Pyrolysis of Potassium Isoamyl Xanthate.- The potassium salt (4.23 g.) was pyrolyzed in a micro-distillation apparatus. The flask was heated by means of a Wood's metal bath for thirty minutes at 230-240°. The infrared spectrum indicated that the distillate was composed of isopentanol and olefinic products. Fractional distillation of this mixture yielded 73% isoamyl alcohol and 27% isoamylene.

Potassium 3-Methylcyclohexyl Xanthate.- The 3-methylcyclohexanol (11.4 g.- 0.1 mole) was reacted with an equivalent



of potassium metal in 50 ml. of dry toluene. The mixture was diluted with 300 ml. anhydrous ether and a solution of carbon disulfide (10 g.- 0.13 mole) in 100 ml. anhydrous ether was added slowly. The mixture was allowed to stir overnight. The potassium salt was recovered by filtration, washed, and dried in vacuo. The salt obtained weighed 20.9 g. (92%).

Pyrolysis of Potassium 3-Methylcyclohexyl Xanthate.- The potassium salt (16.8 g.) was pyrolyzed in a preheated mineral oil bath as previously described. The powdered salt was added slowly from a powder funnel into a mineral oil bath which was maintained at 230-240°. This temperature was held for fifteen minutes after the addition was completed. The pyrolysis products were steam distilled out of the mineral oil, extracted with ether, and dried over magnesium sulphate. The solution was fractionally distilled. The decomposition products were composed of 61% 3-methylcyclohexanol and 39% olefin product (b.p. 104-110°).

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