THE CONVERSION OF PINONIC ACID
INTO HOMOTERFENYL METHYL KETONE AND INTO
2:4-DIMETHYLPHENYLACETIC ACID

Being a Thesis submitted to the
University of London
for the Degree of
Doctor of Philosophy

by

GORDON JOHN BENNETT B.Sc. (LOND.)

SEPTEMBER 1955
ABSTRACT OF THESIS

The rearrangement of trans-pinonic acid into homoterpenyl methyl ketone has been studied in order to elucidate its mechanism. Relatively strong acid-catalysis is necessary for the rearrangement to occur, and the rate of reaction depends upon the strength of the acidic solvent employed. In monochloroacetic acid at 100°, the rearrangement is of the first order with regard to pinonic acid. Formation of homoterpenyl methyl ketone is accompanied by isomerisation of trans-pinonic acid into cis-pinonic acid, which also rearranges to the ketolactone. An intramolecular mechanism is proposed for the rearrangement.

An attempt has been made to determine the mechanism of the conversion of pinonic acid and homoterpenyl methyl ketone into 2,4-dimethylphenylacetic acid by the action of bromine. With pinonic acid, the initial reaction results in the formation of α-bromo-pinonic acid, which has been isolated and characterised. It is believed that under conditions of strong acid-catalysis this readily rearranges to α-bromo-homoterpenyl methyl ketone, which is probably also formed by the action of bromine upon homoterpenyl
methyl ketone. The subsequent cyclisation of the bromo-ketolactone yields 2:4-dimethylphenylacetic acid. Mechanisms of bromination and of cyclisation are discussed.

Pinoic acid is rapidly converted into homoterpenyl methyl ketone when heated with phosphoric acid at 100°. Further heating causes decomposition, with loss of carbon dioxide. 2:4-Dimethylphenylacetic acid is found among the products, which represent the result of a complex process of hydrogen transfer associated with dehydration and decarboxylation. 1:2:4-Trimethyl benzene, 1:2:4-trimethyl cyclohexene, and the lactone of 2-hydroxy 2:4-dimethyl cyclohexylacetic acid have also been identified as products of the reaction. A study of the reactions of the products and of compounds similar to those likely to be present in the reaction-mixture, has afforded evidence relating to the probable mechanism of the reaction.
The work described in this Thesis has been carried out in the Chemical Research Laboratories of Battersea Polytechnic, under the direction of Dr. F. R. Goss. The author wishes to record his appreciation of the guidance and encouragement given by Dr. C. L. Arcus, and to thank Dr. Goss for his interest in this work.

Acknowledgment is given to the Department of Scientific and Industrial Research for the award of a Maintenance Allowance.
CONTENTS

Introduction

Homoterpenyl Methyl Ketone........................................ 1
Pinonic Acid............................................................. 4
The Conversion of Pinonic Acid into
   2:4-Dimethylphenylacetic Acid................................. 11
The Phosphoric Acid - Catalysed
   Decomposition of Pinonic Acid............................. 14

Discussion

The Mechanism of the Rearrangement of Pinonic
   Acid into Homoterpenyl Methyl Ketone.................... 15
The Conversion of Pinonic Acid into
   2:4-Dimethylphenylacetic Acid by the Action
   of Bromine and Hydrochloric Acid......................... 25
The Phosphoric Acid - Catalysed Decomposition
   of Pinonic Acid: the Products and
   Mechanism of the Reaction................................. 36

Summary and Conclusions............................................ 53
The Mechanism of the Rearrangement of Pinonic Acid into Homoterpenyl Methyl Ketone

Experimental

<table>
<thead>
<tr>
<th>CONTENTS (contd.)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Mechanism of the Rearrangement of Pinonic Acid into Homoterpenyl Methyl Ketone</td>
<td>1</td>
</tr>
<tr>
<td>α-Pinene</td>
<td>1</td>
</tr>
<tr>
<td>Preparation of trans-pinonic acid</td>
<td>1</td>
</tr>
<tr>
<td>(±)-trans-Pinonic acid</td>
<td>2</td>
</tr>
<tr>
<td>(+)-trans-Pinonic acid</td>
<td>3</td>
</tr>
<tr>
<td>(±)-Homoterpenyl methyl ketone</td>
<td>4</td>
</tr>
<tr>
<td>Rearrangement in the acidic solvents of Table I</td>
<td>5</td>
</tr>
<tr>
<td>Table I: The Conversion of (±)-trans-Pinonic Acid into (±)-Homoterpenyl Methyl Ketone</td>
<td>7</td>
</tr>
<tr>
<td>Rate of Rearrangement (i)</td>
<td>8</td>
</tr>
<tr>
<td>Table II: The Rearrangement and Isomerisation of Pinonic Acid in Monochloroacetic Acid at 100°.10</td>
<td></td>
</tr>
<tr>
<td>Rate of Rearrangement (ii)</td>
<td>11</td>
</tr>
<tr>
<td>Table III</td>
<td>11</td>
</tr>
<tr>
<td>(+)-Homoterpenyl Methyl Ketone: Mutarotation of Solutions of Pinonic Acid in Monochloroacetic Acid</td>
<td>12</td>
</tr>
</tbody>
</table>
CONTENTS (contd.)

Experimental

Table IV: The Mutarotation of Solutions of (+)-trans-Pinonic Acid in Monochloroacetic Acid at 100\degree ......................... 14

The Formation of 2:4-Dimethylphenylacetic Acid from Pinonic Acid by the action of Bromine........... 15

2:4-Dimethylphenylacetic acid (i)...................... 15
2:4-Dimethylphenylacetic acid (ii)..................... 17
2:4-Dimethylphenylacetic acid (iii)................... 18
Bromo-pinonic acid........................................ 19
Reduction of Bromo-pinonic Acid to Pinonic Acid,... 20
Rearrangement of Bromo-pinonic Acid to 2:4-Dimethylphenylacetic Acid................................. 22

(1) Preparation of hydrochloric-hydrobromic acid mixture............................................. 22

(ii) Rearrangement of the bromo-acid............... 23

Attempt to isolate the bromo-acid without keeping the reaction temperature below 30\degree ........ 24
## Experimental

<table>
<thead>
<tr>
<th>Experimental</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:4-Dimethylphenylacetic Acid from</td>
<td>25</td>
</tr>
<tr>
<td>Homoterpenyl Methyl Ketone</td>
<td></td>
</tr>
<tr>
<td>The rearrangement of (±)-trans-pinonic acid to homoterpenyl methyl ketone</td>
<td>27</td>
</tr>
<tr>
<td>under conditions similar to those employed in the bromination of pinonic</td>
<td></td>
</tr>
<tr>
<td>acid</td>
<td></td>
</tr>
<tr>
<td>The Phosphoric Acid - Catalysed Decomposition</td>
<td>29</td>
</tr>
<tr>
<td>Decomposition of Pinonic Acid in Phosphoric Acid Solution</td>
<td>29</td>
</tr>
<tr>
<td>(i) Extract from the aqueous distillate</td>
<td>31</td>
</tr>
<tr>
<td>(ii) The oil obtained during the steam distillation</td>
<td>32</td>
</tr>
<tr>
<td>(iii) The resin remaining after steam distillation</td>
<td>34</td>
</tr>
<tr>
<td>(iv) The product extracted from the residual aqueous phosphoric acid</td>
<td>35</td>
</tr>
<tr>
<td>(v) 2:4-Dimethylphenylacetic acid</td>
<td>35</td>
</tr>
</tbody>
</table>
## CONTENTS (contd.)

### Experimental

<table>
<thead>
<tr>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Decomposition of Finonic Acid in Phosphoric Acid Solution</td>
<td>36</td>
</tr>
<tr>
<td>(i) 2,4-Dimethylphenylacetic acid</td>
<td>38</td>
</tr>
<tr>
<td>(ii) Examination of the hydrocarbon fractions b.p. 144-166°</td>
<td>38</td>
</tr>
<tr>
<td>(iii) Quantitative nitration</td>
<td>38</td>
</tr>
<tr>
<td>(iv) Attempted ozonolysis of the low-boiling mixture of hydrocarbons</td>
<td>40</td>
</tr>
<tr>
<td>Oxidation of the Lactone $C_{10}H_{16}O_2$</td>
<td>41</td>
</tr>
<tr>
<td>Preparation of $\delta$-n-Butyl-$\gamma'$-dimethyl-$\gamma$-butyrolactone by Reduction of Homoterpenyl Methyl Ketone</td>
<td>41</td>
</tr>
<tr>
<td>(i) Hydrazone of ($\pm$)-homoterpenyl methyl ketone</td>
<td>41</td>
</tr>
<tr>
<td>(ii) Decomposition of the hydrazone</td>
<td>42</td>
</tr>
<tr>
<td>Reduction of ($\pm$)-Homoterpenyl Methyl Ketone without Isolation of the Hydrazone</td>
<td>43</td>
</tr>
<tr>
<td>Determination of equivalent</td>
<td>45</td>
</tr>
<tr>
<td>Preparation of 2-Methyl cyclohexanol</td>
<td>46</td>
</tr>
<tr>
<td>Dehydration of 2-Methyl cyclohexanol</td>
<td>47</td>
</tr>
</tbody>
</table>
## CONTENTS (contd.)

**Experimental**

<table>
<thead>
<tr>
<th>Topic</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preparation of 1:2-Dimethyl cyclohexanol</td>
<td>48</td>
</tr>
<tr>
<td>Dehydration of 1:2-Dimethyl cyclohexanol</td>
<td>49</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>50</td>
</tr>
<tr>
<td>Comparative rates of hydrogenation</td>
<td>51</td>
</tr>
<tr>
<td>Method of Hydrogenation</td>
<td>51</td>
</tr>
<tr>
<td>Results of Hydrogenation</td>
<td></td>
</tr>
<tr>
<td>(i) Cyclohexene</td>
<td>53</td>
</tr>
<tr>
<td>(ii) 1-Methyl cyclohexene</td>
<td>53</td>
</tr>
<tr>
<td>(iii) 1:2-Dimethyl cyclohexene</td>
<td>54</td>
</tr>
<tr>
<td>(iv) &quot;1:2:4-Trimethyl cyclohexene/(\gamma)-cumene mixture&quot;</td>
<td>54</td>
</tr>
<tr>
<td>Decarboxylation of Pinonic Acid, (\alpha)-n-Butyl-(\gamma) dimethyl-(\gamma)-butyrolactone, and the Lactone of 2-Hydroxy 2:4-dimethyl cyclohexylacetic acid.</td>
<td>55</td>
</tr>
<tr>
<td>Table V: Results of Comparative Decarboxylation</td>
<td>56</td>
</tr>
<tr>
<td>The Resistance of 2:4-Dimethylphenylacetic Acid to Decarboxylation.</td>
<td>57</td>
</tr>
<tr>
<td>The Decarboxylation of the Lactone of 2-hydroxy 2:4-dimethyl cyclohexylacetic Acid</td>
<td>57</td>
</tr>
</tbody>
</table>
## INDEX OF ILLUSTRATIONS

<table>
<thead>
<tr>
<th>Fig.</th>
<th>Caption</th>
<th>(follows) page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The Determination of First-Order Kinetics for the Formation of Homoterpenyl Methyl Ketone</td>
<td>16</td>
</tr>
<tr>
<td>2, 3</td>
<td>The Rotatory Power of Solutions of Pinonic Acid in Monochloroacetic Acid at 100°</td>
<td>16</td>
</tr>
<tr>
<td>4</td>
<td>The Rearrangement and Isomerisation of Pinonic Acid in Monochloroacetic Acid</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>The Mechanism of the Rearrangement of Pinonic Acid into Homoterpenyl Methyl Ketone</td>
<td>20</td>
</tr>
<tr>
<td>6</td>
<td>The Products and Mechanism of the Decomposition of Pinonic Acid in Phosphoric Acid</td>
<td>47</td>
</tr>
<tr>
<td>7</td>
<td>Apparatus for the Determination of Comparative Rates of Decarboxylation (exptl.)</td>
<td>55</td>
</tr>
</tbody>
</table>
INTRODUCTION
Homoterpenyl Methyl Ketone

Since Baeyer (Ber., 1895, 29, 326) showed that his "α-Pinonic acid" was isomerised to homoterpenyl methyl ketone by heating at 100° with 50% aqueous sulphuric acid, there has been no attempt to investigate the mechanism of the reaction, and no satisfactory explanation of its course has been put forward, though it has often been employed for preparation of the ketolactone.

Previously to Baeyer's work, Wallach had isolated the same ketolactone from the degradation products of α-terpineol, and deduced the correct structural formula for it (Ber., 1895, 28, 1775). This formula was confirmed almost at once by Tiemann and Semmler (ibid. 1778), who obtained the same compound by the oxidation of pinene. The above authors characterised homoterpenyl methyl ketone by elementary analysis of the ketolactone and of its oxime, by determination of its equivalent by titration, and by its degradation to homoterpenylic and terpenylic acids.

Wallach, Tiemann and Semmler, and Baeyer were all dealing with optically inactive homoterpenyl methyl ketone, which was later synthesised by J. Owen and J. L. Simonsen (J., 1932, 1424) by a route which confirmed its structural formula.
The optically-active isomers of homoterpenyl methyl ketone were first prepared by Barbier and Grignard (Bull. Soc. Chim. de France, 1910, 7, 548) by applying the method of Baeyer to the (+)- and (-)-pinonic acids which they had obtained in the crystalline state. More recently, Delépine and Badoche (Comptes Rendus, 1952, 235, 1455) have prepared (+)-homoterpenyl methyl ketone by the same method, the product having properties in agreement with those previously recorded. Without citing experimental evidence,
these authors proposed the following scheme for the rearrangement:

\[ (4) \quad \rightarrow \quad (5) \quad \rightarrow \quad (3) \]

The rearrangement of pinonic acid into homoterpenyl methyl ketone in media other than aqueous sulphuric acid has not hitherto been studied.

**Pinonic Acid**

Early accounts of the oxidation of pinene often appeared to be contradictory because of the variety of methods used, and the non-homogeneity of the pinene. The hydrocarbon used was a mixture of (+)- and (-)-\(\alpha\)-pinenes in unspecified ratios, and also contained unknown proportions of \(\beta\)-pinene and other hydrocarbons. Consequently, pinonic acid was obtained in solid and in liquid forms, and considerable divergence was shown in the recorded physical properties.

Pinonic acid exhibits geometrical isomerism and each isomer is asymmetric.
The (+)-, (-)-, and (±)- forms of trans-pinonic acid are crystalline solids which have been fully characterised. Only the (-)- form of cis-pinonic acid has been obtained in the pure state, and this is a liquid (Delépine and Badoche, Ann. Chim., 1950, 5, 153-163). (+)- and (±)-cis-Pinonic acids are also liquids, but have not been obtained in a high state of purity.

Throughout the present work, the trans-configuration has been adopted for the solid series of pinonic acids (+)-, (-)-, and (±)-. This is the same as that adopted by Simonsen and Owen ("The Terpenes"), but opposite to that assumed by Delépine (loc. cit.) and others. No essential alteration to the mechanisms which have been deduced (below) becomes necessary if these authors' configurations are adopted.

Evidence relating to the geometrical configuration is summarised below. In all degradations referred to, the
The pinonic acid used was the solid isomer (active or inactive) here called "trans". Baeyer showed that pinonic acid could be degraded stepwise to norpinic acid (Ber., 1896, 29, 3, 1909), the cis-configuration of which was later demonstrated by Perkin and Simonsen (J., 1909, 1176).
Later work has shown that changes of configuration may occur at several points in this scheme (Guha, Ganapathi, and Subramanian, Ber., 1936, 70, 1505; and Grandperrin, Ann. Chim., 1936, 6, 5). In particular, Grandperrin showed that the active (+)-pinic acid obtained in the first stage of the degradation, may have the trans-configuration, since he failed to bring about cyclisation by a variety of methods. A change of configuration at this stage is possible, because a strongly alkaline reagent was used. It has been shown by Delépine (Bull. Soc. Chim. de France, 1936, 3, 1369) that in an alkaline solution, both cis- and trans-pinonic acids are converted into a mixture of both forms (via the enol).

Cyclisation of the amine derived from the oxime of pinonic acid has been claimed by Gallas and Montañés (Anal. Fís. Quím., 1930, 1196).
(15) \[ \text{Na}_2\text{C}_3\text{H}_7\text{OH} \rightarrow \text{then HCl} \]

(16)

Schotten-Baumann benzoylation

\[ \text{(17)} \]

\[ \text{Ac}_2\text{O} \]
It was not found possible however, to characterise the amino pinocamphone and it is not unlikely that changes of configuration occur during the course of these reactions.

The synthesis of (±)-pinonic acid from diethyl trans-pinate by Rao (J. Indian Chem. Soc., 1943, 20, 97) gave a mixture of cis- and trans-isomers, as might be expected from the use of alkaline hydrolysis in the final stage. The semicarbazone of the product was compared with the semicarbazone prepared from a mixture of cis- and trans-pinonic acids which was obtained by treating solid (trans-) pinonic acid with alkali.
I V

Partial Hydrol.

EtOCOCCH₂ (19) → HOCOCCH₂ (20) → Cl.COCH₂ (21)

COOBt

Ph₂NH

COCl

Ph₂N.CO.CH₂ (23)

Ph₂N.CO.CH₂ (22)

SOCI₂

ZnMeI

Ph₂N.CO (25)

CO.CH₃

KOH/MeOH

CO.CH₃

CH₂

CH₂

Ph₂N.CO (4)
The Conversion of Pinonic Acid into 2:4-Dimethylphenylacetic Acid

The formation of 2:4-dimethylphenylacetic acid by the action of bromine upon pinonic acid, was first observed by Barbier and Grignard (Comptes Rendus, 1909, 149, 646) who used the following procedure:

(±)-trans-Pinonic acid (1 mol.), bromine (1 mol.), and water (19 mol.) were heated together at 100° for 14 hr. in an enamelled autoclave. The product was neutralised (Na₂CO₃), and fractionally precipitated with hydrochloric acid. 2:4-Dimethylphenylacetic acid was identified by its m.p., elementary analysis, and m.p. of the amide.

This method was investigated and improved by Harispe (Ann. Chim., 1936, [XI], 6, 249) who employed the following technique:

Pinonic acid (1 mole., 184 g.), bromine (1 mole., 160 g.) and hydrochloric acid (344 g., d 1.19) were shaken together, with cooling, until the initial reaction subsided. The clear amber-coloured solution was then decomposed by heating in a boiling water-bath for 3 hr. Crude 2:4-dimethylphenylacetic acid separated as a solid crust; the pure acid was isolated by esterification, followed by
distillation, and hydrolysis of the ester. An overall yield of 69% of the theoretical (based on pinonic acid) was obtained.

By adding to ice the solution obtained after the initial reaction, Harispe obtained an unidentified and uncharacterised oily substance, containing bromine in quantity approximating to that required for the hypothetical monobromo-pinonic acid. Similar results were obtained by the action of bromine upon homoterpenyl methyl ketone.

Without further evidence, Harispe proposed the following reaction scheme:-
A similar mechanism was proposed for the formation of 2:4-dimethylphenylacetic acid (30) from homoterpenyl methyl ketone, (27) being the initial product of bromination.
The Phosphoric Acid-Catalysed Decomposition of Pinonic Acid.

When pinonic acid is heated with syrupy phosphoric acid, homoterpenyl methyl ketone is first formed; it decomposes on further heating, with loss of carbon dioxide. This decomposition has not hitherto been reported, and was found to occur in the course of an investigation into the possibility of forming carbocyclic compounds related to 2:4-dimethylphenylacetic acid, by removal of the elements of water from homoterpenyl methyl ketone.
DISCUSSION

p. 15  The Mechanism of the Rearrangement of Pinonic Acid into Homoterpenyl Methyl Ketone.

p. 25  The Conversion of Pinonic Acid into 2:4-Dimethylphenylacetic Acid by the Action of Bromine and Hydrochloric Acid.

p. 36  The Phosphoric Acid - Catalysed Decomposition of Pinonic Acid; the Products and Mechanism of the Reaction.
The Mechanism of the Rearrangement of Pinonic Acid into Homoterpenyl Methyl Ketone

Before the kinetic measurements described below were carried out, the rearrangement of pinonic acid into homoterpenyl methyl ketone was studied in solvents other than 50% aqueous sulphuric acid, the only solvent hitherto used for this rearrangement. The percentage of conversion into the ketolactone, after the stated times, was determined with a variety of acid solvents at 100°, the results being collected in Table I. The ketolactone was separated from residual pinonic acid by extraction of the latter with dilute ammonia, which does not affect the ketolactone.

It is apparent from Table I that rearrangement is rapid in the strongly acidic media, phosphoric, trichloroacetic, and 99% formic acids, while acetic acid is without effect, and monochloroacetic and 90% formic acids occupy intermediate positions.

The reaction proceeds smoothly without formation of by-products; prolonged heating in phosphoric acid causes decomposition of the product. This is discussed elsewhere (p. 36). In the presence of 0.1 molecular proportion of the
corresponding sodium salt, the yield of ketolactone in monochloroacetic and formic acids was greatly reduced (experiments 9 and 10, to be compared with experiments 2 and 5 of Table I). This effect is believed to be due to the depression of hydrogen-ion concentration brought about by the presence of the salts, which supply a much increased concentration of the common anion.

**Kinetic Measurements**

Monochloroacetic acid was selected for the solvent to be used in kinetic measurements, as the reaction proceeded at a favourable rate in this acid. Furthermore its vapour pressure at 100° is not too great, and the solution remains quite clear, without much discolouration during the reaction. The rate of rearrangement at 100° in this solvent was determined by isolation of the ketolactone after the recorded intervals (Table II). By plotting the logarithm of the reciprocal of the concentration of pinonic acid remaining, against time, a straight line was obtained \( k_1 = 9.3 \times 10^{-2} \text{ hr}^{-1} \) (Fig. 1). As it was necessary to prepare the solutions at a temperature (80°) above the m.p. of monochloroacetic acid (62°), some rearrangement had already taken place when the
Fig. 1

$\log_{10}\left(\frac{10}{10-x}\right)$ The Determination of First-Order Kinetics for the Formation of Homoterpenyl Methyl Ketone

(See Table II)
Fig. 2

The Rotatory Power of Solutions of Pinonic Acid in Monochloroacetic Acid at 100°.

See Table IV
Fig. 3

The Rotatory Power of Solutions of Pinonic Acid in Monochloroacetic Acid at 100°

See Table IV
solutions were immersed in steam at zero time. The study of the kinetics of this rearrangement by isolation of the product was the method employed after it had been found that a polarimetric method was not practicable. When the rotatory power of solutions of (+)-trans-pinonic acid in monochloroacetic acid at 100° was observed, it was found that the rotation dropped quite rapidly and smoothly until a substantially constant value was reached after about 3 hours (Figs. 2, 3). Isolation of the product revealed that only partial rearrangement to the ketolactone had occurred, while the pinonic acid which was recovered consisted of a mixture of the (+)-trans- and (-)-cis- forms, which, after conversion into their oximes, were separated. The (±)-acid recovered from the kinetic experiments also contained the cis-isomer, which was isolated as its oxime.

The specific rotations (α, 5 in chloroform) of the specimens of optically-active pinonic acid recovered from the kinetic experiments were determined. Values of specific rotation for (+)-trans-pinonic acid and (-)-cis-pinonic acid are known. (+)-trans-Pinonic acid has $[\alpha]^5_{	ext{D}} 92.4^\circ$ (present observation); Delépine and Badoche (Ann. Chim., 1950, 5, 153) record $[\alpha]^5_{	ext{D}} 95^\circ$. (-)cis-Pinonic acid
has \( \alpha \) 5893 - 81.5° (Delépine and Badoche, loc. cit.). By the use of these values, the proportions of (+)-trans- and (-)-cis- acids in the recovered specimens were determined. The concentrations of total, (+)-trans-, and (-)-cis- pinonic acids were plotted against time (Fig. 4).

**The Mechanism of the Rearrangement, and of trans-cis Isomerisation**

The mechanism of the conversion of trans-pinonic acid into the cis-isomer is probably identical with that which has been deduced for the acid-catalysed racemisation of ketones with the structure \( \text{CHRR'CO.R} \) (C. K. Ingold, "Structure and Mechanism in Organic Chemistry", G. Bell and Sons, Ltd., London, 1953, p. 569).
Experimental evidence has shown that rates of racemisation, bromination, and iodination are identical for a given ketone under fixed conditions of acid-catalysis, and are solely dependent upon the rate of formation of the enol (33) (Bartlett and Stauffer, J. Amer. Chem. Soc., 1935, 57, 2580; Ingold and Wilson, J., 1934, 775). When the above mechanism is applied to trans- and cis-pinonic acids
(2, 8), the inversion of configuration at C(3) results in a geometrical isomerisation (pinonic acid is regarded as 3-acetyl-2:2-dimethyl cyclobutyl acetic acid).

\[
\text{trans-} \quad \text{(9)} \\
\text{cis-} \quad \text{(8)}
\]

Experiments carried out with 10% solutions of trans-pinonic acid in monochloroacetic acid at 100° showed that during the first 1.9 hours, cis-pinonic acid accumulates in the solutions more rapidly than does homoterpenyl methyl ketone. Tangents to curves 1 and 4 at the origin (Fig. 4) show that the rate-constant for the trans-acid → cis-acid change is approximately twice that for the trans-acid → ketolactone rearrangement.
Fig. 4

The Rearrangement and Isomerisation of Pinonic Acid in Monochloroacetic Acid at 100° (See Table II)

Homoterpenyl Methyl Ketone 1
Total Pinonic Acid 2
Trans-Pinonic Acid 3
Cis-Pinonic Acid 4

%
The Mechanism of the Rearrangement of Pinonic Acid into Homoterprenyl Methyl Ketone
Fig. (5) shows the most probable mechanism of the rearrangement of pinonic acid to homoterpenyl methyl ketone. (No significance is to be attached to the geometrical configurations given to the ethylenic groups of the enolic forms). Rearrangement of protonated trans- or cis-pinonic acid results in fission of the cyclobutane-ring, with simultaneous formation of the lactone-ring. A study of the molecular models shows that the carboxyl group in the protonated acids is suitably situated to enter into a replacement reaction at C(2); (37) represents the steric relationships and the tautomeric electron-movements which lead to rearrangement.

The rate of formation of homoterpenyl methyl ketone has been found to be proportional to the sum of the concentrations of cis- and trans-pinonic acids. Kinetically, the rearrangement is of the first order, and hence the protonated acids (32) and (32) are kinetically indistinguishable ($k_1$ and $k_1'$ not differing appreciably).
Three apparently possible mechanisms, briefly described below, have been considered and rejected:

(i) If the sole precursor to homoterpenyl methyl ketone were the trans-acid (or its protonated form), then the rate of formation of the ketolactone would diminish rapidly at first, reflecting the rapid reduction of trans-acid concentration which results from its partial conversion into the cis-isomer. First-order kinetics would not apply if the cis-isomer had no part in the rearrangement.

(ii) If the sole precursor to homoterpenyl methyl ketone were the cis-acid (or its protonated form), the rate of formation of the ketolactone would increase at first to a maximum corresponding with the maximum observed in the
concentration of cis-acid. The rate would then diminish, i.e., the ketolactone-concentration/time curve would have a sigmoid form. This is not so.

(iii) A tenable mechanism is that postulating the enol (6) as the sole precursor to the ketolactone.

\[
\begin{align*}
\text{(6)} & \quad \text{H} & \quad \text{CH}_3 \\
& \quad \text{C} & \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{O} \\
& \quad \text{H}^+ & \quad \text{C} & \quad \text{O} \quad \text{C} \\
& \quad \text{CH}_2 \quad \text{CH} & \quad \text{CH} & \quad \text{CH}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{(40)} & \quad \text{H} & \quad \text{CH}_3 \\
& \quad \text{C} & \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{O} \\
& \quad \text{C} & \quad \text{O} \quad \text{C} \\
& \quad \text{CH}_2 \quad \text{CH} & \quad \text{CH} & \quad \text{CH}_2 \\
\end{align*}
\]

\[
\begin{align*}
\text{(3)} & \quad +\text{H}^+ & \quad \text{CH}_3 \\
& \quad \text{O} & \quad \text{C} & \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{O} \\
& \quad \text{CH}_2 \quad \text{C} & \quad \text{O} \quad \text{C} \\
& \quad \text{CH}_2 \quad \text{CH} & \quad \text{CH} & \quad \text{CH}_2 \\
\end{align*}
\]
This is considered to be less probable than the mechanism adopted above, because it involves the taking up of a proton at a point \((C(3))\) from which a proton has immediately before been released to form the enol \((6)\).

These results may be summarised in the following form:

Conversion of pinonic acid into homoterpenyl methyl ketone requires relatively strong acid-catalysis. The rearrangement of \((\pm)\)- and of \((+)\)-trans-pinonic acid in monochloroacetic acid at 100° is kinetically of the first order with regard to pinonic acid. A partial conversion into cis-pinonic acid occurs in the acidic solution, but this isomer also rearranges to homoterpenyl methyl ketone at approximately the same rate as the trans-acid.
The Conversion of Pinonic Acid into
2:4-Dimethylphenylacetic Acid by the Action of
Bromine and Hydrochloric Acid

As described in the experimental section, 2:4-dimethylphenylacetic acid has been prepared from pinonic acid by the procedure of Harispe, a yield of 50% being obtained. In a separate experiment, Harispe's method of isolating the acid from the crude product (by esterification etc.) was replaced by extraction with dilute ammonia followed by sublimation under reduced pressure of the material obtained on acidification of the alkaline extract. This gave a yield of 66% of the acid. It is apparent from this, that the end product of the reaction is 2:4-dimethylphenylacetic acid, which can be readily extracted with dilute ammonia, and not some other compound (such as (28), the lactone of 2-hydroxy 2:4-dimethyl cyclo-hex-3:5-dienyl acetic acid) which might be converted into (41), the methyl ester of 2:4-dimethylphenylacetic acid under the conditions of esterification by the Fischer-Speier method.
The preparation of 2:4-dimethylphenylacetic acid from homoterpenyl methyl ketone has also been carried out, using direct extraction of the acid, 57% of which was obtained.

Bromination of pinonic acid and of homoterpenyl methyl ketone in hydrochloric acid yielded a clear solution, from which the product of bromination could be isolated by pouring on to ice, as described by Harispe. In both instances, the product was a viscous, pale yellow or colourless oil which was kept for long periods in a refrigerator without apparent change. It decomposed slowly at room temperature, and rapidly on heating.

The bromination products of pinonic acid and of homoterpenyl methyl ketone both gave 2:4-dimethylphenylacetic acid on being heated with a mixture of hydrobromic acid and
hydrochloric acid. This mixture was prepared by passing hydrogen chloride into a mixture of concentrated hydrochloric and hydrobromic acids, and approximated in composition to the solvent in the reaction mixture after bromination had taken place (Hydrogen bromide was not given off during bromination, but dissolved in the hydrochloric acid).

During bromination by Harispe's method, the temperature was allowed to rise freely; it increased by about 30° to 40-48°, depending on the initial temperature of the reactants. With homoterpenyl methyl ketone, which is very soluble in concentrated hydrochloric acid, the bromination was almost instantaneous, whereas with pinonic acid it was necessary to shake the suspension for 10 minutes before all of the bromine had reacted.

On stirring a suspension of pinonic acid in the hydrochloric and hydrobromic acid mixture at 48° for 10 minutes, 26% conversion into homoterpenyl methyl ketone took place. These conditions approximate to those in which pinonic acid might be converted to the ketolactone during bromination. Obviously this rearrangement does not take place rapidly enough under these conditions for it to be an essential step in the bromination mechanism.
By preventing the temperature from rising above 30° during the bromination of pinonic acid, and separating the product as described above, a semisolid was obtained from which 2-bromo-pinonic acid (26) was isolated after repeated recrystallisation. This compound was a colourless crystalline substance m.p. 116.5-117° which showed no sign of decomposition after storage for several months at room temperature. Analysis and determination of equivalent indicated the empirical formula C_{10}H_{15}O_{3}Br. On being heated with the hydrochloric-hydrobromic acid mixture, 2:4-dimethylphenylacetic acid was obtained (56%). Reduction with zinc and hydrochloric acid yielded pinonic acid (isolated as its oxime) 5%, and homoterpenyl methyl ketone (isolated as its 2:4-dinitrophenylhydrazone) 10%. Its acidic equivalent, and the isolation of pinonic acid from its reduction-product, demonstrated that the bromo-compound retains the structure of pinonic acid; the formation of ketolactone during the reduction is ascribed to the partial rearrangement of pinonic acid in the acidic reduction-medium.
No compound containing a bromo-methyl group has been encountered, hence the bromo-pinonic acid is considered to be (26) and not (26a), the carbon bridgehead being brominated in preference to the unsubstituted methyl group. This behaviour is similar to that observed in the acid-catalysed bromination of menthone (42) and carvomenthone (44) (Kotz and Steinhorst, Ann., 1911, 372, 13). These gave exclusively the tertiary bromo-derivatives (43) and (45) respectively.
Like pinonic acid itself, the bromo-derivative may show geometrical isomerism. (±)-trans-Pinonic acid was subjected to bromination, and was also obtained (as its
oxime) on reduction of the bromo-compound. However it does not necessarily follow from this, that the bromo-compound must also be assigned the trans-configuration, as a change of configuration may occur in bromination of pinonic acid (via the enol), and during reduction of the bromo-compound.

As the recrystallised bromo-pinonic acid is apparently homogeneous, it is most likely the trans-compound, since this isomer might be expected like trans-pinonic acid to have a lower solubility than the cis-isomer, which would be removed during the recrystallisation.

Neither the cis-isomer, nor bromo-homoterpenyl methyl ketone have been isolated, but both probably form constituents of the viscous oils obtained by "uncontrolled" bromination of pinonic acid and homoterpenyl methyl ketone.
The formation of bromo-homoterpenyl methyl ketone may take place in three different ways:

(1) By a mechanism resembling that proposed for the rearrangement of pinonic acid to homoterpenyl methyl ketone (p. 23):

\[ \begin{align*}
\text{CH}_3 & \quad \text{CO} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{CH}_2 & \quad \text{CH} \quad \text{CH}_2
\end{align*} \]

[Diagram 1]

\[ \begin{align*}
\text{CH}_3 & \quad \text{CO} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{O} \\
\text{H} & \quad \text{H} \\
\text{CH}_2 & \quad \text{CH} \quad \text{CH}_2
\end{align*} \]

[Diagram 2]

A simultaneous shift of electrons involving attack by the carboxyl group upon the carbon atom which carries two \textit{gem}-methyl groups, with fission of the \textit{cyclobutane} ring, and formation of a carbon to bromine bond at the point of fission.
(11) By intermediate formation of the enol of homoterpenyl methyl ketone:

\[
\text{H}^+ \text{CH}_3
\]

\[
\text{O} = \text{C} \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{O}
\]

\[
\text{H}_2\text{C} - \text{C} - \text{C} - \text{CH}_2
\]

\[
\text{H}^+ \quad \text{CH}_3
\]

\[
\text{O} = \text{C} \quad \text{CH}_3 \quad \text{O}
\]

\[
\text{Br-Br} \quad \text{CH}
\]

\[
\text{H}_2\text{C} - \text{C} - \text{C} - \text{CH}_2
\]

\[
\text{HBr} +
\]

\[
\text{CH}_2 - \text{CH} - \text{CH}_2
\]
By rearrangement of the protonated bromo-pinonic acid (46)

In conclusion, Mariage's scheme (p. 13) for the conversion of pinonic acid into 2:4-dimethylphenylacetic acid is reconsidered. The first stage in this scheme is the formation of bromo-pinonic acid (3-acetyl 3-bromo...
2:2-dimethyl cyclobutyl acetic acid) (26), and this is followed by rearrangement of the bromo-acid into bromo-homoterpenyl methyl ketone (27), which can also be prepared by bromination of the ketolactone. The conversion of both pinonic acid and homoterpenyl methyl ketone into 2:4-dimethylphenylacetic acid has now been verified, and 3-bromo-pinonic acid has been isolated as a crystalline substance and characterised. Three possible mechanisms for the formation of this compound are set out above.

There is no evidence to show how the subsequent cyclisation of (27) to 2:4-dimethylphenylacetic acid occurs. The overall reaction involves loss of the elements of water and of hydrogen bromide, and this may occur in two steps or in three; it appears to be impossible to determine the sequence. However it is not likely that Harispe's hydroxy-acid (29) has any reality as an intermediate, the lactone (28) rearranging spontaneously into 2:4-dimethylphenylacetic acid.

Sublimation in vacuo has been shown to be a satisfactory method of isolating 2:4-dimethylphenylacetic acid from the products of reaction, and its isolation without recourse to esterification shows the acid itself to be the main product of the reaction.
The Phosphoric Acid - Catalysed Decomposition
of Pinonic Acid: the Products and Mechanism of the Reaction

The mechanism proposed by Harispe for the conversion of pinonic acid and homoterpenyl methyl ketone into 2:4-dimethylphenylacetic acid requires the intermediate formation of \( \alpha \)-bromo-homoterpenyl methyl ketone (see p. 13), and there seems to be no reason to doubt this. In view of the occurrence of the subsequent cyclisation of this compound, consideration was given to the possibility of bringing about an analogous cyclisation of homoterpenyl methyl ketone itself, in the absence of oxidising agents. Prolonged heating with 50% aqueous sulphuric acid had no effect other than to cause the formation of resin, while the action of phosphorus pentoxide upon a solution of the ketolactone in benzene merely produced a small amount of highly coloured substance which was not examined further.

When the ketolactone was heated with phosphoric acid, decomposition occurred, carbon dioxide being evolved. For investigation of the products of this decomposition, the ketolactone was not prepared separately, but formed in situ, it being known (Table I) that the ketolactone is
formed rapidly from pinonic acid when the latter is heated in phosphoric acid. Accordingly, pinonic acid was heated with phosphoric acid (d 1.72 - 1.74) to 150-165°, when decomposition occurred.

The products of this decomposition were the following:

(i) 2:4-Dimethylphenylacetic acid (30) 3.5%, identified by its m.p. alone, and when mixed with a specimen of the acid prepared by Harispe's method (loc. cit.).

(ii) The lactone of 2-hydroxy 2:4-dimethyl cyclohexyl acetic acid (50) 7.5%. The equivalent, determined by titration, and analytical data, were in agreement with the empirical formula \( \text{C}_{10}\text{H}_{16}\text{O}_2 \). Oxidation with bromine yielded 2:4-dimethylphenylacetic acid.

\[
\begin{align*}
\text{CH}_2\text{CO} & \quad \text{CH}_2\text{COOH} \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{CH}_3 & \quad +4\text{HBr} \\
\text{CH}_3 & \quad \text{CH}_3 \\
(50) & \quad (30)
\end{align*}
\]
(iii) A mixture of 1,2,4-trimethyl benzene (51) and 1,2,4-trimethyl cyclohexene (52) 24.5% (calculated as C₉H₁₆). These were not separated but identified as described below.

(iv) A hydrocarbon-product of high molecular weight and doubtful homogeneity. This was not identified.

(v) A neutral resin, quantitatively the main product.

The separation of these products was achieved, briefly, as follows (a full description is given in the experimental section):-

The reaction mixture was steam-distilled; (i) and (ii) were extracted from the aqueous part of the distillate, and the acid (i) was separated from the lactone (ii) by alkaline extraction. The oily part of the steam-distillate also contained (i) and (ii), together with (iii) and (iv). Alkaline extraction was again used to separate (i). Distillation at atmospheric pressure then separated the hydrocarbon fraction (iii) from (ii) and (iv), which together constituted a high-boiling residue; the latter was separated into its constituents by saponification of (ii)
with alcoholic potash.

A neutral resin (v) remained as a non-volatile residue after steam-distillation. Some 2:4-dimethylphenyl-acetic acid (i) also remained, and was separated from the resin by sublimation in vacuo.

Identification of the constituents (51) and (52) of the hydrocarbon fraction (iii)

The mixture of hydrocarbons was fractionally distilled, 16 fractions being separated within the range 144-166°. Nitration of selected fractions and separation of 3:5:6-trinitro -cumene allowed an approximate estimate of the -cumene content to be made. Under the nitration conditions employed, -cumene yielded 60% of the trinitro-compound, though with mixtures it is probable that the yield of nitro-compound diminishes more rapidly than the -cumene content.

The following facts were ascertained:

(a) The highest-boiling fraction b.p. 165-166° yielded 49% of the trinitro-compound.
(b) The fraction b.p. 153-154° yielded 5% of the trinitro-compound.

(c) Carbon and hydrogen analysis of a fraction b.p. 151-153° indicated that it contained 21% of \( \psi \)-cumene and 79% of 1:2:4-trimethyl cyclohexene.

(d) A fraction b.p. 149-150° was dehydrogenated by boiling with palladised charcoal (Linstead, Millidge, and Thomas, J., 1937, 1146; Linstead, Michaelis, and Thomas, J., 1940, 1139). Its b.p. and refractive index were thereby increased, and the product gave 28% of the trinitro-compound, indicating that the olefinic constituent of the mixture has the same carbon skeleton as \( \psi \)-cumene.

Ozonolysis did not succeed, as no identifiable products were obtained. This was probably due to the formation of stable polymeric ozonides similar to those obtained by Criegee and his co-workers (Ber., 1953, 86, 1; Ann., 1954, 533, 1) by the action of ozone upon 1:2-dimethyl cyclohexene.

Nitration of the mixture yielded 23% of trinitro \( \psi \)-cumene (\( \psi \)-cumene itself yielded 60%). Hence the
mixture contains not less than 38% of \( \gamma \)-cumene. From the refractive indices of the mixture \( (n_D^{25} 1.4780) \), \( \gamma \)-cumene \( (n_D^{25} 1.5020) \), and 1:2:4-trimethyl cyclohexene \( (n_D^{25} 1.4430) \), it was calculated that the mixture contains 41% of olefin and 59% of \( \gamma \)-cumene. In the absence of more reliable data, it was assumed that the mixture consisted of equal proportions of olefin and \( \gamma \)-cumene.

The olefinic bond in the trimethyl cyclohexene was located by comparing the rate of catalytic (Pt\(_2\)) hydrogenation of the unfractionated hydrocarbon-product \( (0.08 \text{ mole}) \) with the corresponding rates for cyclohexene, 1-methyl cyclohexene, and 1:2-dimethyl cyclohexene \( (0.04 \text{ mole}) \).

The order of the respective rates was found to be:

\[
\text{Cyclohexene} > \text{1-Methyl cyclohexene} >> \text{1:2-Dimethyl cyclohexene} = \text{Product}
\]

These results are in good agreement with the general principles determined by Lebedev, Kobliansky, and Yakubchik (J., 1925, 127, 417). These authors studied the relative rates of catalytic hydrogenation of a large number of olefinic substances and showed that in most instances the
presence of \( \alpha \)-substituents retards the rate of hydrogenation.

The hydrocarbon-mixture is apparently free from compounds containing the \(-\text{CH} = \text{CH}-\) and \(-\text{CH} = \text{CMe}-\) groups in the ring. Of all the possible isomers of tetrahydro-\( \psi \)-cumene, only 1:2:4-trimethyl cyclohexene contains the difficultly-hydrogenated tetrasubstituted olefinic bond.

Reviewing the evidence for the structure of the olefinic product, we have:

(a) Dehydrogenation and analytical data indicate it to be a hydro-\( \psi \)-cumene.

(b) Ozonolysis is not practicable, and the results bear comparison with those obtained by Criegee and co-workers when studying the ozonolysis of 1:2-dimethyl cyclohexene.

(c) Hydrogenation data indicate the presence of a tetrasubstituted ethylenic grouping (as in 1:2-dimethyl cyclohexene).

(d) The olefin is produced under conditions which would permit isomerisation of a tetrahydro-\( \psi \)-cumene to the most stable isomer. Of all the possible isomers, only (52)
contains a tetrasubstituted ethylenic group, and this would certainly be the most stable, as it possesses the maximum number of hyperconjugable hydrogen atoms.

The scheme below (Fig. 6) accounts in what is believed to be the simplest way for the formation of the products described. Pinonic acid (\(4\)) is rapidly converted into homoterpenyl methyl ketone (\(3\)) in phosphoric acid (95% conversion after 5 minutes at 100°C (Table I). Homoterpenyl methyl ketone then undergoes ring-closure between one of the gem-methyl groups, and the carbonyl group; the lactone of 2-hydroxy 2:4-dimethyl cyclo-hex-3-enyl acetic acid (\(48\)) is formed. An equilibrium probably exists between this compound and 2:4-dimethyl cyclo-hexa-1:3-dienyl acetic acid (\(49\)). The lactone of 2-hydroxy 2:4-dimethyl cyclohexyl acetic acid is formed by addition of hydrogen to (\(48\)), while dehydrogenation of (\(48\)) (or \(49\)) yields 2:4-dimethylphenylacetic acid. Decarboxylation of (\(48\)) (or \(49\)) and dehydrogenation, yields \(\Psi\)-cumene (\(51\)). Decarboxylation of (\(48\)) (or \(49\)) and hydrogenation yields 1:2:4-trimethyl cyclohexene (\(52\)).

It is not thought that formation of pairs of
hydrogenated and dehydrogenated compounds (e.g. 30 and 50; 51 and 52) implies the actual occurrence of disproportionation at any stage in the scheme. Mechanisms involving transfer of hydrogen may involve compounds which subsequently condense or polymerise to give rise to the resin (which forms the greater part of the product.

Several examples are known of such hydrogen-transfer in the presence of strongly acidic or electrophilic catalysts.

For example:-

(a) The formation of a mixture of m-xylene and 1:5-dimethyl cyclohexene by the dehydration of 2-methyl hept-2-en-6-one in the presence of zinc chloride, phosphorus pentoxide, or dilute sulphuric acid (Wallach, Ann., 1890, 258, 326; Ann., 1913, 395, 80).
(b) The formation of \( \psi \)-cumene and an unidentified hydrocarbon (probably 1:2:4-trimethyl cyclohexene) by the dehydration of thujaketone (2:3-dimethyl hept-2-en-6-one) in the presence of zinc chloride, phosphorus pentoxide, or dilute sulphuric acid (Wallach, Ann., 1893, 275, 174; Ann., 1913, 395, 80).

\[
\begin{align*}
\text{C}_6\text{H}_{12} \xrightarrow{\text{HCl, P_2O_5, H_2SO_4}} \text{C}_6\text{H}_6 + \text{C}_6\text{H}_{12} + \text{H}_2\text{O}
\end{align*}
\]

(c) The formation of 3-methyl xanthene together with unspecified di- and tetra-hydro derivatives by the distillation of 2-methyl \( \alpha - \beta \)-tetramethylene \( \alpha \)-hydroxy benz-\( \alpha \)-pyran with zinc chloride (Borsche and Geyer, Ann., 1912, 393, 48).

\[
\begin{align*}
\text{C}_9\text{H}_{14} \xrightarrow{\text{ZnCl}_2} \text{C}_9\text{H}_{10} + \text{H}_2\text{O etc.}
\end{align*}
\]
(d) The reduction of 1-methyl 4-iso-propyl cyclohexene by cymene in the presence of hydrogen fluoride or sulphuric acid as catalyst. 1-Methyl 4-iso-propyl cyclohexane is formed, while the cymene residues condense to form 1:3:3:6-tetramethyl 1-p-tolyl indan (Ipatieff, Fines, and Oldberg, J. Amer. Chem. Soc., 1948, 70, 2123).
(e) The formation of 1-methyl iso-quinoline from N-acetyl phenylalanine, and of norharman from N-formyl tryptophan, on their being heated with polyphosphoric acid containing phosphorus trichloride, involves elimination of water, loss of carbon dioxide, and dehydrogenation (Snyder and Werber, J. Amer. Chem. Soc., 1950, 72, 2962).
Fig. 6
The Products and Mechanism of the
Decomposition of Pinonic Acid
in Phosphoric Acid
Experimental evidence in favour of the above scheme (Fig. 6) is mainly concerned with the rejection of routes alternative to those described.

A study of the rates of carbon dioxide evolution from the following compounds in phosphoric acid at 160°, has afforded a means of deciding the relative likelihood of certain of these routes.

2:4-Dimethylphenylacetic acid (30) was hardly affected under these conditions, 95% of the acid being recovered after one hour at 160–170°, whence it is certain that γ-cumene is not formed by decarboxylation of this acid.

In 10 minutes, pinonic acid yielded 59% of the possible carbon dioxide, and the decarboxylation did not proceed much further on longer heating (60% after 30 minutes).

The lactone (50) gave 16% of carbon dioxide after 10 minutes, so that a small part of the yield of (52) may be formed from this lactone, which is present only in low concentration in the reaction mixture.

Reduction of homoterpenyl methyl ketone by the
Huang-Minlon procedure (J. Amer. Chem. Soc., 1946, 68, 2487) yielded \( \theta \)-n-butyl \( \gamma\gamma \)-dimethyl \( \gamma \)-butyrolactone (55), which under the same conditions as pinonic acid and the lactone (50) gave 1.4% of the possible carbon dioxide in 10 minutes. Homoterpenyl methyl ketone is therefore not likely to undergo rapid decarboxylation to 2:3 dimethyl hept-2-en-6-one (53) as it differs from (55) only in possessing a carbonyl group at \( \text{C}(3) \) of the side-chain, where this group is unlikely to affect the rate of decarboxylation of the lactone-ring.

The product of the decarboxylation of (50) in phosphoric acid was isolated in a separate experiment. It was a hydrocarbon \( C_{9}H_{16} \), b.p. 144-145°, \( n_{D}^{25} \) 1.4430, which was probably 1:2:4-trimethyl cyclohexene.

![Diagram of chemical structures and reaction](image-url)
The preparation of this hydrocarbon has not hitherto been recorded, but v. Auwers (Ann., 1919, 420, 105) prepared a compound C_{9}H_{16} b.p. 144-146\degree, n_{D}^{20} 1.4432 by the dehydration of 2:4:5 trimethyl cyclohexanol. No proof of its structure was given, but it was assumed to be 1:4:5-trimethyl cyclohexene. Under the conditions of its formation however, (by the action of phosphorus pentoxide), this would be likely to isomerise to the more stable 1:2:4-trimethyl cyclohexene.

Compounds related to those discussed above have been shown to be readily decarboxylated. For example, 4-methyl cyclohex-1-enyl acetic acid decarboxylates on heating to give 1-methyl 4-methylene cyclohexane, (Marckwald
and Meth., Ber., 1906, 39, 2036).

\[
\begin{align*}
\text{CH}_2\text{CO}_2\text{H} & \quad \rightarrow \\
\text{C}_6\text{H}_6 & \\
\text{CH}_3 &
\end{align*}
\]

This hydrocarbon also results from the decarboxylation of 4-methyl cyclohexylidene acetic acid on dry distillation (Wallach, 1909, 365, 255).

\[
\begin{align*}
\text{CH}_3\text{CO}_2\text{H} & \quad \rightarrow \\
\text{C}_6\text{H}_6 & \\
\text{CH}_3 &
\end{align*}
\]

Cyclohexylidene acetic acid also decarboxylates in part on steam distillation, the product being 1-methylene cyclohexane (Wallach, ibid.).
The hydrolysis of the lactones (50) and (55)

During determination of the equivalents of the lactones (50) and (55), it was found that for complete hydrolysis (50) required boiling under reflux for 2 hours with 0.5N alcoholic potash, whereas (55) was completely hydrolysed after standing with 0.5N alcoholic potash at room temperature for 30 minutes.

In review of the results discussed above:

Some of the products of the phosphoric acid-catalysed decomposition of pinonic acid have been identified. These are: 1:2:4 trimethyl benzene (γ-cumene), 1:2:4-trimethyl cyclohexene, the lactone of 2-hydroxy 2:4-dimethyl cyclohexyl acetic acid, and 2:4-dimethylphenyl-acetic acid. A mechanism for the formation of these compounds, involving dehydration, decarboxylation, and transfer of hydrogen, has been put forward. The mechanism is supported by experimental evidence on rates of decarboxylation of compounds which are, or may be, concerned in the reaction, and by analogy with a number of related reactions cited from the literature.
SUMMARY AND CONCLUSIONS

The rearrangement of trans-pinonic acid into homoterpenyl methyl ketone requires relatively strong acid-catalysis (Table I, p. 7).

In monochloroacetic acid at 100°, the rearrangement is of the first order with regard to pinonic acid (Fig. 1). The formation of homoterpenyl methyl ketone is accompanied by the isomerisation of trans- into cis-pinonic acid. Oximes of (-)- and (±)-cis-pinonic acid have been prepared from mixtures of cis- and trans-pinonic acid recovered from the reaction-mixtures containing (+)- and (±)-trans-pinonic acid respectively.

cis-Pinonic acid also rearranges to homoterpenyl methyl ketone at substantially the same rate as does the trans-acid.

Observation of the rotatory power of reaction-mixtures containing (+)-trans-pinonic acid is not suitable for assessing the extent of ketolactone formation, because of the isomerisation of the pinonic acid. By analysis of reaction-mixtures which had been heated for various lengths of time, curves have been constructed which show the changes in concentration of the components as isomerisation
and rearrangement proceed (Fig. 4).

An intramolecular mechanism is proposed for the rearrangement (Fig. 5). Rearrangement of protonated trans- or cis-pinonic acid results in fission of the cyclobutane ring, with simultaneous formation of the lactone-ring (formula 37, p. 22).

The formation of 2:4-dimethylphenylacetic acid by the action of bromine upon pinonic acid and upon homoterpenyl methyl ketone has been verified.

With pinonic acid, the initial reaction results in the formation of $\alpha$-bromo-pinonic acid. This compound has been isolated, and characterised by analysis and by its reduction to pinonic acid and conversion into 2:4-dimethylphenylacetic acid.

The initial product of bromination of homoterpenyl methyl ketone is believed to be $\alpha$-bromo-homoterpenyl methyl ketone, but it has not been found possible to isolate or characterise this compound.

The bromo-ketolactone is probably also formed by rearrangement of $\alpha$-bromo-pinonic acid under conditions of strong acid-catalysis. Under such conditions, the bromo-ketolactone then undergoes cyclisation with loss of
the elements of hydrogen bromide and water, to give 2:4-dimethylphenylacetic acid. Mechanisms of bromination and of cyclisation are discussed.

Pinonic acid is rapidly converted into homoterpenyl methyl ketone when heated with phosphoric acid at 100°. Further heating causes decomposition with loss of carbon dioxide. 2:4-Dimethylphenylacetic acid is found among the products, which represent the result of a complex process of hydrogen transfer associated with dehydration and decarboxylation (Fig. 6). Other compounds which have been identified as products of the reaction are as follows:-

1:2:4-Trimethyl benzene (γ-cumene), identified by formation of the trinitro derivative.

1:2:4-Trimethyl cyclohexene, identified by its resistance to hydrogenation in comparison with cyclohexene, 1-methyl cyclohexene, and 1:2-dimethyl cyclohexene.

The lactone of 2-hydroxy 2:4-dimethyl cyclohexylacetic acid, identified by its oxidation to 2:4-dimethylphenylacetic acid.

A study of the reactions of the products and of compounds similar to those likely to be present in the
reaction mixture, and comparison with related examples from the literature, has afforded evidence relating to the probable mechanism of the reaction.
EXPERIMENTAL SECTION

p. 1  The Mechanism of the Rearrangement of Pinonic Acid into Homoterpenyl Methyl Ketone.

p. 15 The Formation of 2:4-Dimethylphenylacetic Acid from Pinonic Acid by the Action of Bromine.

p. 29 The Phosphoric Acid-Catalysed Decomposition of Pinonic Acid.
The Mechanism of the Rearrangement of Pinonic Acid into Homoterpenyl Methyl Ketone

Rotations of undiluted liquid compounds are for 1, 2.0; those of solutions are for 1, 1.0, unless otherwise stated.

α-Pinene

The proportions of α- and β-pinene in specimens of (-)- and (+)-pinene, from Portuguese and American turpentine respectively, were estimated by determination of the rotatory dispersions \( [\alpha]_{546}^{25}/[\alpha]_{5893}^{25} \) and \( [\alpha]_{546}^{25}/[\alpha]_{5780}^{25} \) and comparison of these values with the tables given by Fugitt, Stallcup, and Hawkins (J. Amer. Chem. Soc., 1942, 64, 2978). A mixture containing 97.5% of α- and 2.5% of β-pinene was then made which had b.p. 156-158°, \( [\alpha]_{5893}^{20} = 0.54° \); this material was oxidised by the method of Delépine (Bull. Soc. Chim. de France, 1936, [V], 3, 1369) except that chloroform was replaced by methylene chloride as extractant.

Preparation of trans-Pinonic Acid (Based on Delépine's Method; loc. cit.)

Potassium permanganate (158 g.), ammonium sulphate (33 g.), water (100 ml.), and crushed ice (1500 g.), were mixed in a thick-walled vessel (Winchester quart bottle, or
1 gallon earthenware jar), and \( \alpha \)-pinene (0.5 mole, 68 g.) was added. After vigorous shaking for 4 hr., the manganese dioxide was filtered off at the pump, and washed with water (4 portions of 100 ml.). The combined filtrate and washings were made alkaline by adding ammonia (10 ml., \( d \) 0.880), and non-acidic substances were extracted with methylene chloride (4 portions of 50 ml.). After acidification of the aqueous liquid with sulphuric acid (50 ml. concentrated acid diluted with 90 ml. of water), the organic acids were extracted with methylene chloride (5 portions of 50 ml.), and the combined extracts were washed with water (4 portions of 50 ml.), dried (\( \text{Na}_2\text{SO}_4 \)), and the solvent removed by distillation. Crude pinonic acid thus obtained (50-60 g.) was recrystallised from benzene or ether.

(\( \pm \))-trans-Pinonic Acid

\( \alpha \)-Pinene (748 g.) having \([\alpha]_{5893}^{20} = 0.54^\circ\), yielded (\( \pm \))-trans-pinonic acid (336 g., from benzene) m.p. 103-104\(^\circ\), which on recrystallisation from hot water had m.p. 105\(^\circ\) (Semicarbazone, prisms from ethanol, m.p. 217\(^\circ\) decomp.

Ammonium (±)-trans-pinonate, on reaction with S-benzyl iso-thiuronium chloride, yielded S-benzyl iso-thiuronium (±)-trans-pinonate, flakes from ethanol, m.p. 152° decomp. (Found: S, 9.0%. C_{18}H_{28}O_{3}N_{2}S requires: S, 9.15%).

(±)-trans-Pinonic acid (1.00 g.) was dissolved in a solution of potassium hydrogen carbonate (0.55 g.) in water (2.0 ml.). A solution of hydroxylamine hydrochloride (0.42 g.) in water (1.00 ml.) was added, and the whole was shaken. The oxime separated and solidified; it was crushed, filtered off, washed with water, and dried in vacuo (H_{2}SO_{4}). It (0.85 g.) on recrystallisation from ethanol, yielded prisms (0.55 g.), m.p. 152° decomp. (Baeyer, Ber., 1896, 22, 24; records p.m. 150°). This method was used for the preparation of all pinonic acid oximes (Delépine, loc. cit.).

(±)-trans-Pinonic Acid

(+)–α– Pinene (68.0 g.), b.p. 154.5–156°,

[α]^{20}_{5893} + 47.0°, d^{19}_{19} 0.360 (from Greek Aleppo turpentine) on similar oxidation gave (±)-trans-pinonic acid (17.3 g., isolated by fractional crystallisation from ether) m.p. 68–69°, 

[α]^{24}_{5893} + 92.4° (c, 5.443 in CHCl_{3}). Its oxime, needles from
ethanol-water (1:4), had m.p. 135.5°, $[\alpha]_{5893}^{20} + 51.7°$
(c, 5.102 in CHCl₃). Found: C, 60.2; H, 8.7; N, 7.3.
Calc. for C₁₀H₁₇O₂N: C, 60.3; H, 8.6; N, 7.05% (Delépine, loc. cit., records m.p. 128°).

(±)-Homoterpenyl Methyl Ketone

The following preparation is based on the brief description given by Baeyer (loc. cit.). (±)-trans-Pinonic acid (6.0 g.) was heated with aqueous sulphuric acid (50%; 60 g.) at 100° for 30 min., and the solution was poured into water (150 ml.). The product was salted out with ammonium sulphate and extracted with chloroform; the extract was washed, dried (Na₂SO₄), and the solvent distilled. The crystalline product (5.4 g.) yielded on recrystallisation from the minimum of boiling ether, (±)-homoterpenyl methyl ketone (3.4 g.), prisms, m.p. 60.5°. Its semicarbazone, hexagonal plates from methanol, had m.p. 206-207° (J. Owen and J. L. Simonsen, J., 1932, 1424; record m.p. 206-207°). Its 2:4-dinitrophenylhydrazone, orange needles from ethanol, had m.p. 163.5° (Found: C, 53.1; H, 5.6; N, 14.9. C₁₆H₂₀O₆N₄ requires: C, 52.7; H, 5.55; N, 15.4%).
Rearrangement in the Acidic Solvents of Table I

(±)-trans-Pinonic acid (1.00 g.) was heated at 100° in the solvent, and for the time, stated in the table. Water (100 ml.) was then added and the whole was made slightly alkaline (to methyl red) with ammonia, and extracted with methylene chloride (successive portions of 25, 20, 15, 10, 10 ml.). The extract was washed with water (2 portions of 25 ml.) and distilled (water forms an azeotrope with methylene chloride). The homoterpneyl methyl ketone was dried at 100° (30 min.) or in vacuo at ordinary temperature.

Unconverted pinonic acid was recovered from the extracted aqueous solution by acidification with hydrochloric acid and extraction as above. These procedures for the isolation of the ketolactone and pinonic acid were used in the rate-measurements, below.

The preparation of the 2:4-dinitrophenylhydrazone of (±)-homoterpneyl methyl ketone was standardised as follows:- to a solution of the ketolactone (1.00 g.; reagents proportional to the actual weight were taken) in warm isopropanol (15 ml.), 2:4-dinitrophenylhydrazine (1.1 g.) was added. The solution was boiled, and addition of a few drops of concentrated hydrochloric acid then precipitated the derivative; further
iso-propanol (15 ml.) was added, and the suspension was cooled and filtered. The 2:4-dinitrophenylhydrazone was washed with iso-propanol (30 ml.), dried at 120° and weighed. Its m.p. and m.p. when mixed with a pure specimen were determined.

In a control experiment (+)-homoterpenyl methyl ketone (0.50 g.) gave 0.95 g. (95%) of the derivative.
Table I
The Conversion of (+)-trans-Finonic Acid into (+)-Homoterpenyl Methyl Ketone

<table>
<thead>
<tr>
<th>Experiment No.*</th>
<th>Acid used as solvent</th>
<th>Quantity of acid</th>
<th>Time (hr.)</th>
<th>Homoterpenyl methyl ketone, yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetic</td>
<td>4.0 g.</td>
<td>4.5</td>
<td>Nil</td>
</tr>
<tr>
<td>2</td>
<td>Formic (90%)</td>
<td>4.0 g.</td>
<td>4.5</td>
<td>55</td>
</tr>
<tr>
<td>3</td>
<td>Formic (99%)</td>
<td>to 10 ml.</td>
<td>2</td>
<td>73</td>
</tr>
<tr>
<td>4a</td>
<td>Monochloroacetic</td>
<td>4.0 g.</td>
<td>3.5</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>to 10 ml.</td>
<td>9</td>
<td>58</td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>to 10 ml.</td>
<td>30</td>
<td>95</td>
</tr>
<tr>
<td>7</td>
<td>Trichloroacetic</td>
<td>4.0 g.</td>
<td>4.5</td>
<td>100</td>
</tr>
<tr>
<td>8</td>
<td>Phosphoric (d 1.72)</td>
<td>4.0 ml.</td>
<td>5 min.</td>
<td>95</td>
</tr>
<tr>
<td>9b</td>
<td>Formic 90%...........</td>
<td>4.0 g.</td>
<td>4.5</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>containing HCO₂Na...</td>
<td>0.53 g.</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10c</td>
<td>Monochloroacetic....</td>
<td>to 10 ml.</td>
<td>9</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>containing CH₂ClCO₂Na...</td>
<td>1.80 g.</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* 1.00 g. of Finonic acid was used in each experiment.

a, b, c: 0.74, 0.85, 0.85 g. of pinonic acid were recovered respectively.
Rate of Rearrangement (1)

Monochloroacetic acid was fused, and 0.05 mol. of concentrated aqueous sodium hydroxide was cautiously added; distillation then gave a main fraction having b.p. 101-102°/25 mm. The liquid acid was allowed to solidify to the extent of about 90% and the remaining liquid was drained off and discarded; the solid was re-melted and the process repeated. The acid so purified had equiv. 94.31 (CH₂Cl·CO₂H requires equiv. 94.50).

(±)-trans-Pinonic acid (1.00 g.) was weighed into a 10 ml. graduated flask and dissolved in monochloroacetic acid at 80°. The solution was made up to the mark, the flask was sealed with a polythene cap, and thereafter immersed in a steam-bath for the time(s) recorded in Table II; homoterpenyl methyl ketone was then isolated as described above.

Specimens of pinonic acid recovered from the rate-experiments were combined, and by washing with ethanol were separated into (±)-trans-pinonic acid, m.p. 102° unchanged by admixture with an authentic specimen, and a liquid mixture of this acid with the (±)-cis-isomer. This mixture was converted into the mixed oximes, from which by fractional
crystallisation from ethanol, there was isolated (±)-cis-pinonic acid oxime, m.p. 171° (Delépine, loc. cit., records m.p. 168°), and also the more soluble trans-oxime, prisms, m.p. 151° alone and when mixed with the specimen described above.
Table II
The Rearrangement and Isomerisation of Pinonic Acid in Monochloroacetic Acid at 100°.
Data relating to 10% solutions of (+)- or (+)-trans-pinonic acid in monochloroacetic acid at 100°.

<table>
<thead>
<tr>
<th>Time (hr.)</th>
<th>Concentrations of compounds present (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(x) Homoterpenyl methyl ketone from (+) from (±)</td>
</tr>
<tr>
<td>½</td>
<td>0.7</td>
</tr>
<tr>
<td>1</td>
<td>1.3</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>2.9</td>
</tr>
<tr>
<td>4</td>
<td>3.4</td>
</tr>
<tr>
<td>5</td>
<td>3.6</td>
</tr>
<tr>
<td>7</td>
<td>5.3</td>
</tr>
<tr>
<td>9</td>
<td>5.8</td>
</tr>
</tbody>
</table>
Rate of Rearrangement (ii)

Five determinations (Table III) of the conversion of (+)-trans-pinonic acid into (+)-homoterpenyl methyl ketone, with recovery of unconverted pinonic acid, were carried out by the method described for the (†)-ketolactone.

The specific rotation (c, 5 in CHCl₃) of the recovered pinonic acid was determined:

<table>
<thead>
<tr>
<th>Reaction-time, hr.</th>
<th>½</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>[α]₅₂⁰³</td>
<td>66.7°</td>
<td>57.4°</td>
<td>47.0°</td>
<td>43.4°</td>
<td>39.7°</td>
</tr>
<tr>
<td>t</td>
<td>22°</td>
<td>22°</td>
<td>21°</td>
<td>20°</td>
<td>22°</td>
</tr>
</tbody>
</table>

The specimens of (+)-ketolactone isolated during these rate-experiments were combined (1.60 g.), dissolved in hot water (20 ml.), treated with charcoal to remove methyl red, extracted with methylene chloride, and twice recrystallised from ether-light petroleum (b.p. 40-60°); the (+)-homoterpenyl methyl ketone formed prisms (0.57 g.), m.p. 46-47°, having [α]₁₆.₅ + 59.6° (c, 5.013 in CHCl₃).

The specimens of semi-solid pinonic acid recovered from the above rate-experiments were pressed on filter paper,
which was then extracted with methylene chloride. The extract yielded a liquid acid (2.16 g.) which was converted into its oxime (1.72 g.); after extraction with boiling ether there remained a product (0.69 g.) m.p. 195°, which by repeated recrystallisation from hot ethanol yielded (-)-cis-pinonic acid oxime, prisms, m.p. 199.5-200°, having \([\alpha]_{D}^{5893} = 34.3°\) (1, 4; c, 0.437 in ether). (Found: C, 60.5; H, 8.7; N, 7.2%). For this oxime, Delépine (loc. cit.) records m.p. 192° and \([\alpha]_{D}^{5893} = 29.5°\) (in ether).

(+)-Homoterpenyl Methyl Ketone: Mutarotation of Solutions of Pinonic Acid in Monochloroacetic Acid

A solution of (+)-trans-pinonic acid (i), (ii), 1.000 g.; (iii), (iv), 1.750 g. in monochloroacetic acid (made up to 10 ml. at 80°) was placed in a 1 dm. sealed end-plate jacketed polarimeter tube maintained at 100° by steam passing freely through the jacket. The rotatory power of the solution was determined at intervals; the first reading was made within 5 min. of the preparation of the solution (Table IV).

The liquid mixture of (+)-trans- and (-)-cis-pinonic acids (6.3 g.) recovered from these polarimetric experiments was heated with thrice its volume of phosphoric acid (d 1.72)
for 10 min. at 100°. The product (5.95 g.), isolated as described for the (+)-ketolactone, was recrystallised from ether and yielded (+)-homoterpenyl methyl ketone (3.5 g.) having m.p. 46.5°, $[\alpha]^{20}_{5893} + 58.6^\circ$ (c, 5.271 in CHCl$_3$), $[\alpha]^{100}_{5893} + 45.5^\circ$ (c, 5.612 in CH$_2$ClCO$_2$H), and $[\alpha]^{100}_{5893} + 45.9^\circ$ (c, 10.000 in CH$_2$ClCO$_2$H; the rotation was unchanged after 4 hr. at 100°). It gave a 2,4-dinitrophenylhydrazone, orange needles from ethanol, m.p. 168.5° (Found: C, 53.0; H, 5.7; N, 15.5%).

Both Barbier and Grignard (loc. cit.) and Delépine and Badoche (Compt. rend., 1952, 235, 1069) record m.p. 47° for (+)-homoterpenyl methyl ketone.
Table IV

The Mutarotations of Solutions of (+)-trans-Pinonic Acid in Monochlorosceletic Acid at 100°.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>[α]100 5893 (i)</td>
<td>5.46</td>
<td>5.18</td>
<td>4.92</td>
<td>4.50</td>
<td>4.10</td>
<td>3.87</td>
</tr>
<tr>
<td>[α]100 5893 (ii)</td>
<td>5.53</td>
<td>5.24</td>
<td>4.99</td>
<td>4.54</td>
<td>4.18</td>
<td>3.90</td>
</tr>
<tr>
<td>[α]100 5893 (iii)</td>
<td>9.34</td>
<td>8.85</td>
<td>8.39</td>
<td>7.69</td>
<td>6.88</td>
<td>6.65</td>
</tr>
<tr>
<td>[α]100 5893 (iv)</td>
<td>9.55</td>
<td>9.07</td>
<td>8.67</td>
<td>7.90</td>
<td>7.33</td>
<td>6.82</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>60</th>
<th>80</th>
<th>100</th>
<th>120</th>
<th>140</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>[α]100 5893 (i)</td>
<td>3.46</td>
<td>3.18</td>
<td>3.02</td>
<td>2.94</td>
<td>2.89</td>
<td>2.89</td>
</tr>
<tr>
<td>[α]100 5893 (ii)</td>
<td>3.44</td>
<td>3.21</td>
<td>3.04</td>
<td>2.92</td>
<td>2.97</td>
<td>2.87</td>
</tr>
<tr>
<td>[α]100 5893 (iii)</td>
<td>5.32</td>
<td>5.41</td>
<td>5.10</td>
<td>4.87</td>
<td>4.77</td>
<td>4.73</td>
</tr>
<tr>
<td>[α]100 5893 (iv)</td>
<td>6.05</td>
<td>5.52</td>
<td>5.18</td>
<td>4.93</td>
<td>4.78</td>
<td>4.71</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>180</th>
<th>195</th>
<th>210</th>
<th>230</th>
<th>240</th>
</tr>
</thead>
<tbody>
<tr>
<td>[α]100 5893 (i)</td>
<td>2.89</td>
<td>-</td>
<td>2.91</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[α]100 5893 (ii)</td>
<td>2.87</td>
<td>-</td>
<td>2.88</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>[α]100 5893 (iii)</td>
<td>4.73</td>
<td>4.67</td>
<td>-</td>
<td>4.67</td>
<td>4.67</td>
</tr>
<tr>
<td>[α]100 5893 (iv)</td>
<td>4.71</td>
<td>4.65</td>
<td>4.63</td>
<td>4.69</td>
<td>4.69</td>
</tr>
</tbody>
</table>

Solutions (1)-(iv) are described in the text.
The Formation of 2:4-Dimethylphenylacetic Acid
from Pinonic Acid by the Action of Bromine

2:4-Dimethylphenylacetic acid (1)

(±)-trans-Pinonic acid (18.4 g.) was suspended in hydrochloric acid (30 ml., d 1.18), and bromine (16.5 g.) was added in one portion. The flask was shaken vigorously and the temperature rose to 47° in 10 min., with disappearance of pinonic acid and bromine.

The clear liquid was heated in a steam bath for 4 hr., cooled, diluted with water (70 ml.), and the resinous product taken up in methylene chloride (30 ml.). This solution was combined with methylene chloride extracts of the aqueous liquid (successive portions of 25, 20, 15, 10, 10 ml.), washed with water, then with excess of dilute aqueous ammonia, and again with water. On distillation of the solvent, a neutral brown oil (1.1 g.) remained.

The ammoniacal and second aqueous washings were combined, acidified with hydrochloric acid, and extracted with methylene chloride (3 portions of 30 ml.). After washing of the combined extracts with water, the solvent was removed by distillation. Crude 2:4-dimethylphenylacetic acid remained as a chocolate-coloured solid (16.6 g.). It was
boiled with cyclohexane (90 ml.) and filtered. The filtrate was boiled for 30 min. with activated charcoal, and again filtered. Impure 2:4-dimethylphenylacetic acid (10.0 g.), m.p. 100-101°, separated as a granular powder on cooling.

Attempts to raise the m.p. of the product by recrystallisation were unsuccessful, owing to the presence of a persistent impurity in the form of a sparingly soluble substance, a small quantity of which was separated by fractional crystallisation. It was a white powder, m.p. 202-203°, which liberated carbon dioxide from a saturated solution of sodium bicarbonate. Tests for nitrogen and halogens were negative; the substance did not sublime at 100°/0.01 mm.

The various fractions of partially purified 2:4-dimethylphenylacetic acid were combined (10.4 g.) and sublimed at 100°/0.01 mm. (8.5 hr.). The sublimate (9.5 g.) had m.p. 104°.

The residue (0.6 g.), m.p. 170°, was extracted with boiling cyclohexane (25 ml.), cooled, filtered off and recrystallised from ethanol-water (1:2) to give a product with m.p. 196° (0.3 g.). A second recrystallisation from ethanol-water (1:1) gave a white powder (0.17 g.), m.p. 207-208°.
Three further recrystallisations from aqueous ethanol gave a white powder m.p. 210-210.5° (Found: C, 72.95; H, 6.65%; equiv., 164.7; M (Rast), (i) 288, (ii) 275).

2,4-Dimethylphenylacetic Acid (ii)

Bromination of pinonic acid and decomposition of the acidic solution were carried out exactly as described above. Neutral products (1.3 g.) and acidic products (15.3 g.) of the decomposition were separated by the same method as before. By sublimation of the crude acid at 100°/0.01 mm. (5 hr.), 2,4-dimethylphenylacetic acid (10.8 g.), m.p. 101° was obtained. After one recrystallisation from cyclohexane (100 ml.), the acid (10.2 g.) had m.p. 104°.

The non-sublimable residue was boiled with chloroform (50 ml.), cooled, and an insoluble powder was filtered off (0.90 g.). After removal of the solvent from the filtrate by distillation, a dark brown gum (2.4 g.) remained. The insoluble powder was recrystallised twice from aqueous ethanol, giving a pale brown powder (0.55 g.) having m.p. 209-210°. Repeated recrystallisation and boiling with activated charcoal did not remove the brown colour, which was eliminated by dissolving the acid (0.47 g.)
in acetone (35 ml.), and passing the solution through a short column (3'' x ½") of freshly heated activated charcoal, the column being finally washed through with more acetone (100 ml.). The combined effluent was evaporated, giving a white solid (0.47 g.), which was recrystallised three times from acetone (10 ml.). The acid so purified was a white crystalline substance, having m.p. 214° (Found: C, 72.95; H, 6.90%; M (Rast), 309).

2:4-Dimethylphenylacetic acid (iii) Preparation based on Harispe's method (loc. cit.).

(±)-trans-Pinonic acid (18.4 g.) in the form of a crystalline powder, was suspended in hydrochloric acid (29 ml., d 1.18), and bromine (5.3 ml.) was added in one portion. On vigorous shaking of the flask, the temperature rose to 48° in 10 min., with disappearance of pinonic acid and bromine.

The clear liquid was heated in a steam bath for 4 hr., cooled, and filtered at the pump (sintered glass filter). After being washed with concentrated hydrochloric acid, the solid was added to methanol (15 ml.); the liquid was then saturated with hydrogen chloride, and boiled under
reflux for 30 min. The mixture was left overnight, then again saturated with hydrogen chloride, boiled for 1 hr., and diluted with water (100 ml.). Extraction with methylene chloride, followed by washing with water, drying (Na₂SO₄), removal of solvent, and distillation, gave methyl 2:4-dimethylphenylacetate (10 g.), b.p. 174-178°/95 mm.

Part of the product (5.0 g.) was left in contact with anhydrous potassium carbonate, and then redistilled; the main fraction was collected at 124-126°/13 mm.

**Hydrolysis of the ester**

Potassium hydroxide (2.0 g.), water (20 ml.), ethanol (5.0 ml.), and the remaining impure ester (5.0 g.) were boiled together under reflux for 1 hr. After cooling and acidification, recrystallisation of the crude product from hot water yielded 2:4-dimethylphenylacetic acid (4.1 g.) in the form of hair-like needles m.p. 105.5°.

**S-Benzyl iso-thiuronium salt**, colourless plates from water, m.p. 164.5° (Found: S, 9.45%. C₁₆H₂₂O₂N₂S requires: S, 9.7%).

**Bromo-Finonic Acid**

(±)-trans-Finonic acid (19.0 g.) was added to a mixture of bromine (16.5 g.) and hydrochloric acid (30 ml.,
in a flask (100 ml.) which was shaken and cooled periodically under the tap, so that the temperature did not rise above 30°. Reaction was complete after 10 min., and the clear solution was then poured on to ice (150 g.), and the flask was rinsed with hydrochloric acid (10 ml., d 1.18).

The aqueous liquid was decanted, and the heavy, white, viscous oil was taken up in methylene chloride (50 ml.); the solution was washed five times with water (100 ml. portions), dried (Na₂SO₄), and the solvent evaporated at reduced pressure. A semi-solid residue (20.5 g.) was obtained which was filtered at the pump, to yield sticky white crystals (5.85 g.). After three recrystallisations from cyclohexane (200 ml.), the product (2.85 g.) had m.p. 114.5-115°. Part of this (0.85 g.) was thrice recrystallised from cyclohexane (80 ml.) and yielded bromo-pinonic acid (0.74 g.), m.p. 116.5-117° (Found: C, 45.9; H, 5.65; Br, 30.25%; equiv., 258. C₁₀H₁₅O₂Br requires: C, 45.65; H, 5.75; Br, 30.35%; equiv., 263).

Reduction of Bromo-Pinonic Acid to Pinonic Acid

The bromo-acid (0.25 g., m.p. 114.5-115°) was added as a fine powder to hydrochloric acid (50 ml., d 1.18), and the suspension was stirred vigorously until a clear solution was obtained. Stirring was continued while zinc dust (0.70 g.)
was added in small portions. As the metal dissolved very rapidly, it was thought that reduction might not be efficient; accordingly, the solution was diluted with water (50 ml.) and more zinc dust (0.70 g.) was added to the clear solution with stirring. The metal dissolved slowly, and after continuation of the stirring for 5 hr. the mixture was left overnight.

Undissolved zinc, and a small amount of insoluble oily material were filtered off, and the filtrate was extracted with methylene chloride (successive portions of 15, 10, 10, 5, 5 ml.). The combined extract was washed once with water (10 ml.) and then shaken with dilute aqueous ammonia (10 ml.). After washing of the methylene chloride with water, solvent was removed by distillation. Impure (±)-homoterpenyl methyl ketone remained as a low-melting solid (0.02 g.). This was converted entirely into the 2:4-dinitrophenylhydrazone (0.035 g.) which had m.p. 153-155°; after one recrystallisation from ethanol it had m.p. 162° and m.p. 163° when mixed with an authentic specimen.

The ammoniacal extract mentioned above was added to the aqueous washings from the following operation, and acidified with dilute hydrochloric acid. After extraction with methylene chloride (5 portions of 5 ml.), the combined
extracts were washed with water and the solvent was removed by distillation. A viscous liquid remained (0.05 g.), which was treated with potassium hydrogen carbonate (0.05 g.) dissolved in the minimum of cold water. A solution of hydroxylamine hydrochloride (0.05 g.) in the minimum of water was then added, and the whole was shaken; the suspension of oily droplets was allowed to stand. After 24 hr., the semi-solid product was filtered off at the pump and pressed on porous plate. This gave a white crystalline powder (10 mg.) m.p. 146-147°. After one recrystallisation from a mixture of ethyl acetate and carbon tetrachloride, the derivative had m.p. 148-149°, and m.p. 149-150° when mixed with an authentic specimen of (±)-trans-pinonic acid oxime having m.p. 152°.

Rearrangement of Bromo-Pinonic Acid to 2:4-Dimethylphenylacetic Acid.

Preparation of hydrochloric-hydrobromic acid mixture

Dry hydrogen chloride (17.5 g.) was passed into an ice-cooled mixture of hydrochloric acid (55.5 ml., d 1.18) and hydrobromic acid (34.5 ml., d 1.43; free from Br₂). More hydrochloric acid (13.4 ml.) and hydrobromic acid (8.3 ml.)
were added, and the "mixed acid" was stored in a tightly stoppered brown glass bottle.

**Rearrangement of the bromo-acid**

Bromo-pinonic acid (0.50 g.) was placed in a small flask (5 ml.) and "mixed acid" (2 ml.) added from a pipette. The mixture, on being heated under reflux on a steam bath, evolved some acidic fumes, and a clear yellow solution was obtained after about 5 min. After 30 min., a pale brown oil began to separate with slow evolution of acidic fumes. At the end of 4 hr., the flask was removed from the steam bath, and, on cooling, the oil solidified. Water (3 ml.) was added, the flask was chilled in ice-water, and the product filtered off at the pump, washed with ice-cold water (10 ml.), and dried in vacuo (H₂SO₄). A pale brown crystalline solid (0.30 g.) m.p. 98-100° was obtained.

Sublimation at 100°/0.1 mm. (1 hr.) gave 2:4-dimethylphenylacetic acid (0.25 g.) having m.p. 103° and 104° when mixed with an authentic specimen. The residue (0.04 g.) was a clear brown gum which dissolved completely in cold chloroform.
Attempt to Isolate the Bromo-acid Without Keeping the Reaction Temperature Below 30°

(±)-trans-Pinonic acid (18.4 g.) was suspended in hydrochloric acid (30 ml., d 1.18), and bromine (16.0 g.) was added in one portion. On vigorous shaking of the flask, the temperature rose to 40° in 10 min. with disappearance of pinonic acid and bromine.

The product of bromination (24.3 g.) was isolated as described above. It was a pale yellow syrup which was not affected by storage in the refrigerator for 24 hr. After being seeded with solid bromo-pinonic acid, and stored in the refrigerator for 7 weeks, the semi-solid obtained was filtered at room temperature at the pump. The filtrate (17.5 g.) was a clear, pale brown syrup, $n_D^{25} 1.5089$. The residue (5.1 g.) was a sticky semi-solid; it was thrice recrystallised from cyclohexane, drained on filter paper, and recrystallised three more times from cyclohexane; (±)-trans-pinonic acid (0.5 g.) m.p. 105-108° was obtained; the m.p. was unchanged by admixture with an authentic specimen of the acid.

Some of the viscous filtrate (0.5 g.) from the bromination product was heated with "mixed acid" (2 ml.) as described above for the conversion of bromo-pinonic acid
into 2:4-dimethylphenylacetic acid. Decomposition proceeded exactly as described for the bromo-acid, except that the oil separating was of a dark brown colour and did not crystallise on cooling, but solidified to a dark brown, brittle resin. The reaction product (0.25 g.) was separated as before. On sublimation at 100°/0.25 mm. (75 min.), white crystals of 2:4-dimethylphenylacetic acid (0.11 g.) were obtained, with m.p. 101°. The residue (0.14 g.) was a dark brown resin which was treated with chloroform (3 ml.) and the insoluble dicarboxylic acid (0.013 g.) filtered off, and washed with a little chloroform; it had m.p. 201-202°.

2:4-Dimethylphenylacetic Acid from Homoterpenyl Methyl Ketone

(±)-Homoterpenyl methyl ketone (18.4 g.) was dissolved in hydrochloric acid (30 ml.), and bromine (16.0 g.) was added in one portion. On shaking the flask, the bromine disappeared at once, and the temperature rose sharply to 50°, with slight evolution of acidic fumes. The clear yellow liquid was cooled under the tap and divided into two equal portions (34.2 g. each). One portion (a) was heated on a steam bath for 4 hr. for decomposition to 2:4-dimethylphenylacetic acid. The other portion (b) was poured on to ice for isolation of the intermediate.
(a) During the decomposition, a brown oil separated, which solidified on cooling, and was taken up in methylene chloride (90 ml.). Separation of the acidic products of the decomposition from the neutral products was carried out by ammoniacal extraction as described above. The neutral product (0.75 g.) was a sweet smelling brown oil, similar to that obtained in the preparation of 2:4-dimethylphenylacetic acid from pinonic acid. The acidic product was a brown solid (7.8 g.) which was sublimed at 100°/0.1 mm. (6 hr.), giving 2:4-dimethylphenylacetic acid (4.7 g.) m.p. 104°; after recrystallisation from cyclohexane (75 ml.) it (3.9 g.) had m.p. 105.5°. A non-sublimable residue (2.30 g.) was also obtained. This was taken up in methylene chloride, filtered, and the residue washed with the same solvent (30 ml.). On drying, this material was found to be the dicarboxylic acid also obtained in the preparation of 2:4-dimethylphenylacetic acid from pinonic acid; it (0.25 g.) had m.p. 203-205°.

On removal of methylene chloride from the filtrate and washings, there remained a dark brown gum (2.00 g.).

(b) The brominated homoterpenyl methyl ketone isolated by pouring the acidic solution on to ice after the initial reaction, was taken up in methylene chloride, washed five
times with water, dried (Na_{2}SO_{4}), and the solvent removed at reduced pressure. A clear, pale yellow syrup remained (12.7 g.); n^25_D 1.4984, which showed no tendency to crystallise after storage in the refrigerator for 4 weeks.

A portion of the bromo-compound (0.5 g.) was dissolved in the "mixed acid" (2 ml.) at room temperature, and the solution was heated on a steam bath for 4 hr. Separation of the reaction product (0.33 g.) was carried out as described above. Sublimation at 100°/0.25 mm. (75 min.) yielded 2:4-dimethylphenylacetic acid (0.19 g.) having m.p. 100°. The non-sublimable residue (0.07 g.) was taken up in cold chloroform, filtered, and the residue washed with the same solvent. On drying, it (5 mg.) had m.p. 202-203°; it was the dicarboxylic acid previously observed.

The Rearrangement of (±)-trans-Pinonic Acid to Homoterpenyl Methyl Ketone under Conditions Similar to those Employed in the Bromination of Pinonic Acid

(±)-trans-Pinonic acid (3.0 g.) was suspended in the "mixed acid" (3.0 ml.), and the suspension was stirred vigorously in a test-tube which was immersed in a stirred oil bath at 48° (thermostat). After 10 min., the clear solution was poured into water (100 ml.), and ammonia
(10 ml., d 0.880) was added. Homoterpenyl methyl ketone was then extracted with methylene chloride (successive portions of 25, 20, 15, 10, 10 ml.), the extracts were washed with water and solvent was removed by distillation; 0.73 g. was obtained, i.e. 26% conversion.

After acidification of the alkaline liquid with hydrochloric acid (10 ml., d 1.18), and extraction with methylene chloride, as before, pinonic acid was obtained (1.88 g., i.e. 63% recovery).
The Phosphoric Acid-Catalysed Decomposition of Pinonic Acid

Decomposition of Pinonic Acid in Phosphoric Acid Solution

(±)-trans-Pinonic acid (80 g.), and phosphoric acid (200 g., d 1.74), were mixed in a round-bottomed flask (1 l.), to which was fitted a Claisen-type distillation head, and double-surface condenser. A thermometer was also fitted, with its bulb immersed in the reaction mixture. The flask was then immersed in an oil bath which had been previously heated to 180°.

As the temperature rose, the pinonic acid dissolved to give a clear solution, and after 10 min., at 150°, decomposition commenced, with steady evolution of carbon dioxide and separation of an oily upper layer. The temperature of the oil bath was maintained at 175°, and the decomposition continued during 10 min., while the temperature of the reaction mixture rose to 160°, and a mixture of colourless oil and water distilled. Heating was then discontinued, but the oil bath was not removed. The internal temperature rose to 165° during 5 min., with only slight evolution of carbon dioxide. On cooling to room
temperature, the reaction mixture was diluted with water (150 ml.) and steam distilled. The steam distillate was collected together with the distillate obtained during the decomposition, the light oil being separated continuously by means of a siphon. The aqueous fraction (4 l.) was collected in successive portions of 1 l., each of which was extracted with methylene chloride (successive portions of 30, 25, 20, 15, 10 ml.). The extracts were combined and the solvent was removed by distillation; a pale yellow oil remained (7.5 g.).

The yellow oil which was collected during the steam distillation, was taken up in methylene chloride, separated from water, and most of the solvent was distilled off on the steam bath.

After cooling, the aqueous phosphoric acid was decanted from the reaction flask, leaving a clear, soft, brown resin, which was washed well with water, drained, and weighed (31.0 g.). The aqueous acid was extracted with methylene chloride (successive portions of 25, 20, 15, 10, 10 ml.), and, after the combined extracts had been washed with water, the solvent was distilled, leaving a pale brown crystalline solid (0.40 g.).
Extract from the aqueous distillate

The pale yellow oil was taken up in methylene chloride (25 ml.) and extracted with sodium carbonate. Acidification of the alkaline extract with dilute sulphuric acid yielded impure 2:4-dimethylphenylacetic acid, white needles (1.5 g.) m.p. 98°.

After being washed with water, the methylene chloride solution, containing non-acidic substances, was distilled. A pale yellow oil remained (5.9 g.). This was dissolved in 0.5N ethanolic potassium hydroxide (75 ml.) and the solution was boiled under reflux for 2 hr. After dilution with water (100 ml.), non-saponifiable substances were extracted with methylene chloride (successive portions of 25, 20, 15, 10, 10 ml.), the combined extracts were washed with water, and the solvent was removed by distillation. The residue (0.1 g.) was not examined further. The alkaline liquid containing the saponifiable substances, was acidified with sulphuric acid, and extracted with methylene chloride (successive portions of 25, 20, 15, 10, 10 ml.). The combined extracts were washed with water and, after removal of the solvent by distillation, there remained a pale red-brown oil (5.6 g.).
The oil obtained during the steam distillation

The pale yellow oil (24.4 g., not completely free from solvent) was taken up in methylene chloride (50 ml.) and extracted with sodium carbonate. Acidification of the alkaline extract yielded a small quantity of pasty solid (0.3 g.) which was not examined further.

The methylene chloride solution was washed with water, and the solvent was then removed by distillation through a short column packed with Fenske helices. The residue (21.1 g.) was distilled from an oil bath through the same column; a pale yellow distillate b.p. 145-160° (13.3 g.), and a high-boiling residue (7.6 g.) were obtained. The distillate was stored over metallic sodium for 12 hr., and then distilled from sodium, the same apparatus as before being used. The entire distillate b.p. 150-170° (11.8 g.) was collected; it was a colourless oil nD^25 1.4780, which on nitration by the method described below yielded 23% of trinitroψ-cumene, m.p. 184° after one recrystallisation from ethanol; the m.p. of this derivative when mixed with an authentic specimen was 185-186°.

The high-boiling residue, referred to above, was dissolved in 0.5N ethanolic potassium hydroxide (50 ml.), and
the solution was boiled under reflux for 2 hr. After dilution with water (100 ml.), the non-saponifiable substances were extracted with methylene chloride (successive portions of 30, 25, 20 ml.), the combined extracts were washed with water and the solvent was removed by distillation, leaving a dark yellow, viscous oil (5.8 g.).

Aqueous washings and the alkaline extract were combined, and washed with methylene chloride. After acidification with dilute sulphuric acid, the liquid was extracted with methylene chloride (successive portions of 25, 20, 15, 10, 10 ml.); the extract was washed with water, and the solvent removed by distillation. A pale red-brown oil remained (1.3 g.). This was combined with the saponifiable material obtained from the aqueous fraction of the steam distillate (5.6 g.), and distilled at reduced pressure. The main fraction (3.4 g.), b.p. 93-97°/0.25 mm., nD²⁵ 1.4683, was the lactone of 2-hydroxy 2:4-dimethylcyclohexylacetic acid. Analytical data, the physical properties of the pure compound, and details of its identification are given below.
The resin remaining after steam distillation

The resin was taken up in methylene chloride (50 ml.), the solution was washed well with water, and the solvent gently boiled off in the sublimation apparatus; the remaining solvent was removed at 100° at the water-pump, after which the pressure was reduced to 0.2 mm. (at the rotary pump) and the resin kept at 100° for 6 hr. A mixture of white crystals and sticky gum sublimed. The sublimate was taken up in methylene chloride (25 ml.) and extracted with dilute aqueous sodium carbonate. On acidification of the alkaline extract with dilute hydrochloric acid, 2:4-dimethylphenylacetic acid was obtained (0.80 g.) m.p. 101-102°. Neutral material from the sublimate was obtained by distilling the solvent; a pale yellow gum (1.0 g.) remained.

Unsublimable resin remaining in the apparatus was taken up in methylene chloride (50 ml.); most of the solvent was then distilled off, the rest being removed at 100° at the water-pump. A soft, brown, clear resin (28.9 g.) remained.
The product extracted from the residual aqueous phosphoric acid

The pale brown crystalline solid (0.40 g.) was taken up in methylene chloride (10 ml.) and separated into neutral (0.1 g.) and acidic (0.2 g.) components by extraction with aqueous sodium carbonate. The neutral material, a brown gum, was not examined further. The acidic component was 2:4-dimethylphenylacetic acid, m.p. 101°.

2:4-Dimethylphenylacetic acid

The three specimens of this acid isolated above (total, 2.4 g.) were combined and recrystallised from hot cyclohexane; the acid was obtained as fluffy white needles (1.85 g.) m.p. 103° alone and 104° when mixed with an authentic specimen having m.p. 105°. A second crop (0.12 g.) m.p. 101-102° was obtained on concentration of the mother-liquor.

A mixture of (±)-trans-pinonic acid m.p. 105-105.5° (0.12 g.) and 2:4-dimethylphenylacetic acid m.p. 105-105.5° (0.12 g.) had m.p. 77-80°.
Decomposition of Pinonic Acid in Phosphoric Acid Solution
(The method described above was developed from the following procedure).

(±)-trans-Pinonic acid m.p. 103.5-104° (80 g.), and phosphoric acid (200 g., d 1.73), were heated together on a steam bath for 30 min. The flask was then fitted for distillation, and the temperature of the contents was raised to 150°. This temperature was maintained for 1 hr., carbon dioxide being steadily evolved without distillation occurring, and a dark oily layer rose to the surface of the liquid. After being cooled, the contents of the flask were diluted with an equal volume of water, and steam-distilled. A light oil (16.75 g.) was separated from the aqueous part of the distillate (3 l.).

When cool, the acidic liquid was decanted from the resinous material remaining in the flask and discarded. The resin was dissolved in methylene chloride (100 ml.) and separated into neutral (32.5 g.) and acidic (3.50 g., mainly 2:4-Dimethylphenylacetic acid) components by extraction with aqueous sodium carbonate (A tendency for emulsions to form made the extraction difficult).

The aqueous portion of the steam distillate was
extracted with methylene chloride, and acidic material removed from the extract by shaking with aqueous sodium carbonate. Acidification of the alkaline liquid gave 2:4-dimethylphenylacetic acid (0.8 g.) m.p. 101º.

A neutral liquid (4.3 g.) was recovered from the methylene chloride extract by distillation. Fractional distillation of the residue gave the lactone of 2-hydroxy 2:4-dimethylcyclohexylacetic acid (1.2 g.), a colourless liquid b.p. 102-103º/0.7 mm., nD^25 1.4683, d^25 1.0288.

(Found: C, 71.5; H, 9.55%; equiv., 169.2. C_{10}H_{16}O_2 requires: C, 71.45; H, 9.55%; equiv., 168.2.)

Distillation of the oil separated from the steam distillate gave two main fractions:

(i) b.p. 149-167º, nD^25 1.4811 (7.35 g.)
(ii) b.p. 92-118º/0.5 mm. (3.65 g.)

(i) Was separated by fractional distillation into 16 fractions, boiling between 144º and 166º. (ii) Was separated by hydrolysis (0.5N ethanolic potassium hydroxide) into the lactone C_{10}H_{16}O_2 b.p. 104-105º/0.7 mm. nD^25 1.4691, and a non-saponifiable fraction b.p. 90-116º/1.0 mm. which was redistilled, giving an unsaturated hydrocarbon fraction b.p. 125-128º/3.5 mm., nD^25 1.5084; probably a mixture (Found: C, 83.1; H, 11.6%).
2:4-Dimethylphenylacetic acid

The crude acid (3.50 g.) extracted from the resinous product of the reaction was recrystallised from cyclohexane and combined (1.35 g.) with the acid extracted from the steam distillate (0.8 g.). Recrystallisation from hot water (1.0 l.) gave 2:4-dimethylphenylacetic acid (2.10 g.) m.p. 105° undepressed by admixture with an authentic specimen.

Examination of the hydrocarbon fractions b.p. 144-166°

The lower-boiling fractions showed strong unsaturation (Br₂/CCl₄) and gave peroxide reactions after a few days exposure to air.

Quantitative nitration

The hydrocarbon fraction (0.29 g.) was added dropwise with shaking to a cooled mixture of nitric acid (2.0 ml., d 1.42) and sulphuric acid (3.0 ml.). After being heated in a steam bath for 10 min., with occasional shaking, the mixture was poured into cold water (100 ml.) and the suspension was allowed to settle (14 hr.). The product was filtered off at the pump and washed with water (100 ml.), followed by ethanol (4 ml.); it was dried in vacuo before determination of the yield, m.p., and m.p. when mixed with
a specimen of 3:5:6-trinitroψ-cumene having m.p. 188-189°.
In a control experiment, ψ-cumene b.p. 167-168° nD25 1.5020
gave 60% of the theoretical yield of the trinitro-compound,
m.p. 183°.

The highest-boiling fraction (b.p. 165-166°,
nD25 1.4967) on nitration gave 3:5:6-trinitroψ-cumene,
having m.p. 183-185°, and mixed m.p. 185-187°. Yield 49%.
A fraction having b.p. 155-157°, nD25 1.4699,
gave a 5% yield of the trinitro-compound m.p. 185° after
one recrystallisation from ethanol; mixed m.p. 186°.
A fraction having b.p. 153-154°, nD25 1.4650,
gave a 5% yield of the trinitro-compound m.p. 184-185°
after one recrystallisation from ethanol; mixed m.p.
186-187°.
A fraction having b.p. 149-150°, nD25 1.4533 (0.38 g.)
was dehydrogenated by boiling with palladised charcoal
(0.059 g.; 7% Pd) for 5 hr. The product had b.p. 154-170°,
nD25 1.4623, and gave a 28% yield of trinitroψ-cumene, m.p.
183-185°, and mixed m.p. 185-187°.
A fraction having b.p. 151-153°, nD25 1.4587, was
analysed
Found: C, 87.65; H, 12.45%
calc. for C₉H₁₂: C, 89.85; H, 10.15%
C₉H₁₄: C, 88.45; H, 11.55%
C₉H₁₆: C, 87.0; H, 13.0%

Attempted ozonolysis of the low boiling mixture of hydrocarbons

The hydrocarbon mixture (1.0 g.) having b.p. 140-167°, nD²⁵ 1.4811 (obtained in a separate decomposition of pinonic acid) was dissolved in acetic acid (3.0 ml.) and treated with ozonised oxygen (7% O₃), the gas being passed in at the rate of 25-30 ml./min.; absorption was complete after 2.5 hr.

Part of the solution (1.0 ml.) was heated to 120°, and acetic acid was then evaporated off in vacuo. The residue dissolved in methanol and on addition to Brady's reagent, it yielded a viscous red oil which did not solidify.

Part of the solution (1.0 ml.) was diluted with water (4 ml.) and boiled under reflux for 40 min. The oily product, and the aqueous liquid both gave a red oil with 2,4-dinitrophenylhydrazine.

Another portion (1.0 ml.) was diluted and boiled under reflux and then steam-distilled. Both distillate and
non-volatile residue gave a red oil with 2,4-dinitrophenyl-hydrazine.

Oxidation of the Lactone $C_{10}H_{16}O_2$

The lactone (0.091 g.), hydrochloric acid (0.17 ml., d 1.18), and bromine (0.061 g.), were heated together in a sealed glass tube at 100° for 1 hr. Acidic products of the reaction were extracted by means of aqueous sodium carbonate, and sublimed at 100°/1.0 mm. (2.5 hr.). A white crystalline sublimate (0.049 g.) was obtained. After two recrystallisations from cyclohexane, and one from hot water, 2,4-dimethyl-phenylacetic acid was obtained, having m.p. 103° undepressed by admixture with an authentic specimen.

Preparation of $\beta$-n-Butyl-$\gamma$-dimethyl-$\gamma$-butyrolactone by Reduction of Homoterpenyl Methyl Ketone

Hydrazone of (i)-homoterpenyl methyl ketone

Hydrazine hydrochloride (10.0 g.), and sodium acetate (NaOOC·CH₃·3H₂O; 15.0 g.) were dissolved together in warm water (25 ml.). Homoterpenyl methyl ketone (24.0 g.) was dissolved in ethanol (25 ml.). The two solutions were mixed and heated under reflux on the steam bath for 20 min.
On cooling, the solution was diluted with water (50 ml.). After 20 hr. at room temperature, the crystals were filtered off, washed with water (100 ml.), and dried in vacuo ($\text{H}_2\text{SO}_4$). The product (3.80 g.) had m.p. 121°.

In view of the low yield, the filtrate and washings were combined, and extracted with methylene chloride (3 portions of 25 ml.). The combined extracts were washed twice with water, and the solvent was removed by distillation. On cooling, the residue solidified to a pasty brown solid (14.1 g.). This was washed with ether and dried as above, giving (+)-homoterpenyl methyl ketone (12.5 g.) m.p. 55-57°.

**Decomposition of the hydrazone**

Potassium hydroxide (3.5 g.) was dissolved in diethylene glycol (25 ml.) by gentle warming over a free, luminous, coal-gas flame. The hydrazone (3.70 g.) was then added, and warming was continued until a clear solution was obtained. This was distilled in a Claisen flask at atmospheric pressure, the thermometer having its bulb immersed in the liquid. Distillation began at 165°, with some effervescence; the temperature rose rapidly, and water distilled. After reaching 205°, the flask was allowed to cool, and arranged for reflux. The liquid was then kept at
205-210° until, after 1.5 hr., the evolution of nitrogen had ceased, and the odour of ammonia could be detected at the top of the condenser. On cooling, the contents of the flask were diluted with water (100 ml.) and extracted with methylene chloride (successive portions of 25, 20, 15, 10, 10 ml.). The aqueous liquid was then acidified with dilute sulphuric acid and extracted with methylene chloride as before. This extract was washed with water, and the solvent removed by distillation. A viscous, dark brown oil remained (2.63 g.), having a strong empyreumatic odour. The oil was distilled at reduced pressure, giving a yellow oil (2.03 g.) b.p. 139-144°/14 mm.

**Reduction of (±)-Homoterpenyl Methyl Ketone without Isolation of the Hydrazone**

Potassium hydroxide (12.5 g.) was dissolved in diethylene glycol (90 ml.) as before. (±)-Homoterpenyl methyl ketone (12.5 g.) was then dissolved in this solution, and an aqueous solution of hydrazine hydrate (5 ml., p. 1.013) was added. The mixture was boiled under reflux for 90 min., in a Claisen flask (250 ml.). Water etc., was then distilled off, with the bulb of the thermometer immersed in the liquid.
Distillation began when the temperature reached 145°. The temperature rose slowly as the distillation proceeded, until evolution of nitrogen began at 190°. At 205°, the effervescence continued after removal of the flame, and the mixture was then heated at this temperature under reflux for 4.5 hr.

To the liquid, after cooling, water (150 ml.) was added. The whole was extracted with methylene chloride (successive portions of 25, 20, 15, 10, 10 ml.). The combined extracts were washed with water, and, after removal of the solvent by distillation, a brown liquid with pleasant odour remained (0.57 g.).

The aqueous alkaline liquid was acidified with dilute sulphuric acid, and extracted as before with methylene chloride. The combined extracts, twice washed with water, were dried over anhydrous potassium carbonate, and the solvent was removed by distillation. A dark brown, viscous oil (10.63 g.) remained which on distillation gave a pale yellow oil with strong empyreumatic odour (6.47 g.), having b.p. 136-141°/13 mm.

Distillation of the material from this and the previous experiment gave a product (5.92 g.) having b.p.
It was twice fractionally distilled and yielded \(\beta\text{-}n\text{-}butyl-\gamma\text{-}dimethyl\gamma\text{-}butyrolactone\) (1.42 g.), b.p. 99.5°/1.2 mm., \(n^\text{D}_{25}\) 1.4470, a colourless oil with faint "oily" odour (Found: C, 70.3; H, 10.6%; equiv., 168.6. \(\text{C}_{10}\text{H}_{18}\text{O}_{2}\) requires: C, 70.6; H, 10.7%; equiv., 170.2).

**Determination of equivalent**

The equivalent of \(\beta\text{-}n\text{-}butyl-\gamma\text{-}dimethyl\gamma\text{-}butyrolactone\) was determined by a semi-micro method. Portions of approximately 0.10 g. of the lactone were hydrolysed with 0.5N ethanolic potassium hydroxide (30 min. at room temperature) and the excess alkali was titrated with 0.4N hydrochloric acid.
Preparation of 2-Methyl cyclohexanol

Aluminium turnings (56.7 g., dried at 100°C), dry iso-propanol (590 ml.), and mercuric chloride (1.0 g.), were boiled together under reflux. When all the aluminium had dissolved (12 hr.), dry, redistilled 2-methyl cyclohexanone (80 g.) was added to the grey suspension and the mixture was boiled under reflux for 30 min. Acetone was then removed by distilling the liquid slowly through a short fractionating column, until the temperature rose to 82°C, and the distillate was free from acetone (150 ml. of distillate were collected).

As much of the solvent as possible was then distilled off at the water-pump, an oil bath which was gradually heated to 150°C being employed. The viscous residue was cooled under the tap and poured promptly with stirring into a mixture of hydrochloric acid (600 ml.) and ice (to make 2.0 l.). During the hydrolysis, the temperature remained below 0°C. Stirring was continued until all of the ice had melted (30 min.); the liquid was allowed to stand; the lower aqueous layer was then siphoned off, and extracted with benzene (3 portions of 100 ml.). The extracts were combined with the oily layer and filtered to remove suspended
black dust. The benzene solution was washed successively with water, very dilute sodium hydroxide (1%), and water, and dried over anhydrous sodium sulphate. Benzene was distilled off at atmospheric pressure, and the residue yielded on distillation a mixture of cis- and trans-2-methyl cyclohexanol (64.3 g., 80% of theoretical), having b.p. 70-74°/19 mm.

**Dehydration of 2-Methyl cyclohexanol**

The carbinol (28.5 g.) was distilled with phosphoric acid (10 ml., d 1.74). A mixture of olefin and water was collected, and distillation ceased when the vapour-temperature reached 114°. The olefin layer was separated from the distillate, and redistilled with more phosphoric acid (10 ml.). After separation of the water from the distillate, the olefin was dried, first over anhydrous potassium carbonate, then over metallic sodium, and then distilled from more sodium. The main fraction had b.p. 108-108.5°, nD\(^{20}\) 1.4473; it was fractionally distilled five times, and yielded a pure specimen (3.0 g.) of 1-methyl cyclohexene having b.p. 109-109.5°, nD\(^{20}\) 1.4484, nD\(^{25}\) 1.4458. Signiado and Cramer (J. Amer. Chem. Soc., 1933,
55, 3326) record b.p. 109-110°, n\text{D}^{20} 1.4498 for this compound, prepared by dehydration of 2-methyl cyclohexanol in the presence of aluminium sulphate.

**Preparation of 1:2-Dimethyl cyclohexanol**

Magnesium turnings were heated at 100° for 10 min., allowed to cool in the desiccator at atmospheric pressure, and then rubbed firmly in a clean, dry mortar, to expose fresh metallic surfaces. The turnings (22.5 g.) were placed in a three-necked flask (1 l.) and covered with sodium-dried ether (200 ml.). The stirrer (mercury-sealed) was started, and methyl bromide gas passed into the mixture (from an ampoule) through an inlet tube reaching to the bottom of the flask. On warming the bottom of the flask with the palm of the hand, a vigorous reaction was initiated, and thereafter the flask was cooled in a bath of water kept at 10-20° by the addition of ice.

After 4 hr., addition of halide (110 g.) was complete, and only a few minute fragments of magnesium remained undissolved. The grey solution was stirred for 30 min. at 15°, then for 30 min. at 35-40° under reflux, and allowed to cool. The inlet tube was replaced by a dropping
funnel through which was added, to the stirred reagent-solution, dropwise during 90 min., a solution of dry, redistilled 2-methyl cyclohexanone (99 g.) in sodium-dried ether (100 ml.).

The magnesium complex was decomposed by adding slowly a saturated solution of ammonium chloride (140 ml., prepared at 25°). Gas was evolved, and the contents of the flask separated finally into a granular white solid, and a clear supernatant liquid. The ethereal solution was decanted, and the solid remaining was first washed with ether (3 portions of 200 ml.), and then shaken with saturated ammonium chloride solution (1350 ml.) until all magnesium compounds had dissolved; the solution was extracted with ether (2 portions of 100 ml.). The combined ethereal solutions were washed with ammonium chloride solution (100 ml.) followed by water (5 portions of 100 ml.), dried (K₂CO₃), and the solvent removed by distillation. Distillation of the product gave a mixture of cis- and trans-1:2-dimethyl cyclohexanol b.p. 67-70°/16 mm. (92.9 g.).

Dehydration of 1:2-Dimethyl cyclohexanol

The carbinol (32.0 g.) was distilled slowly with
iodine (0.2 g.). Dehydration was rapid and almost complete. Distillation began at 90°, a mixture of olefin and water being collected. After 1.5 hr, distillation ceased (vapour temperature 130°), olefin alone distilling. Water was separated from the distillate, and the hydrocarbon was dried over anhydrous potassium carbonate. After redistillation with iodine (0.2 g.), and one washing with potassium carbonate solution, the olefin was dried (K₂CO₃, then Na) and distilled three times, yielding a pure specimen of 1,2-dimethyl cyclohexene (2.37 g.) b.p. 136.5-137°, n° 1.4574.

Hammond and Nevitt (J. Amer. Chem. Soc., 1954, 76 4121) record b.p. 136.2°, n° 1.4587 for this compound, prepared by dehydration of 1,2-dimethyl cyclohexanol in the presence of iodine.

Cyclohexene

The hydrocarbon was first dried over anhydrous potassium carbonate, and then distilled twice from metallic sodium. This gave material having b.p. 81.5-82°, n° 1.4440.
The Comparative Rates of Hydrogenation of Cyclohexene, 1-Methyl Cyclohexene, 1:2-Dimethyl Cyclohexene, and the Hydrocarbon Mixture Believed to Consist of Ψ-Cumene and 1:2:4-Trimethyl Cyclohexene.

Method of Hydrogenation.

Platinic oxide catalyst (15 mg. ±1 mg., "Adams") was weighed in a small glass capsule, which was placed in a hydrogenation flask with methanol (10 ml., redistilled). After flushing of the flask with hydrogen, the gas reservoir was adjusted to full capacity at atmospheric pressure and room temperature, the shaker was started, and the catalyst reduced at a pressure equivalent to a head of about 2 feet of water.

The hydrocarbon (0.004 mol.) was weighed into an ignition tube. Methanol (10 ml.) was added to the contents of the hydrogenation flask, and the ignition tube was placed in an upright position inside the flask, which was then flushed with hydrogen. The apparatus was adjusted as before, the ignition tube was upset, and the hydrocarbon was hydrogenated at a pressure slightly greater than atmospheric. Atmospheric pressure and ambient temperature were noted, and
the volume of hydrogen absorbed was periodically observed after bringing the pressure to atmospheric. Each volume-reading was corrected for vapour pressure of water, and reduced to S. T. P. The percentage of the theoretical maximum of hydrogenation was calculated for each reading.
## Results of Hydrogenation

### Cyclohexene

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>14.8 mg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon</td>
<td>0.3394 g.</td>
</tr>
<tr>
<td>Ambient temperature</td>
<td>23°</td>
</tr>
<tr>
<td>Atmospheric pressure</td>
<td>771 mm.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>Volume absorbed</th>
<th>Percentage of hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 min.</td>
<td>84 ml.</td>
<td>83%</td>
</tr>
<tr>
<td>25 &quot;</td>
<td>90 &quot;</td>
<td>89</td>
</tr>
<tr>
<td>35 &quot;</td>
<td>92 &quot;</td>
<td>91</td>
</tr>
</tbody>
</table>

### 1-Methyl cyclohexene

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>15.0 mg.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrocarbon</td>
<td>0.4166 g.</td>
</tr>
<tr>
<td>Ambient temperature</td>
<td>23°</td>
</tr>
<tr>
<td>Atmospheric pressure</td>
<td>773 mm.</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Time</th>
<th>Volume absorbed</th>
<th>Percentage of hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min.</td>
<td>28 ml.</td>
<td>26.5%</td>
</tr>
<tr>
<td>30 &quot;</td>
<td>33 &quot;</td>
<td>31</td>
</tr>
<tr>
<td>60 &quot;</td>
<td>41 &quot;</td>
<td>39</td>
</tr>
<tr>
<td>90 &quot;</td>
<td>46 &quot;</td>
<td>43.5</td>
</tr>
<tr>
<td>120 &quot;</td>
<td>52 &quot;</td>
<td>49</td>
</tr>
</tbody>
</table>
### 1:2-Dimethyl cyclohexene

<table>
<thead>
<tr>
<th>Time</th>
<th>Volume absorbed</th>
<th>Percentage of hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min.</td>
<td>2.5 ml.</td>
<td>2.5%</td>
</tr>
<tr>
<td>45 &quot;</td>
<td>4.0 &quot;</td>
<td>4.0</td>
</tr>
<tr>
<td>120 &quot;</td>
<td>5.0 &quot;</td>
<td>5.0</td>
</tr>
</tbody>
</table>

### "1:2:4-Trimethyl cyclohexene/γ-Cumene mixture" $n_D^{25}$ 1.4811

<table>
<thead>
<tr>
<th>Time</th>
<th>Volume absorbed</th>
<th>Percentage of hydrogenation</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min.</td>
<td>6 ml.</td>
<td>6%</td>
</tr>
<tr>
<td>105 &quot;</td>
<td>8 &quot;</td>
<td>8</td>
</tr>
<tr>
<td>180 &quot;</td>
<td>9 &quot;</td>
<td>9</td>
</tr>
</tbody>
</table>
Decarboxylation of Pinoic Acid, \( \beta \)-n-Butyl-\( \gamma \)-dimethyl-\( \gamma \)-butyrolactone, and the Lactone of 2-Hydroxy-2:4-dimethylcyclohexylacetic Acid.

The substance to be decarboxylated (200-250 mg.) was weighed accurately into a small round-bottomed flask (5 ml.), and phosphoric acid (1.0 ml., \( d \) 1.74) was added from a pipette, 15 min. being allowed for draining. The flask was then attached to a short reflux condenser fitted with a gas burette which was filled with a colourless mineral oil of low viscosity ("transformer oil"). The reflux condenser was emptied and the apparatus was allowed to reach room temperature; the joint at the top of the condenser was then loosened, and the oil level in the gas burette was adjusted to zero. Atmospheric pressure and room temperature were noted.

The reaction-flask was then immersed in an oil bath thermostatically maintained at 160\(^\circ\), for the specified time, while water was passed through the condenser. After removing the flask from the oil bath and allowing water to drain from the condenser, and the apparatus to return to room temperature, the volume of air displaced was determined and the percentage of decarboxylation was calculated.
Fig. 7
Apparatus for the Determination of Comparative Rates of Decarboxylation
Table (V)

Results of Comparative Decarboxylation

<table>
<thead>
<tr>
<th>Compound deacarboxylated</th>
<th>Weight</th>
<th>Time</th>
<th>Volume</th>
<th>Room</th>
<th>Atmos.</th>
<th>Percentage of decarboxylation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pinonic acid</td>
<td>0.2405 g.</td>
<td>5 min.</td>
<td>17.4 ml.</td>
<td>22°</td>
<td>751 mm.</td>
<td>54.3%</td>
</tr>
<tr>
<td>Fixed</td>
<td>0.2407 g.</td>
<td>10 min.</td>
<td>18.8 &quot;</td>
<td>23°</td>
<td>751 &quot;</td>
<td>58.5%</td>
</tr>
<tr>
<td>Fixed</td>
<td>0.2420 g.</td>
<td>30 min.</td>
<td>19.0 &quot;</td>
<td>22°</td>
<td>769 &quot;</td>
<td>60.4%</td>
</tr>
<tr>
<td>Lactone of 2-hydroxy-2,4-dimethyl cyclohexylacetic acid</td>
<td>0.2478 g.</td>
<td>10 min.</td>
<td>5.6 ml.</td>
<td>25°</td>
<td>764 mm.</td>
<td>15.6%</td>
</tr>
<tr>
<td>Fixed</td>
<td>0.2393 g.</td>
<td>30 min.</td>
<td>13.2 &quot;</td>
<td>22°</td>
<td>769 &quot;</td>
<td>33.7%</td>
</tr>
<tr>
<td>β-n-Butyl-γ-dimethyl-γ-butyrolactone</td>
<td>0.2375 g.</td>
<td>10 min.</td>
<td>0.8 ml.</td>
<td>23°</td>
<td>759 mm.</td>
<td>1.4%</td>
</tr>
<tr>
<td>Fixed</td>
<td>0.2384 g.</td>
<td>30 min.</td>
<td>1.8 &quot;</td>
<td>25°</td>
<td>759 &quot;</td>
<td>5.2%</td>
</tr>
</tbody>
</table>
The Resistance of 2:4-Dimethylphenylacetic Acid to
Decarboxylation

2:4-Dimethylphenylacetic acid (1.00 g.) and
phosphoric acid (10 ml., d 1.74) were heated together under
reflux in a flask which was immersed in an oil bath at
160-170° for 1 hr. On cooling, the contents of the flask
were dissolved in dilute aqueous sodium carbonate (500 ml.).
The alkaline solution was extracted with methylene chloride
(successive portions of 25, 20, 15, 10, 10 ml.). After
washing of the extract with water, and distillation of the
solvent, there remained no residue.

The alkaline solution was acidified with dilute
sulphuric acid, and extracted with methylene chloride
(successive portions of 50, 40, 30, 20, 10 ml.). The
combined extracts were washed with water, and on distillation
of the solvent there remained 2:4-dimethylphenylacetic acid
(0.95 g.), m.p. 104-105°.

The Decarboxylation of the Lactone of 2-hydroxy-2:4-dimethyl
cyclohexylacetic Acid

The lactone n^D_{25} 1.4688 (3.25 g.) was dissolved in
phosphoric acid (13 ml., d 1.74), and the pale brown solution
was heated under reflux in an oil bath which was thermostatically kept at a temperature of 160°. Slow effervescence occurred, with formation of a colourless oil which floated on the surface of the mixture. After 3 hr., the reaction mixture was cooled, diluted with water (15 ml.), and the oil taken up with ether (10 ml.), washed several times with water, dried (Na₂SO₄), and the ether distilled. On distillation of the residue, a colourless oil b.p. 135-150° (0.80 g.) was collected. A high-boiling brown oil remained (1.12 g.).

The distillate was redistilled, and the main fraction b.p. 142-150° was dried over metallic sodium; further distillation yielded a colourless hydrocarbon (0.25 g.) b.p. 144-145° nD²⁵ 1.4430 (Found: C, 86.75; H, 13.35. C₉H₁₆ requires: C, 87.0; H, 13.0%).

On distillation, the high-boiling residue yielded as the main fraction, a yellow oil b.p. 120-200°/0.6 mm. nD²⁵ 1.4876, which was partly soluble in dilute sodium hydroxide.
The Mechanism of the Rearrangement of Pinonic Acid into Homoterpenyl Methyl Ketone.

By C. L. Arcus and G. J. Bennett.


The rearrangement of pinonic acid (I) to homoterpenyl methyl ketone (VII) requires relatively strong acid-catalysis. The rearrangement of (+)- and of (−)-trans-pinonic acid, in monochloroacetic acid at 100°, is of the first-order with regard to pinonic acid. A partial conversion into cis-pinonic acid occurs in the acidic solution, but this isomer also rearranges to homoterpenyl methyl ketone.

An intramolecular mechanism, represented in (IX), is proposed for the rearrangement.

Pinonic acid (I), on being heated with 50% sulphuric acid, is converted in high yield into homoterpenyl methyl ketone (VII) (Baeyer, Ber., 1896, 29, 326); the (+)- and the (−)-form of this compound have been obtained from (+)- and (−)-pinonic acid (Barbier and Grignard, Bull. Soc. chim. France, 1910, 7, 548). The structure of homoterpenyl methyl ketone has been ascertained by degradation (Tiemann and Semmler, Ber., 1895, 28, 1778) and by synthesis (J. Owen and Simonsen, J., 1932, 1424).

The data relating to the degradation and synthesis of pinonic acids (Baeyer, Ber., 1896, 29, 3, 1909; Perkin and Simonsen, J., 1909, 95, 1176; Gallas and Montañes, Anal. Fis. Quim., 1930, 28, 1196; Grandperrin, Ann. Chim., 1936, 6, 5; Guha, Ganapathi, and Subrahmanian, Ber., 1937, 70, 1505; Rao, J. Indian Chem. Soc., 1943, 20, 97) yield no decisive evidence on geometrical configurations, mainly owing to the use (largely unavoidable) of reagents which catalyse enolisation, leading to geometrical isomerisation. The assignment of geometrical configurations to (+)- and (±)-pinonic acids made by Simonsen and L. N. Owen (“The Terpenes,” University Press, Cambridge, 1949, Vol. II, p. 147)—that the solid acids are trans and the liquid acids cis—has been adopted. The opposite configurations have been used by Delépine and Badoche (Compt. rend., 1962, 233, 1435), but no
essential alteration to the mechanisms which have been deduced (below) becomes necessary if these authors' configurations are adopted.

The essential step in the conversion of (I) into (VII) is the rearrangement of an aceto-cyclobutylacetic acid to a keto-γ-lactone. Reaction schemes postulating the intermediate tertiary alcohol (VIII) have been proposed (Simonsen and Owen, op. cit., p. 117; Delépine and Badoche, loc. cit.), but no experimental evidence for its occurrence has been adduced.

In experiments preliminary to rate-measurements, the percentage conversion of pinonic acid into homoterpenyl methyl ketone, in acid solvents at 100° for stated times, has been determined; the results are collected in Table 1. In a number of instances the keto-lactone was converted into its 2:4-dinitrophenyl-hydrazone, of which the yield (based on the pinonic acid) is given in the last column.

It is apparent from Table 1 that the strongly acidic media, phosphoric, trichloroacetic, and 99% formic acids, cause rapid rearrangement, that acetic acid is ineffective, and that monochloroacetic and 90% formic acids occupy an intermediate position.

The rearrangement proceeds smoothly, and no by-products have been encountered; prolonged heating in phosphoric acid effects a breakdown of homoterpenyl methyl ketone which is to be described later.

### Table 1. The conversion of (±)-pinonic acid into (±)-homoterpenyl methyl ketone.

<table>
<thead>
<tr>
<th>Expt. no.*</th>
<th>Acid</th>
<th>Quantity (g)</th>
<th>Time (hr.)</th>
<th>Yield (%)</th>
<th>from 2:4-dinitrophenyl-hydrazone</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetic</td>
<td>4.0</td>
<td>4.5</td>
<td>55</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>Formic (99%)</td>
<td>4.0</td>
<td>4.5</td>
<td>51</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>Formic (99%)</td>
<td>to 10 ml.</td>
<td>2</td>
<td>73</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>Monochloroacetic</td>
<td>4.0</td>
<td>3.5</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>Trichloroacetic</td>
<td>to 10 ml.</td>
<td>9</td>
<td>58</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>Phosphoric (d 1.72)</td>
<td>to 10 ml.</td>
<td>30</td>
<td>95</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>Phosphoric (d 1.72)</td>
<td>containing H-CO2Na</td>
<td>0.53 g.</td>
<td>100</td>
<td>94</td>
</tr>
<tr>
<td>8</td>
<td>Formic (90%)</td>
<td>4.0</td>
<td>5 min.</td>
<td>95</td>
<td>92</td>
</tr>
<tr>
<td>9</td>
<td>Monochloroacetic</td>
<td>4.0</td>
<td>4.5</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>10</td>
<td>Monochloroacetic</td>
<td>to 10 ml.</td>
<td>9</td>
<td>5</td>
<td>4</td>
</tr>
</tbody>
</table>

* 1.0 G. of (±)-pinonic acid in each expt.

An acid containing 0.1 molecular proportion of its sodium salt was used as solvent in two experiments (9, 10; cf. 2, 5); in each instance the yield of homoterpenyl methyl ketone was markedly depressed, and 85% of the pinonic acid was recovered. This effect is ascribed to the lowering of hydrogen-ion concentration by the buffering action of the salts.

**Kinetic Measurements.**—Monochloroacetic acid was selected for use in a kinetic study of the conversion of (±)- and of (±)-pinonic acid into (±)- and (±)-homoterpenyl methyl ketone. The rate of rearrangement at 100° was determined by isolation of the keto-lactone after the recorded intervals (see Figure). The plot of log₁₀ [pinonic acid]⁻¹ *versus* time is linear, and yields a first-order rate constant $k = 9.9 \times 10^{-4}$ hr⁻¹.

When solutions of (±)-pinonic acid in monochloroacetic acid at 100° were studied polarimetrically, a considerable change in rotatory power was observed before conversion into homoterpenyl methyl ketone had proceeded very far. This mutarotation was found to be due to a partial conversion of (±)-trans- into (−)-cis-pinonic acid; the oxime of the latter was prepared from the pinonic acid recovered from "mutarotated" solutions. In addition, the oxime of (±)-cis-pinonic acid was prepared from pinonic acid recovered from the rate-experiments with (±)-trans-pinonic acid.

The specific rotations ($\epsilon$, in CHCl₃) of the specimens of optically active pinonic acid recovered from the kinetic experiments were determined. The corresponding value is known for (±)-trans-pinonic acid: $[\alpha]_{5893}^\circ = 92.4°$ (present observation; Delépine and Badoche, *Ann. Chim.*, 1950, 5, 153, record $[\alpha]_{5893}^\circ = 95°$), and for (−)-cis-pinonic acid: $[\alpha]_{5893}^\circ = 81.5°$ (*idem, loc. cit.*), whence were calculated the proportions of these isomers...
in the above specimens of pinonic acid. The concentrations of total, trans-, and cis-pinonic acid are plotted versus time in the Figure.

The Mechanism of Rearrangement, and of trans-cis-Isomerisation.—The mechanism of the conversion of trans- into cis-pinonic acid is probably identical with that for the acid-catalysed racemisation of ketones CHRR'CO·R" (Bartlett and Stauffer, J. Amer. Chem. Soc., 1933, 55, 4992; 1935, 57, 2580; Ingold and Wilson, J., 1934, 773). When this mechanism is applied to trans- and cis-pinonic acid (I—V), the inversion of configuration at C(1) results in the appropriate geometrical isomerisation.

During the first 1-9 hours cis-pinonic acid accumulates in the system more rapidly than does homoterpenyl methyl ketone, and, from tangents drawn at the origin to curves 3 and 1, the rate constant for trans-acid \( \rightarrow \) cis-acid is approximately twice that for trans-acid \( \rightarrow \) keto-lactone.

The mechanism of the rearrangement of pinonic acid to homoterpenyl methyl ketone is, most probably, that shown in formulae (I—VII). (The geometrical configurations given to the ethylenic groups of the enols have no significance.) The act of conversion of the cyclobutane into the lactone ring is the rearrangement of the protonated trans- or cis-pinonic acid (II or IV). Models of these molecules show the carboxyl group to be well placed to enter into a replacement reaction at C(1). The steric relations, together with the tautomeric electron movements whereby rearrangement occurs, are represented in (IX).

It has been found, above, that the rate of formation of homoterpenyl methyl ketone is proportional to the total concentration of (trans-+ cis-)pinonic acid, and it is inferred from this result that the rate constants \( k_1 \) and \( k_2 \), relating to (II) and (IV) respectively, do not differ appreciably.

Three apparently possible mechanisms, briefly described below, have been considered and rejected.
The rate of formation of homoterpenyl methyl ketone is, as has been stated, proportional to the concentration of \((\text{trans-} + \text{cis-})\)-pinonic acid: were the imws-acid (or its proton adduct) the sole precursor, then the curve for the formation of the keto-lactone (curve 1) would show an initial rapid fall in slope, and were the cis-acid (or its proton-adduct) the sole precursor, this curve would have a sigmoid form.

A tenable mechanism is that postulating the enol (III) as the sole precursor to the keto-lactone:

\[
\begin{align*}
\text{Me} & \quad \text{H} \\
\text{CH}_3 & \quad \text{CH}_3
\end{align*}
\]

This is considered less probable than the mechanism adopted above, because it involves the taking up of a proton at a point (C(III)) from which a proton has earlier been released to form the enol.

**EXPERIMENTAL**

Rotations are for \(l, 2-0 \) unless otherwise stated.

The proportions of \(\alpha\)- and \(\beta\)-pinene in specimens of \((-\) - and \((+\) -pinene from American and Portuguese turpentines were estimated by determination of the rotatory dispersions \([\alpha]_{D}^{25} + \text{[}\alpha\text{]}_{D}^{25}\) and \([\alpha]_{D}^{20} + [\alpha]_{D}^{25}\) and comparison of these values with the Tables given by Fuguitt, Stallcup, and Hawkins \((J. \text{ A m e r . C h e m . S o c .}, \ 1942, \ 64, \ 2978)\). A mixture containing 97-5\% of \(\alpha\)- and 2-5\% of \(\beta\)-pinene was then made which had b. p. 156—158°, \([a\] +93°; this material (748 g.) was oxidised by Delépine's method \((B u l l. \text{ S o c. c h i m . F r a n c e ,} \ 1936, \ 3, \ 1369)\) except that chloroform was replaced by methylene chloride as extractant; it yielded \((\pm\) -trans-pinonic acid (336 g., from benzene), m. p. 103—104°, which on recrystallisation from hot water had m. p. 105° [semicarbazone, prisms (from ethanol), m. p. 217° (decomp.)]; Ruzicka and Pontalti \((H e l v . \ C h i m . A c t a , \ 1924, \ 7, \ 494)\) record m. p. 208°.

Ammonium \((\pm\) -trans-pinonate, on reaction with S-benzylthiuronium chloride, yielded S-benzylthiuronium \((\alpha\) -trans) -pinonate, flakes (from ethanol), m. p. 152° (decomp.) \((F a e y e r , \ B e r ., \ 1896, \ 29, \ 24, \ r e c o r d s \ m . \ p . \ 150°)\).

The following method was used for the preparation of all pinonic acid oximes: \((\pm\) -trans-pinonic acid \((0-0 \ g.)\) was dissolved in a solution of potassium hydrogen carbonate \((0-55 \ g.)\) in water \((2-0 \ m l.); a solution of hydroxylamine hydrochloride \((0-42 \ g.)\) in water \((1-0 \ m l.)\) was added and the whole was shaken. The oxime separated and solidified; it was crushed, filtered off, washed with water, and dried \(i n \ v a c u o \) \((H_2S0_4)\). It \((0-85 \ g.)\), on recrystallisation from ethanol, yielded prisms \((0-55 \ g.),\) m. p. 152° (decomp.) \((B a e y e r , \ B e r ., \ 1896, \ 29, \ 24, \ r e c o r d s \ m . \ p . \ 150°)\).

\((-\) -\(\alpha\)-Pinene \((68-0 \ g.),\) b. p. 154-5—156°, \([a\] +93°, \(\text{[}\alpha\text{]}_{D}^{25} + 47-0°,\) on similar oxidation gave \((\pm\) -trans-pinonic acid \((17-3 \ g.; \ i s o l a t e d \ b y \ f r a c t i o n a l \ c r y s t a l l i s a t i o n \ f r o m \ e t h e r),\) m. p. 68—69°, \([\alpha]_{D}^{25} + 92-4° \ (c \ 5-443 \ i n \ C H C l_3)\). Its oxime, needles from ethanol—water \((1:4,\) had m. p. 135-5°, \([\alpha]_{D}^{25} + 51-7° \ (c \ 5-102 \ i n \ C H C l_3)\) \((F a e y e r , \ C, 60-2; H, 8-7; N, 7-3. \ C a l c . \ f o r C_{10}H_{16}O_3N: \ C, 60-3; H, 8-6; N, 7-05%).\) Delepine \((l o c. \ c i t.)\) records m. p. 128°.

\((-\) -Homoterpenyl Methyl Ketone.—The following preparation is based on the brief description given by Baeyer \((l o c. \ c i t.)\). \((\pm\) -trans-Pinonic acid \((6-0 \ g.)\) was heated with aqueous sulphuric acid \((50\% ; \ 60 \ g.)\) at \(100°\) for 30 min., and the solution was poured into water \((150 \ ml.).\) The product was salted out with ammonium sulphate and extracted with chloroform; the extract was washed and dried \((N aS0_4),\) and the solvent distilled. The crystalline product \((5-4 \ g.)\) yielded, on recrystallisation from the minimum of boiling ether, \((\pm\) -homoterpenyl methyl ketone \((3\) -4 g.),) prisms, m. p. 60-5°. Its semicarbazone, hexagonal plates from methanol, had m. p. 206—207°; J. Owen and Simonsen \((J., \ 1932, \ 1424)\) record m. p. 206—207°. Its 2:4-dinitrophenylhydrazones, orange needles from ethanol, had m. p. 163-5° \((F a e y e r , \ C, 53-1; H, 5-6; N, 14-9. \ C_{16}H_{14}O_3N_2 \ r e q u i r e s \ C, 52-7; H, 5-55; \ N, 15-4%).\)

Rearrangement in the acidic solvents of Table 1. \((\pm\) -trans-Pinonic acid \((1-00 \ g.)\) was heated at \(100°\) in the solvent, and for the time, stated in the Table; water \((100 \ ml.)\) was then added and the whole was made slightly alkaline (to methyl red) with ammonia and extracted with methylene chloride \((25,20,15,10,10 \ m l. \ p o r t i o n s \ s u c c e s s i v e l y)\); the extract was washed with
water (2 x 25 ml.) and distilled (water forms an azeotrope with methylene chloride). The homoterpenyl methyl ketone was dried at 100° (30 min.) or in vacuo at ordinary temperature.

Unconverted pinonic acid was recovered from the extracted aqueous solution by acidification with hydrochloric acid and extraction as above.

(These procedures for the isolation of the keto-lactone and pinonic acid were used in the rate-measurements, below.)

The preparation of the 2 : 4-dinitrophenylhydrazone of (±)-homoterpenyl methyl ketone was standardised as follows: to a solution of the keto-lactone (1-00 g.; reagents proportional to the actual weight were taken) in warm propan-2-ol (15 ml.), 2 : 4-dinitrophenylhydrazine (1-1 g.) was added; the solution was boiled, and addition of a few drops of concentrated hydrochloric acid then precipitated the derivative; further propan-2-ol (15 ml.) was added, and the suspension was cooled and filtered. The 2 : 4-dinitrophenylhydrazone was washed with propan-2-ol (30 ml.), dried at 120°, and weighed. Its m. p. and mixed m. p. were determined.

In a control experiment (±)-homoterpenyl methyl ketone (0-50 g.) gave 0-95 g. (95%) of the derivative.

Rate of rearrangement. Monochloroacetic acid was fused, and 0-05 mol. of concentrated aqueous sodium hydroxide was cautiously added; distillation then gave a main fraction having b. p. 101—102°/25 mm. The liquid was allowed to solidify to the extent of about 90% and the remaining liquid was drained off and discarded; the solid was re-melted and the process repeated; the acid so purified had equiv. 94-31 (Gale, for CH₂Cl-CO₂H : equiv., 94-50).

(±)-trans-Pinonic acid (1-00 g.) was weighed into a 10-ml. graduated flask and dissolved in monochloroacetic acid at 80°; the solution was made up to the mark, the flask was sealed with a Polythene cap, and thereafter immersed in a steam-bath for the time(s) recorded in the Figure; homoterpenyl methyl ketone was then isolated as described above. The quantities of keto-lactone formed by rearrangement of (dr)- and (-)-pinonic acid, together with those calculated from the first experimental point (t = ½ hr.) by use of the first-order rate-constant k = 9-9 x 10⁻² hr⁻¹, are as follows:

<table>
<thead>
<tr>
<th>t (hr.)</th>
<th>Pinonic acid</th>
<th>Homoterpenyl methyl ketone</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>isolated (g.)</td>
<td>calc. (g.)</td>
</tr>
<tr>
<td>½ hr.</td>
<td>+</td>
<td>±</td>
</tr>
<tr>
<td>1 hr.</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>2 hr.</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>3 hr.</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

Specimens of pinonic acid recovered from the rate-experiments were combined and washed with ethanol, whereby they were separated into (±)-trans-pinonic acid, m. p. and mixed m. p. 102°, and a liquid mixture of this acid and the (±)-cis-isomer. This mixture was converted into the mixed oximes, from which, by fractional crystallisation from ethanol, there were isolated (±)-cis-pinonic acid oxime, m. p. 171° [Delépine (loc. cit.) records m. p. 168°], and also the more soluble trans-oxime, as prisms, m. p. 151° alone and when mixed with the specimen above.

(±)-Homoterpenyl Methyl Ketone.—Mutarotation of solutions of pinonic acid in monochloroacetic acid. A solution of (±)-trans-pinonic acid [(i), (ii) 1-000 g.; (iii), (iv) 1-750 g.] in monochloroacetic acid (to 10 ml. at 80°) was placed in a 1-dm. jacketed polarimeter tube with sealed end-plates, maintained at 100° by steam passing freely through the jacket. The rotatory power of the solution was determined at intervals (Table 2); the first reading was made within 5 min. of the preparation of the solution.

The liquid mixture of (±)-trans- and (−)-cis-pinonic acids (6-3 g.) recovered from these

<table>
<thead>
<tr>
<th>Table 2.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time (min.): 0 5 10 20 30 40 60 80 100</td>
</tr>
<tr>
<td>(i)</td>
</tr>
<tr>
<td>(ii)</td>
</tr>
<tr>
<td>(iii)</td>
</tr>
<tr>
<td>(iv)</td>
</tr>
</tbody>
</table>

| Time (min.): 120 140 150 180 195 210 230 240 |
| (i) | a₁₀₀ | 2-94° | 2-89° | 2-89° | — | 2-89° | 2-91° |
| (ii) | a₁₀₀ | 2-92 | 2-87 | 2-87 | — | 2-87 | 2-88 |
| (iii) | a₁₀₀ | 4-87 | 4-77 | 4-73 | 4-67° | — | — | 4-67° | 4-67° |
| (iv) | a₁₀₀ | 4-93 | 4-78 | 4-71 | 4-65 | — | 4-63 | 4-69 | 4-69 |
polarimetric experiments was heated with thrice its volume of phosphoric acid \((d 1.72)\) for 10 min. at 100°. The product (5.95 g.), isolated as described for the \((\pm)\)-keto-lactone, was recrystallised from ether and yielded \((+)-\)homoterpenyl methyl ketone (3.5 g.), m. p. 46-5°, 
\[\{x\right\}^\circ_{D} +58-6° (c 5.271 \text{ in } \text{CHCl}_3), \{x\right\}^\circ_{D} +45-5° (c, 5-612 \text{ in CH}_2\text{C}=\text{O}_2\text{H}) \text{ and } [x]^{20} +45-8° (c, 10-000 \text{ in CH}_2\text{Cl}-\text{CO}_2\text{H}; \text{ the rotation was unchanged after 4 hr. at 100°}); \text{ it gave a 2:4-}
\text{dinitrophenylhydrazone, orange needles (from ethanol), m. p. 168-5° (Found : C, 53-0; H, 5-7; N, 15-5%). \Both Barbier and Grignard (loc. cit.) and Delépine and Badoche (Compt. rend., 1952, 235, 1069) record m. p. 47° for \((+-)-\)homoterpenyl methyl ketone.}

\text{Rate of rearrangement.} \Five determinations (cf. Figure) of the conversion of \((+-)-\)trans-
\text{pinonic acid into \((+-)-\)homoterpenyl methyl ketone, with recovery of unconverted pinonic acid,}
\text{were carried out by the method described for the \((\pm)\)-keto-lactone. The specific rotation}
\text{(c, 5 in CHCl}_3\) \text{of the recovered pinonic acid was determined :}

<table>
<thead>
<tr>
<th>Reaction-time (hr.)</th>
<th>0-5</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>( [x]_{D} )</td>
<td>+66-7°</td>
<td>+57-4°</td>
<td>+47-0°</td>
<td>+43-4°</td>
<td>+39-7°</td>
</tr>
<tr>
<td>( t )</td>
<td>22°</td>
<td>22°</td>
<td>21°</td>
<td>20°</td>
<td>22°</td>
</tr>
</tbody>
</table>

\text{The specimens of \((+-)-\)keto-lactone isolated during these rate-experiments were combined}
\text{(1.60 g.), dissolved in hot water (20 ml.), treated with charcoal to remove methyl red, extracted}
\text{with methylene chloride, and twice recrystallised from ether-light petroleum (b. p. 40—60°);}
\text{the \((+-)-\)homoterpenyl methyl ketone formed prisms (0.57 g.), m. p. 46—47°, } [x]^{20} +59-6°
\text{(c, 5-013 in CHCl}_3\). \text{The specimens of semisolid pinonic acid recovered from the above rate-experiments were}
\text{pressed on filter paper; the solid was removed and the paper extracted with methylene chloride.}
\text{The extract yielded a liquid acid (2.16 g.) which was converted into its oxime (1.72 g.); after}
\text{extraaction with boiling ether there remained a product (0.69 g.), m. p. 195°, which by repeated}
\text{recrystallisation from hot ethanal yielded \((-)-\)cis-pinonic acid oxime, prisms, m. p. 199-5—200°,}
\text{\([x]_{D}^{\circ} -34-8° (c, 4; c, 0-437 \text{ in ether) (Found : C, 60-5; H, 8-7; N, 7-2%). \text{For this oxime Delépine (loc. cit.) records m. p. 192° and } [x]_{D}^{\circ} -29-8° \text{ in ether).}}

\text{Thanks are expressed to the Government Grants Committee of the Royal Society and to}
\text{Imperial Chemical Industries Limited for grants, and to the Department of Scientific and}
\text{Industrial Research for a maintenance grant (to G. J. B.).}

\text{BATTERSEA POLYTECHNIC, LONDON, S.W.11. [Received, March 18th, 1955.]

PRINTED IN GREAT BRITAIN BY RICHARD CLAY AND COMPANY, LTD.,
BUNGAY, SUFFOLK. 551