STEREOCHEMISTRY OF REDUCTION
BY SOLUTIONS OF ALKALI METAL IN AMINES

by
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INTRODUCTION

It was first reported by R. A. Benkeser, in an investigation of silicon free radicals, that arylsilanes absorbed large amounts of lithium metal when dissolved in anhydrous ethylamine. The results obtained at this time indicated that six equivalents of lithium were absorbed for each phenyl group in the arylsilane molecule. It appeared that complete saturation of the phenyl rings by lithium was taking place, and indicated that far more reduction of the aromatic rings was occurring than had been observed previously in the sodium-liquid ammonia system.

Benkeser later reported that benzene is reduced by lithium-ethylamine to cyclohexene. This is a unique feature in that the reduction tends to leave an unreduced double bond. Further investigation at different temperatures indicated that at -78°C the monoolefin tends to form as the major product, whereas at 17°C (reflux) a mixture was obtained of the monoolefin and saturated hydrocarbon. Benkeser reported a 45 per cent yield of 1-ethylcyclohexene and a 55 per cent yield of ethylcyclohexane at 17°C, whereas at -78°C a 75 per cent yield of 1-ethylcyclohexene with only a trace of completely saturated compound was obtained.
He pointed out that the lithium-ethylamine reduction system is more potent than either lithium or sodium in anhydrous liquid ammonia. One of the factors causing the difference was attributed to the increased basicity of ethylamine as compared to liquid ammonia.

Benkeser proposed a hypothesis in which there is a rapid 1,4-addition of lithium. The organometallic thus produced reacts with solvent to give 1,4-dihydro product, which then rearranges in the basic medium to the more stable conjugated olefinic system. Then another 1,4-addition of lithium occurs, followed by reaction with solvent so that a monociclenin is formed, with or without rearrangement.3

It was established by Campbell that the reduction of acetylenes by sodium and liquid ammonia involves a trans-addition of hydrogen.4 Reductions of acetylenes were carried out in lithium-amine systems by Benkeser. He reported that he obtained a "good yield" of trans-olefins.5

Attempts to replace ethylamine with higher molecular weight amines gave poorer yields, perhaps because lithium becomes less soluble as the ratio of nitrogen to carbon decreases.6,7

The potential advantage of the high boiling point (117°) of ethylenediamine, as well as its favorable ratio of one carbon atom to one nitrogen atom, caused Reggel to investigate the lithium-ethylenediamine system.7 His results showed it to be a convenient and effective method for
carrying out reductions of organic compounds. Although lithium-ethylenediamine is the most powerful reducing system, as compared to other metal-amine systems, it is the least selective. In contrast to the sodium-liquid ammonia and to the lithium-ethylamine systems, which will reduce acetylenes only to olefins, the lithium-ethylenediamine combination will reduce acetylenes to alkanes. By this system many substances, including olefins, phenol, and even coal, which are difficult to reduce by chemical means, are easily reduced.

Reggel showed that the extent of reduction increases with an increase in the amount of lithium used and that adding the lithium metal at a rapid rate to the solution caused more extensive reduction than slow addition.

The present investigation consists of a series of experiments in which toluene and mesitylene were subjected to homogeneous and heterogeneous reductions in lithium-ethylamine and lithium-ethylenediamine systems in order to determine the stereospecificity of the reduction and to compare the effects of the different amines and reduction conditions on the stereospecificity of the reduction.
DISCUSSION

A study has been made of the stereospecificity of the lithium-ethylamine and lithium-ethylenediamine reduction systems. The reductions were carried out both homogeneously and heterogeneously to determine the effect of the conditions on the yields of monoolefin and on the stereospecificity of the reduction. In the homogeneous reactions, the amount of lithium used was limited by the amount soluble in the amine, whereas in the heterogeneous reduction the amount of lithium used was determined by the persistence of the blue color. It was found that in the heterogeneous reductions when the blue color persisted for longer than 30 min, the reduction was essentially complete. The amount of reduction in the homogeneous case was dependent on the solubility of the lithium in the amine. About equal quantities of the two amines were used, and since the solubility of lithium was much greater in ethylenediamine than in ethylamine, in the one case a larger mole excess of lithium was present in the reduction.

The first experiment was performed according to the procedure outlined by McDonald, but it was found to be more convenient to modify his procedure to allow better control of the reaction. McDonald's method called for all the lithium
to be present initially in the reaction flask and the drop-wise addition of the amine. The reaction was rather violent during the early stages, especially with ethylenediamine. For this reason, the procedure outlined by Reggel for ethylenediamine was tried and proved to be more satisfactory. By this method, the reaction was easily controlled by the persistence of the blue color and the evolution of gas. In all experiments the amine was placed in the reaction flask first, and in the homogeneous reaction, the lithium then added to the amine, and the aromatic compound added drop-wise to the mixture. In the heterogeneous experiments the amine and aromatic compound were mixed and the lithium added to the mixture. The results of these experiments are reported in Tables I and II.

The amount of toluene remaining after experiments 1 and 2 seemed to show that there was too much toluene to be reduced for the amount of solvent (100 g.) and lithium used. Benkeser used 250 g. of ethylamine and Reggel used 300 g. of ethylenediamine for the same amount of toluene (0.2 mole). For this reason the amount of toluene was decreased to 0.1 mole.

The homogeneous reactions gave lower yields of remaining hydrocarbons, which were mainly methylcyclohexane. This is attributed to the decreasing concentration of lithium in solution. The homogeneous reduction had a limited amount of lithium present, and as the reaction proceeded,
Table I

Reduction of Toluene

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Toluene moles</th>
<th>Lithium moles</th>
<th>Amine g.</th>
<th>Yield, Percent</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>toluene</td>
</tr>
<tr>
<td>1</td>
<td>0.2</td>
<td>0.6</td>
<td>100, I</td>
<td>26.1</td>
</tr>
<tr>
<td>2</td>
<td>0.2</td>
<td>1.2</td>
<td>100, I</td>
<td>28.3</td>
</tr>
<tr>
<td>4</td>
<td>0.1</td>
<td>0.9</td>
<td>135, II</td>
<td>30.8</td>
</tr>
<tr>
<td>5</td>
<td>0.1</td>
<td>1.0</td>
<td>135, II</td>
<td>13.9</td>
</tr>
</tbody>
</table>

a Experiments 2 and 3 were heterogeneous and 1 and 4 were homogeneous.

b Amine I was ethylamine and Amine II was ethylenediamine.

c The olefin was 1-methylcyclohexene.

d The residue was mainly methylcyclohexane, but also included some colored by-products and polymeric materials.
### Table II

**Reduction of Mesitylene**

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Mesitylene moles</th>
<th>Lithium moles</th>
<th>Amine b</th>
<th>Yield, Percent</th>
<th>Percent residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.1</td>
<td>0.8</td>
<td>135, II</td>
<td>mesitylene 3.4</td>
<td>66.5</td>
</tr>
<tr>
<td>6</td>
<td>0.1</td>
<td>1.5</td>
<td>135, II</td>
<td>8.3</td>
<td>53.7</td>
</tr>
<tr>
<td>7</td>
<td>0.077</td>
<td>0.9</td>
<td>100, I</td>
<td>4.2</td>
<td>62.3</td>
</tr>
<tr>
<td>8</td>
<td>0.1</td>
<td>1.2</td>
<td>100, I</td>
<td>6.1</td>
<td>58.1</td>
</tr>
</tbody>
</table>

a. Experiments 5 and 7 were homogeneous, and 6 and 8 were heterogeneous.

b. Amines I was ethylamine and Amines II was ethylenediamine.

c. The olefin was determined as total olefin by bromine titration.

d. The residue was mainly 1,3,5-trimethylcyclohexane, but also included some colored by-products and polymeric materials.
the concentration of lithium decreased. However, in the heterogeneous reduction the solution was saturated with lithium metal so that as the reaction progressed there was a constant concentration of metallic lithium present through a major fraction of the reaction.

This may show that the rate of the reaction is dependent on the concentration of lithium present, and that the rate of reaction in the homogeneous reduction would decrease as the reaction uses up the metallic lithium. Thus in the length of time the reaction was run not all of the aromatic compound would be reduced.

Reggel reported that N-lithioethylenediamine, \( \text{H}_2\text{NC}_2\text{H}_4\text{NHLi} \), which is first formed by reaction of the metal with the solvent, catalyzes the isomerization of olefins

\[
\text{Li} + \text{H}_2\text{NC}_2\text{H}_4\text{NH}_2 \rightarrow \frac{1}{2}\text{H}_2 + \text{LiNHC}_2\text{H}_4\text{NH}_2
\]

I

and the dehydrogenation of cyclic dienes. He reported that 4-vinylcyclohexene was isomerized and dehydrogenated to ethylbenzene. He proposed that this occurs in two steps: first an isomerization to the conjugated diene,

\[
\begin{array}{c}
\text{CH} = \text{CH}_2 \\
\text{C}_2\text{H}_5
\end{array}
\]

II

followed by a concerted reaction in which I and II form a
cyclic intermediate, making use of the bidentate character of I.

A modification of this sequence, such as

\[
\text{CH}_3 + 2e^- + \text{RNH}_2 \rightarrow \text{CH}_3 + \text{H}_2 + \text{CH}_3
\]

could alternatively explain the large amount of unreduced aromatic compound and the low yield of remaining hydrocarbon in the lithium-ethylenediamine homogeneous reduction, because of the reversibility of the initial reduction step, which in the overall process simply consumes the lithium by producing hydrogen from the solvent, the aromatic compound playing the role of a catalyst.

The effect of the homogeneous reduction would be to lower the yield of methylcyclohexene and leave more unreduced toluene, whereas the heterogeneous reduction with the excess of metallic lithium would give greater reduction and a larger yield of reduced products, methylcyclohexene and methylcyclohexane.

In the lithium-ethylamine and lithium-ethylenediamine reductions of mesitylene there is a possibility of two isomers: cis-1,3,5-trimethylcyclohexene, III and
trans-1,3,5-trimethylcyclohexene, IV.

Four experiments, two homogeneous and two heterogeneous, were carried out with mesitylene. The results of these experiments are found in table II.

The total olefin concentration was determined by bromine titration of the reduction mixture (see Experimental). A standard sample of the cis-isomer was prepared and infrared spectra of several dilutions taken. A standard curve was made of absorbance vs. concentration to determine the concentration of cis-isomer in the reduction products.

Trisubstituted ethylenes give an infrared band at about 950 cm.$^{-1}$ The location of this band is dependent on the structure of the alkyl groups. Rasmussen states that the strain caused by a six member ring shifts the band to a higher frequency, i.e., a lower wave number. And it is implied by Hoffman that the strain added by cis-methyl groups shifts the band to still lower wave numbers.

This shifting of bands was found to be true. In the infrared spectrum of 1-methylcyclohexene, a cyclic trisubstituted ethylene, there was a band at 932 cm.$^{-1}$, whereas in the infrared spectrum of cis-1,3,5-trimethylcyclohexene
the band had shifted to about 909 cm\(^{-1}\).

In the preparation of the standard curves the following bands were used: for toluene, the characteristic aromatic band at 1604 cm\(^{-1}\), 1-methylcyclohexene 932 cm\(^{-1}\), mesitylene 1609 cm\(^{-1}\), and cis-1,3,5-trimethylcyclohexene 909 cm\(^{-1}\).

In the spectra of the reduced products from experiments 5-8, there was the typical trisubstituted ethylene band at 932 cm\(^{-1}\), but no band at 909 cm\(^{-1}\). From this data it is seen that no cis-1,3,5-trimethylcyclohexene is formed, but rather, it is assumed that the trans-isomer is the only isomer formed.

That the reduction forms no cis-isomer was not what would be expected from a carbanion intermediate. A carbanion, unlike a carbonium ion which is planar, has a definite conformation,

\[
\begin{align*}
\text{V} & : C' \cdots - C \cdots - C'' \cdots \Theta \\
\text{VI} & \cdots C' \cdots C'' \cdots \Theta
\end{align*}
\]

although V and VI are easily interconverted. From this it would be expected that the thermodynamically more stable isomer would be formed.

Klyne reported\(^{11}\) that of the isomeric dimethylcyclohexenes, the isomer that can take up a diequatorial conformation is the most stable one. This form would be
the cis-1,3,5-trimethylcyclohexene.

Therefore the stereospecificity of the reaction must not be determined by the stability of the final product, but rather by the stability of an intermediate.

Benkeser initially proposed an hypothesis in which lithium adds directly to the ring,

\[
\text{H} + 2 \text{Li} \rightarrow \text{H Li}\]

and does not involve any solvated electrons in the reduction.

In the reduction when metallic lithium was added to the amine, an intense blue color appeared almost immediately. This has been attributed to the characteristic blue color of solvated electrons.

McDonald reported that in reactions with amines where the lithium is not appreciably soluble and the blue color not formed, there is no reduction.

It would seem reasonable that the lithium would give up an electron to a solvent molecule, which then transfers it to the ring. This mechanism would allow
resonance stabilization of the intermediates. It would be a stepwise addition, alternately of solvated electrons and protons from the solvent molecules. \textsuperscript{3,6,12}

According to this proposed mechanism, the amine acts as a Brønsted acid toward the carbanions.

The formation of saturated hydrocarbons must involve a 1,2-addition with no resonance stabilization of the intermediates. This would be a higher energy process and it does not occur in the sodium-liquid ammonia system. \textsuperscript{7}
EXPERIMENTAL

**Materials.**—Metallic lithium in the form of a heavy wire was used throughout the investigation. Toluene (Braun Chemical Company) was dried over magnesium sulfate and distilled through a Todd column. Mesitylene (Eastman Kodak White Label) was purified in the same manner. The infrared spectra of toluene\(^{13}\) and mesitylene\(^{14}\) were very similar to standards in the A. E. I. tables. The ethylamine (Eastman), which was anhydrous, was used directly. Ethylenediamine (Eastman) was refluxed over sodium for a few days and distilled directly into a pressure-equalizing dropping funnel to avoid excessive exposure to the atmosphere.

**Equipment.**—All reactions with ethylamine were run in 500 ml. three neck ground-glass joint flasks fitted with a pressure-equalizing dropping funnel with a nitrogen inlet, a cold finger condenser equipped with a calcium chloride drying tube, and a Hershberg stirrer. After the amine was added, the dropping funnel was replaced with a stoppered straight reflux condenser. Throughout the rest of this experimental section this apparatus shall be referred to as apparatus A. The reactions with ethylenediamine were run in 500 ml. three neck ground-glass joint flasks fitted with a Hershberg stirrer, a pressure-equalizing dropping funnel.
with a nitrogen inlet, and with a reflux condenser with a nitrogen outlet equipped with a calcium chloride drying tube. After the liquid was added, the dropping funnel was replaced by a thermometer dipping below the surface of the liquid. Throughout the rest of the experimental section this apparatus shall be referred to as apparatus B.

Nitrogen was purified by passing it through a heated column of copper turnings and dried by passing through a column of silica gel. The pure dry nitrogen was passed through the apparatus previous to the addition of any materials.

A continuous liquid-liquid extractor was used to extract the products from the reaction mixture.

Products were identified by use of a Carl Zeiss refractometer and a Beckman IR-4 spectrophotometer, with optics and cells of sodium chloride.

Procedures for the Reactions with Lithium-Ethylamine and Lithium-Ethylene diamine.--In the reactions of lithium-ethylamine and lithium-ethylenediamine there were four procedures used, two homogeneous and two heterogeneous.

A. Procedure I.--Ethylamine Homogeneous Reduction.--The cold finger condenser of apparatus A was filled with a mixture of Dry Ice, chloroform, and carbon tetrachloride, and the apparatus was swept with purified nitrogen. A 100 g. sample of ethylamine (2.2 moles) was added to the reaction flask and stirred. Lithium was added through the
straight condenser in pieces about 1.5 in. long, 4-8 pieces (0.4-0.8 g.) being added in each portion. The rate of addition was controlled by hydrogen evolution and the persistence of the blue color. The addition of the metal took place over a period of one to two hours. Lithium was added until no more would dissolve. Any excess lithium was then filtered out by pouring the mixture through a glass wool filter into a second apparatus which was swept with nitrogen. The substrate was then added dropwise to the blue lithium amine solution over a period of one to two hours. After all the substrate had been added, the mixture was allowed to stir at reflux for 3-8 hours. After the reaction was complete, the solution was cooled to Dry Ice temperature and water was added slowly. Considerable heat was evolved, and after a little water had been added, the mixture became solid, requiring efficient stirring. After enough water had been added to dissolve most of the solid, the temperature was allowed to rise slowly, and sufficient dilute sulfuric acid was added to dissolve any lithium hydroxide remaining in the solid state.

The reaction mixture was then extracted with ether by use of a continuous liquid-liquid extractor. The ether-ethyl solution was then dried over calcium chloride and the ether distilled off. The residual products were then diluted to 25 ml. with anhydrous carbon tetrachloride and analyzed by the infrared spectrophotometer.
B. Procedure II.—Lithium-Ethylamine Heterogeneous Reduction—The reaction was carried out in the same manner as the homogeneous lithium-ethylamine reduction except that the substrate was first dissolved in the ethylamine and the lithium was added in small portions to the mixture to maintain the blue color. The mixture was allowed to stir at reflux for 3-8 hours. After the reaction was complete, the solution was cooled to Dry Ice temperature. The solution was hydrolyzed and the products isolated and identified as in Procedure I.

C. Procedure III.—Lithium-Ethylenediamine Homogeneous Reduction.—Apparatus B was flushed with dry nitrogen, 150-200 ml. of ethylenediamine was added, and the amine was heated to 90-100°. The lithium was then added in portions, as in Procedure I, over a period of one to two hours, until no more lithium would dissolve. Any excess of lithium was filtered out by a glass wool filter as in Procedure I. The substrate to be reduced was then added dropwise to the homogeneous solution at a temperature of 90-100°, and the mixture was then stirred for two to five hours. The flask was cooled in ice, and water was added until most of the solid which first formed had dissolved. The products were isolated and analyzed in the manner of Procedure I.

D. Procedure IV.—Lithium-Ethylenediamine Heterogeneous Reduction—The reaction was carried out in the
same manner as the homogeneous lithium-ethylenediamine reduction except that the substrate and ethylenediamine were mixed and heated, and small portions of lithium added to the mixture as in Procedure II. The mixture was allowed to stir for 3-8 hours at 100°. The mixture was hydrolyzed and the products isolated and identified as in Procedure I.

**Analysis of Products.**—The concentration of the original aromatic materials remaining unreacted and the 1-methylcyclohexene concentration were determined by infrared spectrophotometry. The amount of saturated hydrocarbon was calculated by difference.

**Preparation of Standard Curves.**—Three or four dilutions of toluene, 1-methylcyclohexene, mesitylene, and cis-1,3,5-trimethylcyclohexene were made with micropipets and their spectra taken on the Beckman IR-4. Plots of absorbance vs. concentration were in accordance with Beer's Law.

$$E_\nu = \frac{1}{cL} \log_{10}(I_0/I)$$

In this relationship $E_\nu$ is the molecular extinction coefficient, $c$ is the concentration expressed in moles per liter, $L$ is the cell length in centimeters, and $\log_{10}(I_0/I)$ is the observed absorbance.$^{15}$

**Determination of Total Olefin Content in the Mesitylene Reaction Mixtures.**—The total amount of olefinic material in the reduction products was determined by titration
of an aliquot of the mixture with a standard bromine-acetic acid solution as described by Uhrig and Levin.\textsuperscript{16} Due to the color of the products, the endpoint was not clear. Therefore a slight excess of bromine solution was added and the solution back titrated with standard thiosulfate solution. The amount of olefin was determined according to the formula

\[
\text{mg. olefin in sample} = \frac{(\text{mg. Br}_2/\text{ml. Br}_2 \text{ reagent})(\text{ml. Br}_2 \text{ reagent consumed})}{\text{Theoretical bromine addition number}} \times (100)
\]

**Attempted Analysis by Gas Phase Chromatography.**—

A Cenco 70150 Vapor Phase Analyzer was used with a 5 ft. x \( \frac{1}{4} \) in. column of copper tubing. The column was packed with squalane on C-22 firebrick by the use of a electric vibrator. Eggertsen and Groenings had used a similar column on the separation of seven-carbon saturates.\textsuperscript{17}

Samples of toluene, methylcyclohexane, and 1-methylcyclohexene were run on this column at a column temperature of 125\(^\circ\), a flow rate of 10 ml./16.2 sec., and a head pressure of 29.5 mm. with helium as the carrier gas. Individual samples emerged at 17 min. for methylcyclohexane, 20 min. for 1-methylcyclohexene, and 22 min. for toluene. An 80 ml. sample of the products from Exp. 1 were analyzed and only two peaks were observed, with poor resolution.

A similar set of runs were made with a 20 ft. x \( \frac{1}{4} \) in. column of copper tubing with squalane on C-22 firebrick
and under the same conditions. Individual samples emerged at 48.25 min. for methylcyclohexane, 60.13 min. for l-methylcyclohexene, and 62.48 min. for toluene. A mixture of equal quantities of the three materials was run, and a peak emerged after the same time as methylcyclohexane and one other peak about twice as large in area as the first peak after about 61 min.

An 80 μl. sample in ether of the products from Exp. 1 gave no resolution under the same conditions.

Clearly these squalane columns were not satisfactory. Keulemans\textsuperscript{18} stated that there must be a certain compatibility between the stationary phase and the components. For an efficient separation the components of the mixture and the stationary phase should show some resemblance. Seemingly an unsaturated compound should be a better stationary phase than squalane because of the similarity of two of the components.

**Preparation of l-methylcyclohexene.**—Using the method of Signaigo and Cramer,\textsuperscript{19} 42 g. (0.25 mole) of cyclohexanone was converted to l-methylcyclohexanol. The alcohol boiled at 150-160°.

In the dehydration of l-methylcyclohexanol to l-methylcyclohexene, two procedures were attempted. The first of these was unsatisfactory.

**A. Procedure I.**—Into a 500 ml. ground glass joint flask, equipped with a pressure-equalizing dropping funnel,
a condenser set up for distillation, and a thermometer below the surface of the solid, 50 g. of anhydrous aluminum sulfate was placed. A small amount of 1-methylcyclohexanol was added through the dropping funnel and the mixture was heated. The dehydration began at 150° and the olefin and water distilled slowly and evenly. The remainder of the alcohol was then slowly added as the distillation continued. The product was dried over calcium chloride and distilled. The olefin boiled at 109-110°; n^24_d 1.4510. The infrared spectrum was compared with the A. P. I. standard, and at 3500 cm. a band was observed which did not appear in the standard. A peak at this wave number is characteristic of an alcohol. The product was then refluxed with sodium metal for 3 hr. and distilled. The olefin boiled at 106-7°; n^24_d 1.4481. The yield was 1 g., or 2.7% of the theoretical yield. The infrared spectrum of this product was very similar to that of the standard.

B. Procedure II.---Into a 100 ml. one neck ground-glass jointed flask equipped with a condenser for distillation, 48.6 g. (0.43 mole) of 1-methylcyclohexanol was added to 0.2 g. of iodine, and the mixture was slowly distilled. The distillate was washed with sodium thiosulfate solution and with distilled water, and dried over calcium chloride. The product was then refluxed with sodium for 3 hours and distilled from the sodium. The olefin boiled at 106-7°;
Preparation of 3,5-dimethylcyclohexanol.--Two hydrogenations of 3,5-dimethylphenol were tried, one low pressure and one high pressure. Neither method was successful.

**A. Procedure I.**--Into a hydrogenation vessel was placed 30.5 g. (0.25 mole) of 3,5-dimethylphenol that had been recrystallized three times from 66-75° ligroin, 0.3 g. of platinum oxide (Adams' catalyst) and 50 ml. of anhydrous ethanol. The Adams' catalyst was prepared according to the procedure of Adams. 22 The hydrogenation was started at 4.5 atm., and after a small initial drop in pressure, essentially no hydrogen was absorbed during 10 hours. The catalyst was filtered out, the solvent was distilled off, and the starting material was recovered.

**B. Procedure II.**--According to the procedure of Baker, 23 30.5 g. (0.25 mole) of 3,5-dimethylphenol, 0.6 g. of platinum oxide, and 25 ml. of glacial acetic acid, were placed in an autoclave. The hydrogenation was run at 40 atm. for 12 hr. at 80°. The catalyst was filtered off and the solution was poured into aqueous sodium hydroxide and boiled with excess alkali to remove any acetate esters; the product was extracted with ether. The ethereal solution was dried over anhydrous magnesium sulfate and the ether removed by distillation. The product was distilled to give
two fractions: the first boiling at 79°C (15 mm.), $n_d^{31.5}$ 1.4393, and the main fraction, boiling at 132°C (15 mm.), which was unreacted starting material. The yield of the alcohol was about 1 g., or 2.1% of the theoretical yield.

**Attempted Reduction of 3,5-dimethylphenol to 3,5-dimethylcyclohexanone.**—Two chemical reductions were tried, one by the lithium-ethylamine heterogeneous method, using 200 g. of ethylamine, 30.5 g. (0.25 mole) of 3,5-dimethylphenol, and 20.7 g. (3.0 moles) of lithium according to the procedure of R. A. Benkeser.²⁴ The mixture was extracted with ether, and the extract was dried over magnesium sulfate. The ether was distilled off, leaving unreacted starting material. The second method was by lithium and ethylenediamine heterogeneous procedure, using 300 ml. of ethylenediamine, 30.5 g. (0.25 mole) of 3,5-dimethylphenol, and 18.6 g. (2.7 moles) of lithium. The mixture was extracted with ether, and the extract was dried over magnesium sulfate. The ether was distilled off leaving unreacted starting material.

**Preparation of 3,5-dimethylcyclohexanone.**—In accord with the procedure of Sandborn,²⁵ 50 g. (0.4 mole) of 3,5-dimethylcyclohexanol (Aldrich Chemical Co.) was oxidized to 3,5-dimethylcyclohexanone with sodium dichromate. The product was extracted with ether, dried over magnesium sulfate, and the ether removed by distillation. The product was then distilled at reduced pressure to give two fractions: b.p.
62-64° (6.5 mm.), and 66-68° (6.5 mm.).

Preparation of cis-3,5-dimethylcyclohexanone.---The pure cis-dimethylketone was obtained by converting the crude cis-ketone (62-64° fraction) to its semicarbazone, and recrystallizing the semicarbazone from aqueous ethanol. The recrystallization gave white plates, m.p. 198-9°, lit. 200-201°.5°.26

Preparation of cis-1,3,5-trimethylcyclohexene.---
The semicarbazone was hydrolyzed with ethanolic hydrochloric acid, dried over magnesium sulfate and distilled. The pure cis-3,5-dimethylcyclohexanone was converted to 1,3,5-trimethylcyclohexanol by the method of Signaigo and Cramer.19 The alcohol boiled at 178-9°, nD 1.4392. The alcohol was dehydrated according to the procedure of Edgar, et. al.,21 to cis-1,3,5-trimethylcyclohexene. The olefin boiled at 82° (4 mm.); nD 1.4475. The overall yield was 4 g. of cis-isomer, or 8% of the theoretical yield from the original commercial dimethylcyclohexanol mixture of isomers.

Attempted preparation of trans-1,3,5-trimethylcyclohexene.---The crude trans-dimethylketone (66-68° fraction) was converted to its semicarbazone and converted to trans-1,3,5-trimethylcyclohexene by the same method as the cis-isomer. There was not enough of the olefin obtained to utilize further.
CONCLUSIONS

The results of this work show that no cis-1,3,5-trimethylcyclohexene is formed in the reduction of mesitylene. Since there is a possibility of only the two isomers, cis and trans, the olefin must be entirely trans-1,3,5-trimethylcyclohexene. If the carbanion mechanism of Birch is correct, the stereospecificity in this case must be dependent on the stability of an intermediate, rather than the stability of the final product. If it were dependent on the stability of the final product, the cis-isomer would be the preferred product.

The heterogeneous reduction with lithium-ethylene-diamine was the most powerful in that it produced more saturated hydrocarbon. This could be attributed to the increased solubility of the metallic lithium and the higher temperature at which the reduction was run.

In the homogeneous reactions, there was less reduction, possibly because of the decreasing concentration of lithium available. This could cause the rate of reduction to decrease and the reduction to be incomplete in the time allowed for reaction.

The data showed that mesitylene was more readily reduced than was toluene.
Further work on the homogeneous reduction could show if the reduction is dependent on the concentration of lithium. A series of homogeneous reactions which were run for different lengths of time with the same quantities of amine and lithium would show whether the reduction rate was slowed by the decreasing amount of lithium. Also, if the amount of amine and lithium were increased and reactions run for a specific length of time, it could be determined if the concentration of lithium is a factor in the rate of the reaction.

A study in which 1,4-cyclohexadiene was added to a homogeneous mixture of lithium and ethylenediamine to determine if the N-lithoethylenediamine would rearrange and dehydrogenate the diene to benzene would show whether there is a reversibility of the first step of the reduction.

Gas Phase Chromatography was used in an attempt to analyze the products. Although it was unsuccessful in this investigation, it has the most promise. Further work using Gas Phase Chromatography to analyze the products would be the best way to find the concentration of each of the products. An unsaturated stationary phase would be the most compatible to the reduction products and probably would be a good column material to use.
BIBLIOGRAPHY


