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THE REDUCTION OF p-TOLYL METHYL ETHER

A Dissertation

Submitted to the Faculty

Of the Graduate School of the University of Louisville

In Partial Fulfillment of the

Requirements for the Degree

Of Master of Science.

Department of Chemistry

By

Gustav Paul Dinga

Year

1949

NAME OF STUDENT: Gustav Paul Dinga

TITLE OF THESIS: The Reduction of p-Tolyl

Methyl Ether.

APPROVED BY READING COMMITTEE COMPOSED OF THE
FOLLOWING MEMBERS:

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DATE: May 7, 1949.

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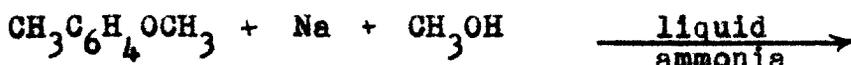
The writer wishes to acknowledge his appreciation to Max Ingersoll Bowman for his direction and advice throughout the research for this thesis. He is indebted to his wife, Eunice Viola Dinga, who assisted in the preparation of the manuscript and in the proof reading of this material.

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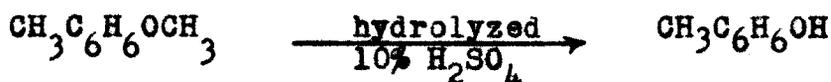
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I. INTRODUCTION

This research is a continuation of the work initially started by Arthur J. Birch² involving the reduction of 4-methylanisole (one mole) with 1.9 moles of sodium and methyl alcohol in liquid ammonia, as indicated:



4-methylanisole
(p-tolyl methyl ether)



dihydro 4-methylanisole
83.9% of theoretical yield

4-methyl-1,3-cyclohexadien-1-ol



4-methyl-2-cyclohexen-1-one
33.0% of theoretical yield

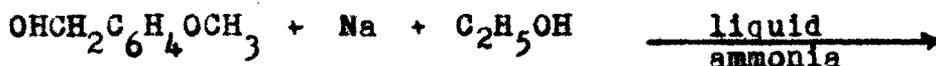
The 4-methyl-2-cyclohexen-1-one reacted with semicarbazide and 2,4-dinitrophenylhydrazine reagent to give the usual ketone derivatives, melting points 188-189°C. and 158-159°C., respectively. The melting point of 4-methyl-2-cyclohexen-1-one

semicarbazone is different from the supposedly identical compound prepared by Kotz and Steinhort¹¹, reported melting point 184-185°C.

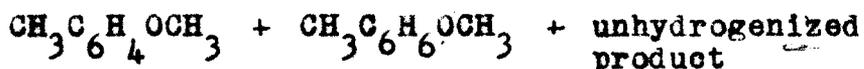
The theories regarding the mechanism of this reaction and related experiments have been published by C.A. Kraus¹², H. Levy and A.C. Cope¹⁴, Chablay⁷, A. A. Morton¹⁵, Piazoia¹⁶, Einhorn and Ehret⁸, K. Campbell and B. Campbell⁶, Kazanskii¹⁰, and Beilstein references to Behal¹.

It may be interesting to note that the two hydrogens added to the benzenoid structure during reduction are attached to the second and fifth carbon atom. This was indicated by Birch² in his initial paper.

Arthur Birch continued the reduction methods with anisyl alcohol³ or p-methoxyphenyl carbinol. The reduction of anisyl alcohol with sodium and ethyl alcohol in liquid ammonia gave the following products: p-tolyl methyl ether, 29%; dihydro p-tolyl methyl ether, 7%; and unhydrogenated product, 59%. The above reaction occurred as follows:



anisyl alcohol



p-tolyl methyl ether dihydro p-tolyl
ether methyl ether

The semicarbazone derivative of dihydro-p-tolyl methyl ether melted between 188-189°C., indicating that it was probably 4-methyl-2-cyclohexen-1-one semicarbazone, melting point 188-189°C.²

The p-tolyl methyl ether, boiling point 175-177°C., corresponds to the same physical constant given by Heilbron⁹ (b.p. 175-176°C.). The other products described in Birch's article were not of immediate interest to the type of research performed for this paper.

The research involving reduction by dissolving metals was extended by Birch in a third paper⁴ which presented a more thorough examination of reduction with sodium and alcohol in liquid ammonia. Various methoxy benzenes

were examined but the reduction of dimethyl-p-toluidine and p-tolyl methyl ether was of primary interest.

The reductions were carried out by three methods. Method A utilized sodium and excess alcohol in liquid ammonia, adding two hydrogens to the benzenoid structure. Method B included the procedure of method A followed by further action by an increased quantity of sodium and liquid ammonia, adding four hydrogens to the benzenoid structure. Method C utilized reduction in ether with calcium hexamine (prepared by reacting calcium with liquid ammonia), adding four hydrogens to the benzenoid nucleus.

The reduction of a substance by method A, with sodium and alcohol in liquid ammonia, added two hydrogens to the benzenoid nucleus to form a dihydro compound. The reaction involved 7.0 g. of substance, 7.0 g. sodium, 15.0 g. ethyl alcohol and 130 ml. of liquid ammonia. The sodium was added to the solution in 45 minutes and allowed to react with rapid stirring until the blue color (formed by sodium and ammonia) disappeared. The pasty mass, formed during the

the reduction, was cautiously decomposed with 100 ml. of water and the oil (dihydro compound) was extracted with ether and distilled.

The methoxy alkyl dihydrobenzene, formed by reduction method A, was shaken with a saturated solution of sodium bisulfite (10.0 g.) for twelve hours to form a solid sodium bisulfite addition product. The addition product was decomposed with a solution of sodium carbonate (5.0 g.) in 15 ml. of water to form an oil. The oil (β,γ -unsaturated ketone), obtained from the hydrolyzed methoxy alkyl dihydrobenzene, was extracted with ether and distilled under reduced pressure.

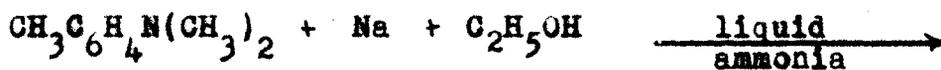
The β,γ -unsaturated ketone 2,4-dinitrophenylhydrazone was prepared by adding an excess of 2,4-dinitrophenylhydrazine, dissolved in 5% sulfuric acid and ethyl alcohol, to methoxy alkyl dihydrobenzene or β,γ -unsaturated ketone. The 2,4-dinitrophenylhydrazone derivative was washed with aqueous sodium carbonate and water to remove any acid that would probably isomerize it on recrystallization. The 2,4-dinitrophenylhydrazone derivative was isomerized to α,β -unsaturated

ketone 2,4-dinitrophenylhydrazone by refluxing for three minutes with a few drops of sulfuric acid in alcohol or benzene.

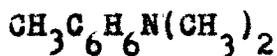
The α,γ -unsaturated ketone was shaken with aqueous semicarbazide and sodium acetate to form a semicarbazone derivative. It should be noted that the sodium acetate was not added until the unsaturated ketone had been dissolved in the aqueous semicarbazide.

The reduction of a compound by method B or C added four hydrogens to the benzenoid structure to form a tetrahydro compound, consequently, these two reduction methods were not utilized in this research.

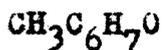
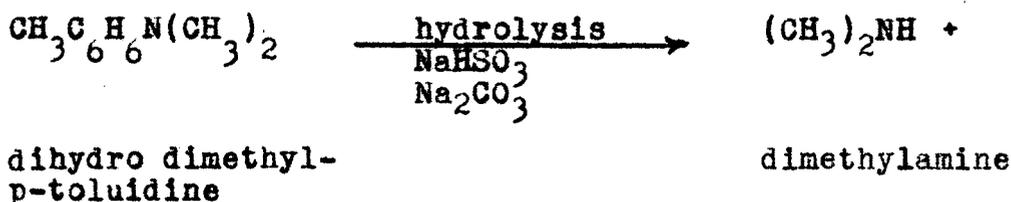
The reduction of dimethyl-p-toluidine and hydrolysis of the product to the α,γ -unsaturated ketone, by method A, gave the following products:



dimethyl-p-toluidine



dihydro dimethyl-p-toluidine



4-methyl-3-cyclohexen-1-one

The reduction of dimethyl-p-toluidine (7.0 g.) formed 4.1 g. of 4-methyl-3-cyclohexen-1-one, boiling point 74°C. at 17 mm. pressure or 169-172°C. at 755 mm. pressure. A quantitative analysis of the unsaturated ketone indicated the empirical formula C₇H₁₀O. A spectroscopic analysis indicated an absence of a maximum wave length at 2260 A. (mol. 870) confirmed as , - unsaturated ketone.

The reaction of 2,4-dinitrophenylhydrazine, dissolved in 5% sulfuric acid and ethyl alcohol, with the dihydro compound or 4-methyl-3-cyclohexen-1-one formed orange prisms, m.p. 120-121°C., wavelength max. 3680 A. and max. 20,200, identified as 4-methyl-3-cyclohexen-1-one 2,4-dinitrophenylhydrazone. The quantitative analysis

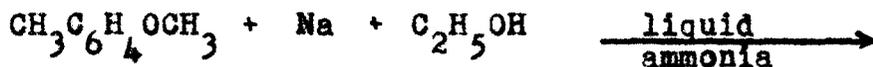
of the derivative indicated the empirical formula
 $C_{13}H_{14}O_4N_4$.

The reaction of semicarbazide with the dihydro compound or 4-methyl-3-cyclohexen-1-one formed a colorless crystalline material, m.p. 188-189°C., wavelength max. 2330 A. and max. 11,300, identified as 4-methyl-3-cyclohexen-1-one semicarbazone.

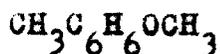
The 4-methyl-2-cyclohexen-1-one was prepared by refluxing 4-methyl-3-cyclohexen-1-one with 3% aqueous sulfuric acid for six hours.

The reduction of dimethyl-p-toluidine by method B or C formed tetrahydro dimethyl-p-toluidine which hydrolyzed to 4-methyl cyclohexanone.

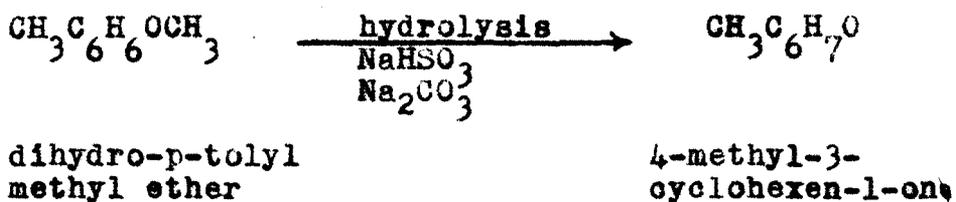
The reduction of p-tolyl methyl ether by method A and hydrolysis of the dihydro compound formed the following products:



p-tolyl methyl ether



dihydro p-tolyl methyl ether



The reduction of p-tolyl methyl ether (7.0 g.) produced 5.0 g. of dihydro-p-tolyl methyl ether, b.p. 167-170°C., 71.4% of theoretical yield. The dihydro compound was shown to be 94% pure by the formation of a 2,4-dinitrophenylhydrazone derivative, m.p. 120-121°C. (identical to the 2,4-dinitrophenylhydrazone prepared from dihydro 4-methyl anisole, dihydro dimethyl-p-toluidine and 4-methyl-3-cyclohexen-1-one).

The semicarbazone of 4-methyl-3-cyclohexen-1-one or dihydro-p-tolyl methyl ether was colorless crystalline material, m.p. 188-189°C.,

max. 2330 Å. and max. 11,300, identified as 4-methyl-3-cyclohexen-1-one semicarbazone. It is interesting to note that Birch's original paper² identified the semicarbazone of 4-methyl-2-cyclohexen-1-one with the same melting point as that of 4-methyl-3-cyclohexen-1-one semicarbazone, m.p. 188-189°C.

The reduction of p-tolyl methyl ether by

method B formed 0.7 g. of methyl-1-cyclohexene, b.p. 105-110°C., 10% of theoretical yield. This liquid product reacted with 2,4-dinitrophenylhydrazine reagent to form nitroloperidine of methyl-1-cyclohexene, m.p. 146-147°C.

The reduction of p-tolyl methyl ether with sodium and a reducing alcohol in liquid ammonia is of primary interest. But, the other reduction products mentioned in the introduction may be formed in the reduction of p-tolyl methyl ether, consequently, it becomes advantageous to utilize the material as a basis for an understanding of the experimental results.

II. OBJECTIVE

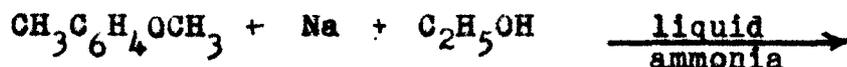
The initial objective has been to become acquainted with the technique of handling the reduction of p-tolyl methyl ether, consequently, model experiments were performed that correlated with the procedures presented by Birch in the original literature.^{2,3,4}

Generally, the reduction of p-tolyl methyl ether (also identified as p-cresyl methyl ether, methyl-p-tolyl ether and 4-methyl anisole) proceeds according to the data given in the original literature, consequently, with the establishment of success in various reductions it becomes of interest to reduce p-tolyl methyl ether by other methods.

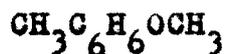
III. EXPERIMENTAL

A. Reduction of p-tolyl methyl ether with sodium and alcohol in liquid ammonia.

1. One mole of p-tolyl methyl ether reacted with 3.96 moles of sodium and an excess of ethyl alcohol in liquid ammonia to form dihydro p-tolyl methyl ether, as follows:



p-tolyl methyl ether



dihydro p-tolyl methyl ether

The reduction involved 19.7 g. of p-tolyl methyl ether, 14.0 g. sodium and 45 ml. of ethyl alcohol in 300 ml. of liquid ammonia. The sodium was added to the solution of p-tolyl methyl ether, ethyl alcohol and liquid ammonia in 40 minutes with intermittent shaking. The blue color of the reacting material had not disappeared in four hours, therefore, the material was left overnight, in the reaction flask (Dewar flask),

to complete reaction and permit evaporation of the liquid ammonia. The gray solid formed during the reduction was decomposed with ice and water to form an oil layer which was extracted with ether.

The aqueous layer gave a negative test with 2,4-dinitrophenylhydrazine reagent, thus, indicating the absence of any dihydro compound.

The ether-oil layer was dried over calcium sulfate (Drierite) and fractionally distilled as follows:

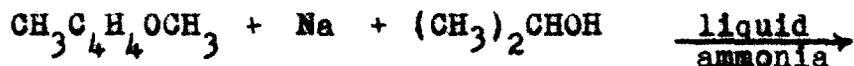
Fraction	B.P. °C.	ml.	M.P. °C. of 2,4-DNPH	g. of 2,4- DNPH	% of dihydro comp'd.
1	30-60	33	110-117	0.2	0.2
2	66-167	37	115-121	0.6	0.7
3	167-170	3	-	-	-
4	172-173	14	-	-	-
5	174	5	-	-	-
residue	above 174	-	-	-	-

2,4-DNPH-indicates 2,4-dinitrophenylhydrazone.

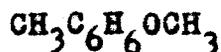
The constitution of each fraction was tentatively concluded to be the following: fraction 1, predominantly diethyl ether;

fraction 2, ethyl alcohol and diethyl ether; fraction 3, colorless liquid, boiling point 167-170°C., tentatively identified as dihydro p-tolyl methyl ether, b.p. 167-170°C.⁴, 15% of theoretical yield; fraction 4, probably unreacted p-tolyl methyl ether; fraction 5, unreacted p-tolyl methyl ether; residue, an insufficient quantity for identification. The hydrolysis of the tentatively identified dihydro compound is described in part four.

2. One mole of p-tolyl methyl ether reacted with 5.25 moles of sodium and excess of anhydrous isopropyl alcohol in liquid ammonia to give dihydro p-tolyl methyl ether, as indicated:



p-tolyl methyl ether



dihydro p-tolyl methyl ether

The reduction involved 50 ml. of p-tolyl methyl ether, 48.5 g. sodium, 100 ml. anhydrous isopropyl alcohol and 750 ml. of liquid ammonia. The sodium was added to the reacting materials (in a Dewar flask) in $1\frac{1}{2}$ hours. After five hours an additional 10 ml. of anhydrous isopropyl alcohol was added to enhance the disappearance of the blue coloration in the mixture. The evaporation of the liquid ammonia left a gray residue which was decomposed with cold water. The oil was extracted with ether and dried over calcium sulfate (Drierite).

The aqueous layer gave a negative test with 2,4-dinitrophenylhydrazine indicating the absence of any dihydro p-tolyl methyl ether.

The ether-oil layer was fractionally distilled and the various fractions tested with 2,4-dinitrophenylhydrazine reagent as follows:

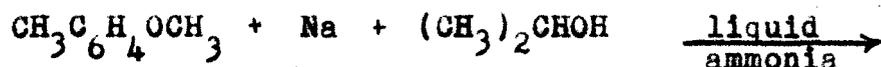
Fraction	B.P. °C.	ml.	M.P. °C. of 2,4- DNPH	g. of 2,4- DNPH	% of dihydro comp'd.
1	30-80	140	-	-	-
2	87	12	118-121	0.6	2.6
3	168-170	25	-	-	-
4	172-175	2	108-110	0.5	12.0
residue	above 175	2	111-118	0.8	20.0

2,4-DNPH-indicates 2,4-dinitrophenylhydrazone.

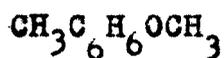
The 2,4-dinitrophenylhydrazine reagent consists of 2,4-dinitrophenylhydrazine dissolved in isopropyl alcohol and 5 percent sulfuric acid.

The various fractions were summarized as follows: fraction 1, predominantly diethyl ether; fraction 2, isopropyl alcohol and other higher boiling material; fraction 3, a colorless liquid, b.p. 167-170°C., tentatively identified as dihydro p-tolyl methyl ether, b.p. 167-170°C.⁴, 50% of theoretical yield; fraction 4, a solution of unreacted p-tolyl methyl ether and dihydro p-tolyl methyl ether which was indicated by the formation of 2,4-dinitrophenylhydrazone; residue, similar to fraction 4 with a higher percentage of dihydro p-tolyl methyl ether.

3. One mole of p-tolyl methyl ether reacted with 5.35 moles of sodium and an excess of anhydrous isopropyl alcohol in liquid ammonia to give dihydro p-tolyl methyl ether as follows:



p-tolyl methyl ether



dihydro p-tolyl methyl ether

The reduction utilized 35 ml. of p-tolyl methyl ether, 36.0 g. sodium, 100 ml. isopropyl alcohol and 800 ml. of liquid ammonia. The sodium was added in 1 3/4 hours and allowed to react until the blue coloration disappeared. When the reduction was completed the ammonia was allowed to evaporate by removing the material from the Dewar flask. The gray solid was decomposed with ice and water to form an oil layer which was extracted with ether.

The aqueous layer gave a negative test with 2,4-dinitrophenylhydrazine reagent, indicating the absence of any reduction product.

The ether-oil layer, which was dried over Drierite, was fractionally distilled and the various fractions were tested with 2,4-dinitrophenylhydrazine reagent as follows:

Fraction	B.P. ^{°C.}	ml.	M.P. ^{°C.} of 2,4- DNPH	g. of 2,4- DNPH	% of dihydro comp'd.
1	35-80	40	-	-	-
2	145-165	3	117-121	0.4	6.6
3	167-170	14	-	-	-
residue	-	-	-	-	-

2,4-DNPH-indicates 2,4-dinitrophenylhydrazone.

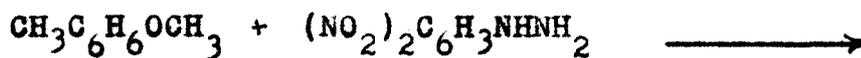
The constitution of each fraction was tentatively concluded to be as follows: fraction 1, predominantly diethyl ether and isopropyl alcohol; fraction 2, unidentified higher boiling material with a small amount of dihydro p-tolyl methyl ether; fraction 3, a colorless liquid, b.p. 167-170^{°C.}, tentatively identified as dihydro p-tolyl methyl

ether, b.p. 167-170°C.⁴, 40% of theoretical yield; residue, an insufficient quantity for identification.

The tentatively identified dihydro compound reacted with semicarbazide hydrochloride to form a small quantity of semicarbazone, m.p. (154°) 165-187°C. (unidentified).

4. The various colorless liquid fractions from the three previous preparations, tentatively identified as dihydro p-tolyl methyl ether, b.p. 167-170°C.⁴, were combined (refractive index 1.4891 at 20°C, no previous literature reference) and treated as follows:

Procedure A involved the reaction of dihydro p-tolyl methyl ether (1.08 g.) with an excess of 2,4-dinitrophenylhydrazine reagent to form the following product:



dihydro p-tolyl methyl ether 2,4-dinitrophenylhydrazine



4-methyl-3-cyclohexen-1-one 2,4-dinitrophenylhydrazone

The orange crystalline solid, 1.3 g., m.p. 115-117°C., was tentatively identified as 4-methyl-3-cyclohexen-1-one 2,4-dinitrophenylhydrazone, m.p. 120-121°C.⁴, 50% of theoretical yield.

Procedure B involved the reaction of dihydro p-tolyl methyl ether (1.6 g.) with an excess of semicarbazide hydrochloride and sodium acetate to form the following product:

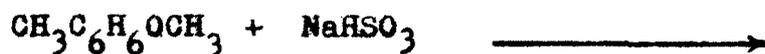


dihydro p-tolyl methyl ether semicarbazide

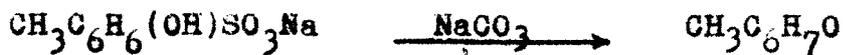
high melting semicarbazone, unidentified

The material was allowed to react for three days with no occurrence of any solid semicarbazone, consequently, the mixture was heated for one hour between 90-100°C. and cooled to form 1.0 g. of an unidentified buff solid, m.p. 245-247°C. A mixed melting point with a similiar semicarbazone, obtained by Dr. Max I. Bowman when refluxing the semicarbazone of 3-methyl-2-cyclohexen-1-one with an excess of semicarbazide hydrochloride, was 245-246°C. The above results tentatively indicated that the higher melting semicarbazone is not derived from the ketones but from the semicarbazide hydrochloride.

Procedure C involved the reaction of dihydro p-tolyl methyl ether (20.0 g.) with an excess of sodium bisulfite (25.0 g.) and 10.0 g. of sodium carbonate to form the following products:



dihydro p-tolyl methyl
ether



sodium bisulfite addition
compound of 4-methyl-3-
cyclohexen-1-one

4-methyl-3-
cyclohexen-
1-one

A yellow viscous solid formed after shaking the dihydro compound with sodium bisulfite for 24 hours. The filtration of the mixture gave a buff solid, 4-methyl-3-cyclohexen-1-one bisulfite addition compound, which was decomposed with 10.0 g. of sodium carbonate (dissolved in 30 ml. of water) to form an oil which was extracted with ether and dried over magnesium sulfate.

The aqueous layer reacted with 2,4-dinitrophenylhydrazine reagent to form 0.7 g. of an unidentified dark red solid, m.p. 133-165°C.

The ether-oil layer was fractionally distilled and the various fractions

treated with 2,4-dinitrophenylhydrazine reagent as follows:

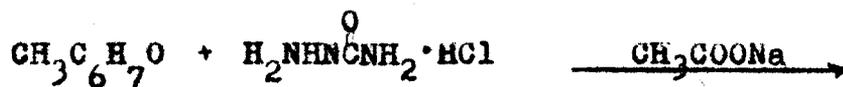
Fraction	B.P. ^{°C.}	ml.	M.P. ^{°C.} of 2,4- DNPH	g. of 2,4- DNPH	% of dihydro comp'd.
1	36-65	15	122-123	0.4	1.1
2	169-173	10	-	-	-
residue	above 173	4	-	-	-

The various fractions were identified as follows: fraction 1, predominantly diethyl ether and a small quantity of 4-methyl-3-cyclohexen-1-one; fraction 2, a colorless liquid, b.p. 169-173^{°C.}, identified as 4-methyl-3-cyclohexen-1-one, b.p. 169-172^{°C.},⁴, approximately 50% of theoretical yield; residue, unidentified material which gives a negative test with an excess of hydroxylamine hydrochloride and sodium acetate.

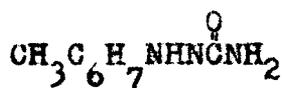
The 4-methyl-3-cyclohexen-1-one was indirectly identified when 2,4-dinitrophenylhydrazine reagent reacted with the unsaturated ketone present in fraction one to form an orange crystalline solid (re-crystallized from methyl alcohol and

ether) m.p. 122-123°C., identified as 4-methyl-3-cyclohexen-1-one 2,4-dinitrophenylhydrazone, m.p. 120-121°C.⁴

The composition of fraction two was further established when 1.2 g. of the unsaturated ketone reacted with an excess of semicarbazide hydrochloride and sodium acetate to form the following product:



4-methyl-3-cyclohexen-1-one semicarbazide hydrochloride



4-methyl-3-cyclohexen-1-one semicarbazone

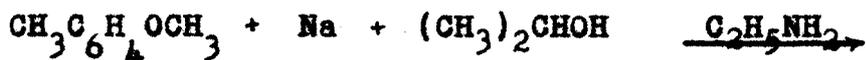
The reaction formed 1.2 g. of a white solid (recrystallized from methyl alcohol and ether), m.p. 188-189°C., identified as 4-methyl-3-cyclohexen-1-one semicarbazone, m.p. 188-189°C.⁴, 80% of theoretical yield.

The refractive index of 4-methyl-3-cyclohexen-1-one was 1.47085 at 21°C., no previous literature reference.

Various attempts to prepare the oxime of 4-methyl-3-cyclohexen-1-one, formerly prepared by Behal as indicated by Beilstein¹, have been unsuccessful.

B. Reduction of p-tolyl methyl ether with sodium and alcohol in ethyl amine.

1. One mole of p-tolyl methyl ether reacted with 3.79 moles of sodium and anhydrous isopropyl alcohol in ethylamine as follows:



p-tolyl methyl ether

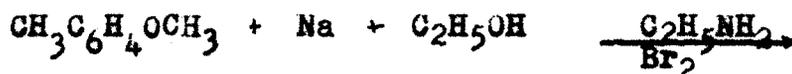
no reduction product

The reaction involved 9.7 g. of p-tolyl methyl ether, 7.0 g. sodium, 19 ml. anhydrous isopropyl alcohol and 90 ml. of ethylamine. The sodium, which reacted in a mild manner, was added in twenty minutes. The material, which contained unreacted sodium after 48 hours, indicated the absence of any reduction product when treated with 2,4-dinitrophenylhydrazine reagent. The partially solid material, after 72 hours, was decomposed with water to form

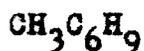
an oil which was extracted with ether.

The various tests of the ether-oil and aqueous layers with 2,4-dinitrophenylhydrazine reagent indicated the absence of a reduction product.

2. One mole of p-tolyl methyl ether was reduced with 3.79 moles of sodium, ethyl alcohol in ethylamine and bromine, as follows:



p-tolyl methyl ether



methyl-1-cyclohexene

The reduction utilized 9.7 g. p-tolyl methyl ether, 7.0 g. sodium, 29 ml. ethyl alcohol, 80 ml. ethylamine and 4 ml. of bromine. The sodium was added to the solution in ten minutes and after 1½ hours no further reaction was perceptible,

consequently, 19 ml. of ethyl alcohol was added to initiate further activity. The reduction was incomplete after 24 hours (indicated by unreacted sodium), therefore, an additional 20 ml. of ethyl alcohol and 4 ml. of bromine were added to the reaction mixture in an attempt to obtain a complete reduction.

The white material formed during the reaction was decomposed with water and the oil was extracted with ether. The ether-oil layer, dried over calcium sulfate (Drierite), was fractionally distilled as follows:

Fraction	B.P. ^o C.	ml.
1	60-90	64
2	97-110	6
residue	-	-

The constitution of each fraction was as follows: fraction 1, predominantly diethyl ether and ethyl alcohol; fraction 2, a cloudy liquid, b.p. 97-110^oC., tentatively identified as methyl-1-cyclohexene, b.p.

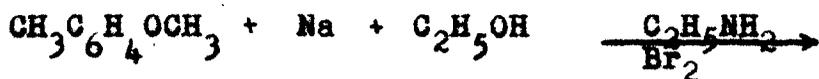
105-110°C.⁴ and 110-111°C.¹³; residue, insufficient quantity for identification.

The liquid obtained in fraction two was treated with 2,4-dinitrophenylhydrazine reagent to form an orange crystalline solid, m.p. 138-148°C., tentatively identified as nitrolpiperidine of methyl-1-cyclohexene, m.p. 146-147°C.⁴

The aqueous layer reacted with 2,4-dinitrophenylhydrazine reagent to form an orange crystalline material, m.p. 141-145°C., tentatively identified as nitrolpiperidine of methyl-1-cyclohexene, m.p. 146-147°C.⁴

The use of bromine as a catalyst was an extension of Einhorn's and Ehret's⁸ method which utilized bromine in the benzene ring as a means of facilitating reduction with sodium and amyl alcohol.

3. One mole of p-tolyl methyl ether reacted with 5.26 moles of sodium and ethyl alcohol in ethylamine and bromine, as follows:



p-tolyl methyl ether

no reduction product

The reaction involved 9.7 g. of p-tolyl methyl ether, 9.7 g. sodium, 20 ml. ethyl alcohol mixed with 2 ml. of bromine and 80 ml. ethylamine. The sodium was added in 15 minutes and after four hours of stirring the material was decomposed with water. A small quantity of unreacted sodium was detected, probably indicating incomplete reduction of the p-tolyl methyl ether.

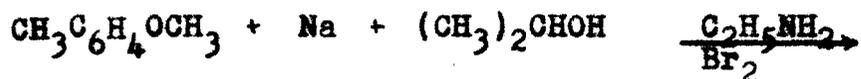
The oil, formed by decomposition of the material, was extracted with ether, dried over magnesium sulfate and fractionally distilled, as indicated:

Fraction	B.P. ^o C.	ml.
1	36-75	30.0
2	168-172	0.5
3	172-174	7.0
4	175	2.0
residue	-	-

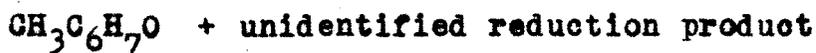
The various fractions gave negative tests with 2,4-dinitrophenylhydrazine reagent, indicating the absence of any reduction product.

The aqueous layer also gave negative results with 2,4-dinitrophenylhydrazine reagent, indicating the absence of a reduction product.

4. One mole of p-tolyl methyl ether reacted with 5.26 moles of sodium and anhydrous isopropyl alcohol in ethylamine and bromine, as follows:



p-tolyl methyl ether



4-methyl-2-cyclohexen-1-one

The reduction utilized 9.7 g. of p-tolyl methyl ether, 9.7 g. sodium, 4 ml. bromine and 80 ml. of ethylamine. The

sodium was added to the p-tolyl methyl ether and ethylamine in 15 minutes and after 1½ hours anhydrous isopropyl alcohol mixed with 3 ml. of bromine was added to the reaction mixture. The reduction was not completed after 2 hours, therefore, 20 ml. of anhydrous isopropyl alcohol and one ml. of bromine was added to the reactants in an attempt to complete the reaction. A solid product formed by the reaction was decomposed with water and the oil layer was extracted with ether.

The ether-oil layer was dried over magnesium sulfate and fractionally distilled as indicated:

Fraction	B.P. °C.	ml.
1	70-85	100
2	89-108	20
residue	-	-

The constitution of each fraction was as follows: fraction 1, predominantly diethyl ether with a small quantity of ethylamine; fraction 2, contained two immiscible

liquids which were further identified; residue, insufficient quantity for identification.

Fraction 2 was treated with diethyl ether in an attempt to separate any organic material from the two immiscible liquids. The supposedly ether-organic layer was fractionally distilled and each fraction reacted with 2,4-dinitrophenylhydrazine reagent, as follows:

Fraction	B.P. ^{°C.}	ml.	M.P. ^{°C.} of 2,4- DNPH	g. of 2,4- DNPH	% of dihydro comp'd.
1	35-60	2	-	-	-
2	(168)172-175	6	172-175	0.2	1.5
residue	above 175	2	132-135	0.1	4.3

2,4-DNPH-indicates 2,4-dinitrophenylhydrazone.

The various fractions indicated the following: fraction 1, predominantly diethyl ether; fraction 2, colorless liquid that reacted with 2,4-dinitrophenylhydrazine reagent to form dark red needle crystals, m.p. 172-174^{°C.}, tentatively identified as

4-methyl-2-cyclohexen-1-one 2,4-dinitrophenylhydrazone, m.p. 173-174°C.⁴; residue, a high boiling liquid, b.p. 175°C. and higher, which forms a red-orange solid with 2,4-dinitrophenylhydrazine reagent, m.p.

132-135°C., corresponding to the physical properties of pure 4-methyl cyclohexanone, b.p. 165-172°C.⁴, and 4-methyl cyclohexanone 2,4-dinitrophenylhydrazone, m.p. 133-134°C.⁴ The mixed melting points of the above 2,4-dinitrophenylhydrazone derivatives indicated they are not the same.

2,4-DNPH of	(a)	(b)	(a-b)
M.P. °C.	132-135	133-134	119-120

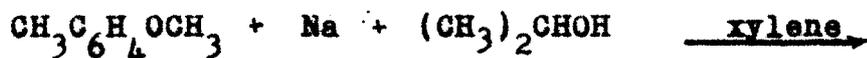
- (a) 2,4-DNPH of residue.
- (b) 2,4-DNPH of pure 4-methyl cyclohexanone.
- (a-b) Mixture of (a) and (b).

2,4-DNPH-indicates 2,4-dinitrophenylhydrazone.

The aqueous layers obtained in this analysis gave negative tests with 2,4-dinitrophenylhydrazine reagent, indicating the absence of a reduction product.

C. Reduction of p-tolyl methyl ether by other methods.

1. One mole of p-tolyl methyl ether reacted with 5.26 moles of sodium and isopropyl alcohol in xylene, as indicated:



p-tolyl methyl ether

no reduction product

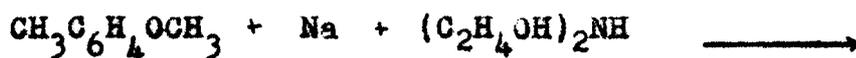
The reaction involved 7.0 g. of p-tolyl methyl ether, 7.0 g. sodium, 30 ml. isopropyl alcohol (reducing alcohol) and 100 ml. of xylene. The sodium was added to the solution in 45 minutes and the mixture was slowly refluxed with continuous stirring until the sodium had entirely dissolved.

The two immiscible layers, that were obtained when the white solid formed during the reaction was decomposed with water, were

tested with 2,4-dinitrophenylhydrazine reagent and semicarbazide hydrochloride. The negative tests obtained with these reagents indicated the absence of a reduction product.

It may be interesting to note that Birch obtained a reduction of m-tolyl methyl ether with potassium, isopropyl alcohol and light petroleum.⁵ The above reaction with xylene, which gave negative results, was an attempt to duplicate this type of reduction.

2. One mole of p-tolyl methyl ether reacted with 5.25 moles of sodium in diethanolamine, as follows:



p-tolyl methyl ether diethanolamine

unidentified reduction product

The reaction involved 7.0 g. of p-tolyl methyl ether, 7.0 g. sodium and

150 ml. of diethanolamine (utilized as a reducing alcohol and solvent). The sodium was added to the material in 45 minutes and the mixture was refluxed until the reaction had gone to completion.

The solid material that formed during the reaction was decomposed with water and the oil was extracted with ether.

The ether-oil layer was fractionally distilled as follows:

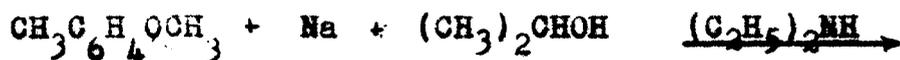
Fraction	B.P. ^{°C.}	
1A	38-120	colorless liquid
1B	173	cloudy liquid
residue	above 173	brown liquid

The various fractions gave negative tests with 2,4-dinitrophenylhydrazine reagent and semicarbazide hydrochloride, indicating the absence of any reduction product.

The solvent-aqueous layer gave a red-orange solid with 2,4-dinitrophenylhydrazine reagent, m.p. 125-130^{°C.}, tentatively indicating some type of reduction

product that was not a derivative of dihydro p-tolyl methyl ether, m.p. 120-121°C.⁴

3. One mole of p-tolyl methyl ether reacted with 5.26 moles of sodium and isopropyl alcohol in diethylamine, as follows:



p-tolyl methyl ether

unidentified reduction product

The reduction involved 7.0 g. p-tolyl methyl ether, 7.0 g. sodium, 45 ml. isopropyl alcohol and 30 ml. of diethylamine. The sodium was added to the material in 45 minutes and the mixture was stirred until the reaction had gone to completion. The addition of water to the mixture formed an oil layer which was extracted with ether.

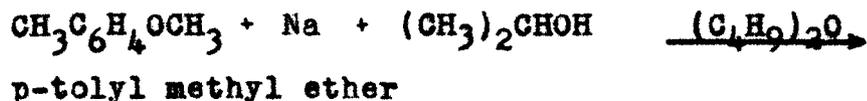
The ether-oil layer was fractionally distilled, as follows:

Fraction	B.P. °C.
a	55-85
b	85-100
c	100-105
residue	gray solid

The various fractions gave negative tests with semicarbazide hydrochloride and 2,4-dinitrophenylhydrazine reagent indicating the absence of a reduction product.

The aqueous layer, as in the previous reduction, gave an orange-red solid with 2,4-dinitrophenylhydrazine reagent, m.p. 125-130°C., tentatively indicating that the reduction product was not the 2,4-dinitrophenylhydrazone of dihydro p-tolyl methyl ether, m.p. 120-121°C.⁴

4. One mole of p-tolyl methyl ether reacted with 3.79 moles of sodium and anhydrous isopropyl alcohol and 120 ml. of dibutyl ether, as follows:



unidentified reduction product

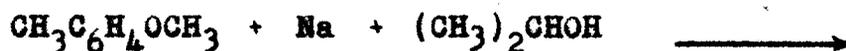
The reduction utilized 9.7 g. of p-tolyl methyl ether, 7.0 g. sodium, 30 ml. anhydrous isopropyl alcohol and 120 ml. of dibutyl ether. The reaction of the refluxing material with sodium was terminated in 45 minutes by the removal of unreacted sodium. The oil formed, when decomposing the material with water, was extracted with ether.

The ether-oil layer reacted with 10.0 g. of sodium bisulfite (saturated solution) to form an unidentified solid which was decomposed with sodium carbonate to form a liquid product, b.p. 167-168°C., corresponding to dihydro p-tolyl methyl ether, b.p. 167-170°C.⁴ The failure of the material to give a positive test with 2,4-dinitrophenylhydrazine reagent indicated the absence of a dihydro compound.

The aqueous layer was treated with 10.0 g. of sodium bisulfite and 6.0 g. of sodium carbonate to give a non-aqueous layer which reacted with 2,4-dinitrophenylhydrazine reagent to form an orange-yellow

solid, m.p. 130-136°C. (146°). The results indicated a tentatively unidentified reduction product.

5. One mole of p-tolyl methyl ether reacted with 1.64 moles of sodium in anhydrous isopropyl alcohol and hydroxylamine hydrochloride, as follows:



p-tolyl methyl ether

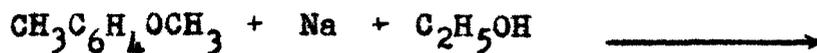
unidentified liquid $\xrightarrow{\text{NH}_2\text{OH}\cdot\text{HCl}}$ no reduction product

The reaction utilized 9.7 g. of p-tolyl methyl ether, 3.0 g. sodium and 40 ml. of anhydrous isopropyl alcohol. The sodium was refluxed with p-tolyl methyl ether and anhydrous isopropyl alcohol for 1 1/3 hours. The unreacted sodium was removed and hydroxylamine hydrochloride was added with 20 ml. isopropyl alcohol and 4.4 ml. of concentrated hydrochloric acid (36.7%

assayed). After refluxing for two hours the products gave negative tests with 2,4-dinitrophenylhydrazine reagent, indicating the absence of a reduction product.

The above reaction with hydroxylamine hydrochloride, which gave negative results, was an attempt to duplicate a similar reduction utilized by Shaw¹⁷ when reducing pyridine.

6. One mole of p-tolyl methyl ether reacted with 1.93 moles of sodium in ethyl alcohol, as follows:



p-tolyl methyl ether

no reduction product

The reaction involved 4.9 g. of p-tolyl methyl ether, 1.4 g. sodium and 20 ml. of ethyl alcohol (utilized as a solvent and reducing alcohol). The sodium was added in 45 minutes and as the reaction

progressed over a period of 96 hours various fractions of the material were tested, at different time intervals, with 2,4-dinitrophenylhydrazine reagent in an attempt to note any reduction product that would be formed. The negative tests obtained with 2,4-dinitrophenylhydrazine reagent indicated the absence of any reduction product.

IV. SUMMARY

1. One mole of p-tolyl methyl ether was reduced with 3.96 moles of sodium and ethyl alcohol in liquid ammonia to form a colorless liquid, b.p. 167-170°C., tentatively identified as dihydro p-tolyl methyl ether, b.p. 167-170°C.⁴; 15% of theoretical yield.

2. One mole of p-tolyl methyl ether was reduced with 5.25 moles of sodium and excess anhydrous isopropyl alcohol in liquid ammonia to form a colorless liquid, b.p. 168-170°C., tentatively identified as dihydro p-tolyl methyl ether, b.p. 167-170°C.⁴, 50% of theoretical yield.

3. One mole of p-tolyl methyl ether was reduced with 5.35 moles of sodium and an excess of anhydrous isopropyl alcohol in liquid ammonia to give a colorless liquid, b.p. 167-170°C., tentatively identified as dihydro p-tolyl methyl ether, b.p. 167-170°C.⁴, 40% of theoretical yield. The semicarbazone of the dihydro compound, m.p. (154°) 165-187°C., was unidentified.

4. The tentatively identified dihydro p-tolyl methyl ether, from the three previous experiments, was combined and gave a refractive index of 1.4891 at 20°C., no previous literature reference.

The dihydro p-tolyl methyl ether formed the following derivatives: first, the 2,4-dinitrophenyl hydrazone, m.p. 115-117°C., tentatively identified as 4-methyl-3-cyclohexen-1-one 2,4-dinitrophenylhydrazone, m.p. 120-121°C.⁴; second, the semicarbazone, m.p. 245-247°C., was the same as the semicarbazone prepared by Dr. Max I. Bowman when refluxing 3-methyl-2-cyclohexen-1-one with semicarbazide hydrochloride, m.p. 245-246°C., mixed m.p. 245-246°C.; third, the bisulfite addition compound was decomposed with sodium carbonate to form 4-methyl-3-cyclohexen-1-one, b.p. 169-173°C., identical to the unsaturated ketone obtained by Birch, b.p. 169-172°C.⁴

The 4-methyl-3-cyclohexen-1-one formed the following derivatives: the 2,4-dinitrophenylhydrazone, m.p. 122-123°C., identified as 4-methyl-3-cyclohexen-1-one 2,4-dinitrophenylhydrazone, m.p. 120-121°C.⁴; and the semicarbazone, m.p. 188-189°C., identified as

4-methyl-3-cyclohexen-1-one semicarbazone, m.p.
188-189°C.⁴

The refractive index of 4-methyl-3-cyclohexen-1-one was 1.47085 at 21°C., no previous literature reference.

5. One mole of p-tolyl methyl ether was not reduced with 3.79 moles of sodium and anhydrous isopropyl alcohol in ethylamine.

6. One mole of p-tolyl methyl ether reacted with 3.79 moles of sodium and ethyl alcohol in ethylamine and bromine to give a colorless liquid and its 2,4-dinitrophenylhydrazone derivative, b.p. 97-110°C. and m.p. 139-148°C., respectively. The products were tentatively identified as methyl-1-cyclohexene, b.p. 105-110°C.⁴ and the nitrolpiperidine of methyl-1-cyclohexene, m.p. 146-147°C.⁴

7. One mole of p-tolyl methyl ether was not reduced with 5.26 moles of sodium and ethyl alcohol in ethylamine and bromine. Note: not the same procedure as in the previous reduction.

8. One mole of p-tolyl methyl ether reacted with 5.26 moles of sodium and anhydrous isopropyl alcohol in ethylamine and bromine to give a colorless liquid which formed a 2,4-dinitrophenylhydrazone derivative, m.p. 172-175°C., tentatively identified as 4-methyl-2-cyclohexen-1-one 2,4-dinitrophenylhydrazone, m.p. 173-174°C.⁴ The reduction also gave an unidentified 2,4-dinitrophenylhydrazone derivative, m.p. 132-135°C.

9. One mole of p-tolyl methyl ether was not reduced with 5.26 moles of sodium and isopropyl alcohol in xylene.

10. One mole of p-tolyl methyl ether was reduced with 5.26 moles of sodium in diethanolamine to give an unidentified reduction product which formed a 2,4-dinitrophenylhydrazone derivative, m.p. 125-130°C.

11. One mole of p-tolyl methyl ether was reduced with 5.26 moles of sodium in isopropyl alcohol in diethylamine to give an unidentified

reduction product which formed a 2,4-dinitrophenylhydrazone derivative, m.p. 125-130°C.

12. One mole of p-tolyl methyl ether was reduced with 3.79 moles of sodium and anhydrous isopropyl alcohol in dibutyl ether to give an unidentified reduction product which formed a 2,4-dinitrophenylhydrazone derivative, m.p. 130-136°C.(146°).

13. One mole of p-tolyl methyl ether was not reduced with 1.64 moles of sodium in anhydrous isopropyl alcohol and hydroxylamine hydrochloride.

14. One mole of p-tolyl methyl ether was not reduced with 1.93 moles of sodium in ethyl alcohol.

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