SYNTHESIS AND ATTEMPTED BECKMANN REARRANGEMENT OF SOME 2-ALKYLTETRALONE OXIMES

Thesis for the Degree of M. S.

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Martin Robert Leven

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This is to certify that the

thesis entitled

SYNTHESIS AND ATTEMPTED BECKMANN REARRANGEMENT
OF SOME 2-ALKYLTETRALONE OXIMES

presented by

MARTIN ROBERT LEVEN

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Harold Hart
Major professor

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SYNTHESIS AND ATTEMPTED BECKMANN REARRANGEMENT OF SOME 2-ALKYLTETRALONE OXIMES

By

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INTRODUCTION

In order to determine the configuration of 2-alkyl-α-tetralone oximes, the synthesis of 2-methyl, 2-ethyl and 2-isopropyl-α-tetralone oximes and a study of their Beckmann rearrangement was undertaken. The Beckmann rearrangement of 2-alkyl-α-tetralone oximes may lead to two possible structural isomers, ortho-amino-γ-phenyl-α-alkylbutyrolactam or ortho(3-amino-propyl)-benzoic acid lactam.

Ungnade and McLaren (2) were able to rearrange a series of alkylcyclohexanone oximes in sulfuric acid and found that the 2-alkyl compounds gave single products on rearrangement. Isolation and identification of these lactams indicated that the oximes were in all cases anti to the alkyl group.

Schroeter's results on the Beckmann rearrangement of α-tetralone oximes were anomalous to those of the cyclohexanone series (2). He reported the end product of the rearrangement of α-tetralone oxime to be α-naphthylamine. However, Schroeter employed acetic anhydride, acetic acid and gaseous hydrogen chloride to bring about the rearrangement.

Sulfuric acid and phosphorus pentachloride were not cited in the literature as rearranging mediums for the 2-alkyl-α-tetralone oximes. It is one of the purposes of this investigation to report the results obtained with these reagents.

HISTORICAL

Beckmann rearrangements of 2-alkylcyclanone oximes have been studied extensively in the cyclohexanone (1) and cyclopentanone (3) series. The rearrangement may possibly lead to the formation of two structural isomers (Fig. 1).

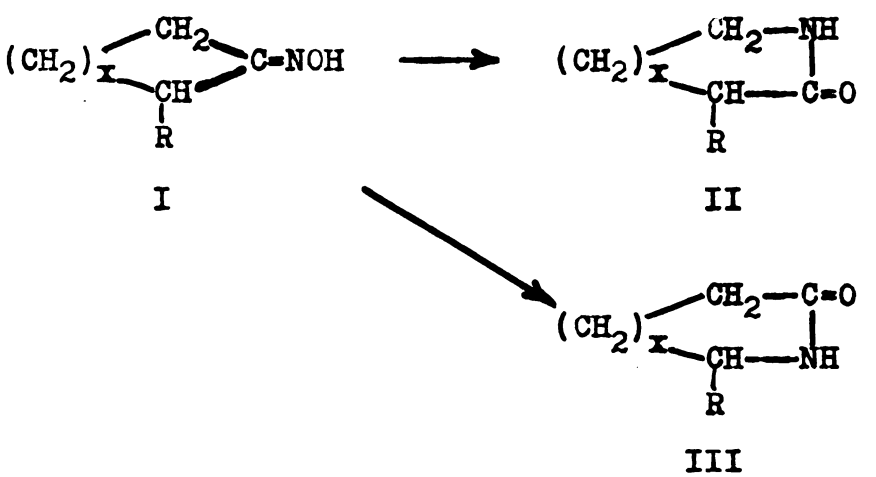

Fig. 1

Hildebrand and Bogert (3) studied the rearrangement of 2-methyl, 2-ethyl and 2-n-propylcyclopentanone oximes and 2-methylcyclohexanone oxime in a sulfuric acid medium. In all cases, the rearranged product was found to be represented by III in Fig. 1.

Ungnade and McLaren (1) were able to rearrange a series of mono-, di- and trialkylcyclohexanone oximes. The cyclohexanone oximes with one α-alkyl group gave

single products on sulfuric acid rearrangement which had the 2-keto-7-alkylhexamethyleneimine structure (Fig. 2).

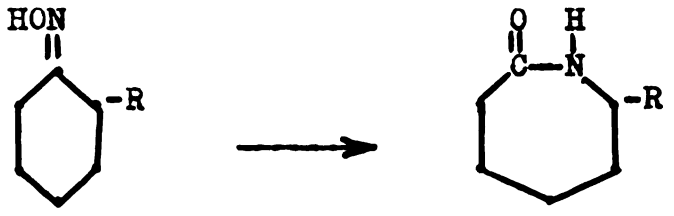

Fig. 2

When other alkyl groups were substituted on the α-alkylcyclohexanone oxime, the Beckmann rearrangement followed the same course as indicated in Fig. 2. Unsymmetrical alkylcyclohexanone oximes that did not contain an α-substituent were found to give a mixture of the two possible isomers upon rearrangement. Rearrangements were successfully carried out on 2-methyl-, 4-methyl-, 2,4,6-trimethyl-, 2,3,5-trimethyl-, 2,4-dimethyl-, 2,5-dimethyl-, 3,5-dimethyl- and 2-t-butyl-4-methylcyclohexanone oximes. Only one rearranged product was isolated in all of these instances. With the unsymmetrically substituted cyclohexanone oximes without the α-substituent, both of the possible isomers were isolated and identified.

The oximes of α-tetralone should behave in a manner similar to those of the cyclohexanone and cyclopentanone series. The work of Schroeter, however, showed that α-tetralone oximes gave unusual products when subjected to the Beckmann rearrangement (2).

Schroeter was able to treat α-tetralone oxime or the acetyl ester of α-tetralone oxime with a Beckmann reagent which consisted of acetic anhydride and acetic acid saturated with gaseous hydrogen chloride. The end product was found to be α-naphthylamine. Schroeter was also able to get an "α-naphthylamine rearrangement" with substituted α-tetralone oximes such as 5- or 7-nitro-, 6- or 7-chloro- and 6-methoxy-α-tetralone oxime. The proposed and rather unbelievable mechanism for the rearrangement has the title of "the gap molecular theory" or "the univalent nitrogen hypothesis." (Fig. 3)

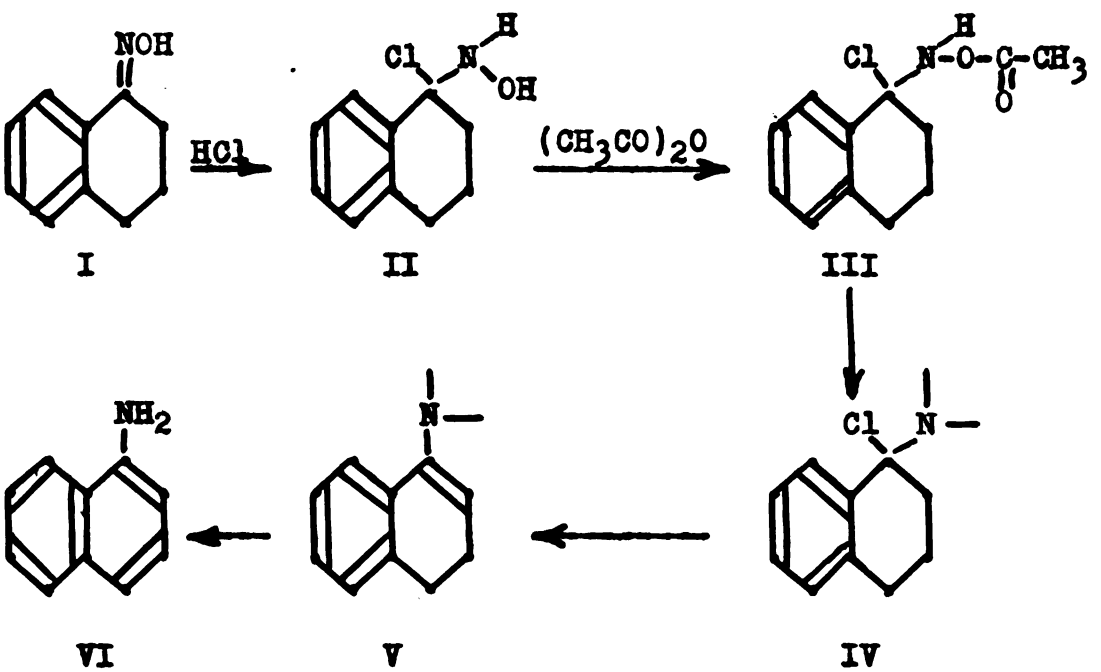

Fig. 3

The α-naphthylamine rearrangement was carried out in an open container. Schroeter also carried out a rearrangement of 5,8-dimethyl-α-tetralone oxime acetate using Beckmann's reagent in a closed system. The lactam

Fig. 3

of (2,5-dimethyl-6-amino-γ-phenyl)-n-butyric acid was isolated (Fig. 4).

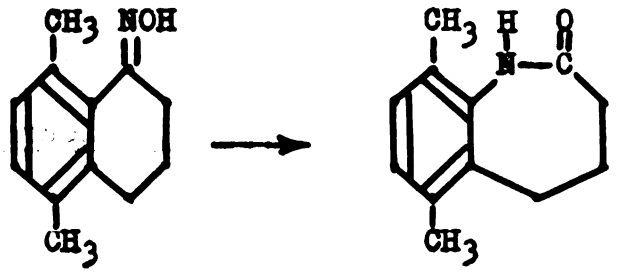

Fig. 4

Since the end product was what might be expected in a normal Beckmann rearrangement, the configuration of the oxime was established. The normal Beckmann rearrangement was also given with α-tetralone oxime p-toluenesulfonate.

Smith (4), using the Schmidt reaction on α-tetralone, was able to isolate homodihydrocarbostyryl (ortho-amino-γ-phenyl-n-butyrolactam) in 85% yield. The solvent for the Schmidt reaction was trichloroacetic acid. When the oxime of α-tetralone was warmed to 60° in trichloroacetic acid, the trichloroacetate of α-tetralone oxime was the only product isolated.

Smith also attempted the rearrangement of the potassium α-tetralone oxime-O-sulfonate in a hydrogen chloride solution of dioxane (5). The end product was largely α-tetralone, but he also reported 12% α-naphthylamine. Small amounts of homodihydrocarbostyryl were formed when the potassium α-tetralone oxime-O-sulfonate was warmed in dry pyridine.

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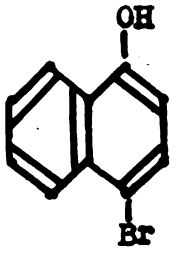
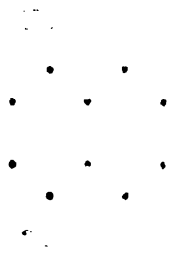
EXPERIMENTAL

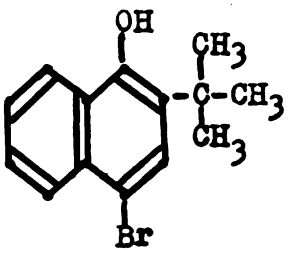
4-Bromonaphthol (6)



In a 250-ml. flask there was placed 26 g. (0.102 mole) of finely divided iodine in 60 ml. of glacial acetic acid. After the addition of 5 ml. of bromine to the solution, the flask was placed on a steam bath and warmed to 50°. When the solution was removed from the steam bath and cooled, 14 g. (0.096 mole) of α-naphthol in 45 ml. of glacial acetic acid was added. The contents of the flask were mixed by shaking and then allowed to stand at room temperature for one hour. The solution was then added to 16 g. of sodium bisulfate in 700 ml. of water. The resulting crude precipitate of 4-bromo-α-naphthol was filtered, washed with water and air dried. For each gram of compound, 45 ml. of 33% ethanol was used for recrystallization. From this process, 20 g. (93% yield) of colorless needles melting at 127-129° (uncorrected) was obtained.

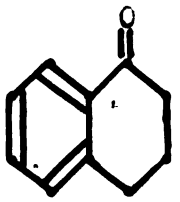


Attempted Preparation of 2-t-Butyl-4-bromo-α-naphthol



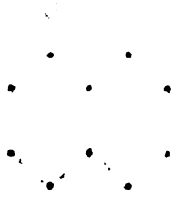
Using the alkylating vessel described by Stillson et al. (7), 20 g. (0.089 mole) of 4-bromo-α-naphthol was dissolved in 300 ml. of p-xylene and 5 ml. of concentrated sulfuric acid and alkylated at 65-70° with 12 g. (0.21 mole) of isobutylene. After fifteen minutes of alkylation, the solution turned black. The entire alkylation took one and one-half hours. The black solution was then neutralized with sodium bicarbonate, washed with water and dried over anhydrous sodium sulfate. A precipitate was formed in the organic layer during the process of neutralization. The precipitate and solvent were transferred to a Vigreaux column and the solvent was removed in vacuo. The residue consisted of a black gummy resinous material which could not be recrystallized to give a sharp melting point. Four to five grams of this material was obtained.

1-Keto-1,2,3,4-tetrahydronaphthalene (α-tetralone) (8)



Five hundred grams of commercial tetralin (3.78 moles) was placed in a one-liter round-bottomed flask equipped with a fritted glass bubbler, thermometer and a series of reflux condensers. The type of reflux condensers used was a Liebig condenser surmounted by a Freidrick and a Graham condenser. Since rubber stoppers contaminate the subsequent reactions, only ground glass equipment was used. A rapid stream of air was drawn through the tetralin by applying suction from an aspirator pump attached to the uppermost condenser. The air current was continued for fifty to fifty-five hours. The contents of the flask was maintained at 78° by means of a Glas-col heater.

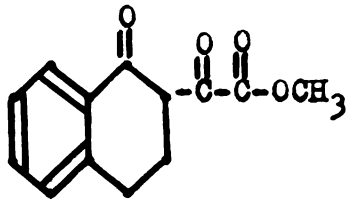
At the end of this period, the warm partially oxidized tetralin was poured into 500 ml. of 2 N sodium hydroxide which had been placed in a two-liter flask. During the addition of the partially oxidized tetralin, vigorous mechanical stirring was maintained while the temperature was kept below 70° by adding ice when necessary. This temperature was maintained for at least ten minutes. The mixture was then cooled to room temperature



and nearly neutralized with 6 N sulfuric acid (about 160 ml.). The upper tetralin and α-tetralone layer, which was now colored dark orange, was separated and washed with 100 ml. of .5 N sulfuric acid and then with 100 ml. of 1% ferrous sulfate. If an emulsion formed during the ferrous sulfate addition, the solution was acidified, followed by the addition of 25 to 60 g. of sodium chloride. The lower layer was removed and the upper tetralin-α-tetralone layer was dried over 25 g. of anhydrous sodium sulfate. It was then fractionally distilled through a 30-cm. column packed with #8 glass helices. The unchanged tetralin distilled at 65-72° at 2 mm. (70-85°/4 mm., 59-69°/1 mm.). The temperature then rose and the fraction distilling at 105-107° at 2 mm. (115-118°/5 mm.), (113.5-116°/4 mm.), (123-124°/9 mm.) was practically pure α-tetralone. If rubber-stoppered equipment was used, a fraction distilling at 96-98°/3 mm. was obtained. This material was not analyzed.

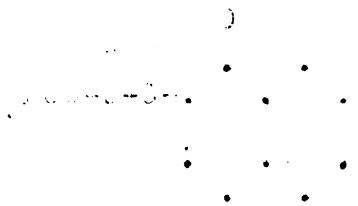
It was noted that if the recovered tetralin was used in a future oxidation, the yield of α-tetralone increased to as much as 80%. If the tetralin was oxidized for the first time, the yield of α-tetralone varied from 75-85 g. (46-55% of the theoretical amount based on the tetralin not recovered).

Methyl-α-tetralone-2-glyoxylate (9)



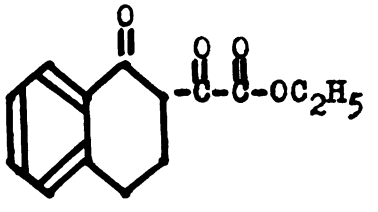
The equipment used in the procedure was a 500-ml. two-necked flask fitted with an addition tube, an inlet for nitrogen gas, a reflux condenser and a separatory funnel. Commercial sodium methoxide (17.28 g., 0.32 mole) and 37.76 g. (0.32 mole) of methyl oxalate was placed in the flask with 160 ml. of anhydrous benzene and refluxed for fifteen minutes. An atmosphere of dry nitrogen was maintained from this point until the end of the glyoxylation. At the end of the fifteen minutes, not all of the solid material had dissolved. After allowing the mixture to cool to room temperature, a solution of 23.36 g. (0.16 mole) of α-tetralone in 80 ml. of dry benzene was added. The flask was swirled until a definite yellow color formed throughout the mixture. The flask was then immersed in a water bath which was maintained between 15-20° for four hours. During this four-hour period the contents of the flask were shaken from time to time.

At the end of the four-hour period 200 ml. of water was added, and the sodium salt of the glyoxylate was extracted into the water layer. The benzene was then



extracted with 200 ml. of 20% sodium hydroxide and then again with 200 ml. of water. Ice was added, and the alkaline solution was then neutralized with cold 1:1 hydrochloric acid. The resulting yellow precipitate was kept cold for three hours to facilitate the complete precipitation. The yellow crystals were then filtered and washed with water and while they were still wet, recrystallized from aqueous methanol. Thirty-five grams (82% yield based on the α-tetralone) of yellow plates melting at 54-56° were isolated.

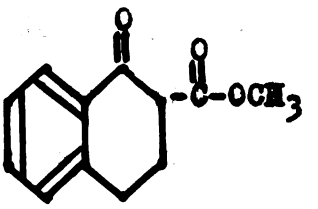
Ethyl-α-tetralone-2-glyoxylate



To a 500-ml. two-necked flask equipped with a mercury sealed stirrer and a reflux condenser surmounted by a separatory funnel, 12 g. of sodium and 250 ml. of absolute ethanol was added. When the mixture was cooled to room temperature, a solution of 35 g. (0.23 mole) of α-tetralone in 71 g. (0.36 mole) of cold ethyl oxalate was poured into the flask. The resultant mixture was stirred for one hour while the flask was immersed in an ice bath. The ice bath was removed, and the stirring was continued for an additional hour without application

of heat. While the solution was kept cold, 150 ml. of cold water was added followed by dilute sulfuric acid until neutral to litmus. The yellow crystals were filtered and recrystallized from methanol. Forty-four grams (67%) of yellow crystals (plates) melting at 46-47° were isolated.

Methyl-α-tetralone-2-carboxylate (9)



Twenty-four grams (0.10 mole) of methyl-α-tetralone-2-glyoxylate was placed in an eight-inch Pyrex test tube and heated on an oil bath to 150°. Powdered glass (12 g.) was added, and the temperature was raised to 180-190° and kept there for thirty minutes. At the end of this time carbon monoxide ceased to be evolved. After the contents of the test tube had cooled to room temperature, the carboxylate was extracted from the glass with acetone. The acetone extracts were then warmed and treated with carbon black and filtered. The acetone was evaporated, and the viscous material remaining was cooled and scratched with low boiling petroleum ether until crystals formed. These crystals were recrystallized from 50 ml. of 60-70° petroleum ether and 5 ml. of acetone.

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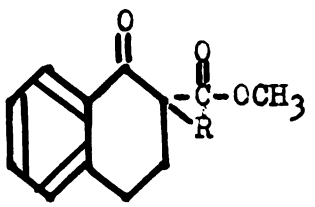
Colorless plates melting at 83-84° were obtained. The yield was 15 g. (74%).

The Alkylation of Methyl-α-tetralone-2-carboxylate (9,10)



Methyl iodide, ethyl iodide, isopropyl iodide, isopropyl bromide and isopropyl chloride were used in the alkylation of the carboxylate. The following general procedure applied to all of the alkylations:

To 5 g. (0.22 mole) of sodium and 95 ml. of anhydrous methyl alcohol was added a solution of 18 g. (0.09 mole) of methyl 1-keto-1,2,3,4-tetrahydronaphthalene-2-carboxylate in 50 ml. of anhydrous methyl alcohol and 50 ml. of dry benzene. The mixture, at this point, became distinctly red in color.

To the red solution was added the appropriate alkyl halide.

methyl iodide (38 g., 0.27 mole)

ethyl iodide (42 g., 0.27 mole)

isopropyl iodide (45 g.,026 moles)

After the addition of the alkyl iodides, the red solution was refluxed for three hours. In the case of the methyl and ethyl iodides, the solutions gradually changed color until they were practically yellow, but in the instance

of isopropyl iodide, the solution remained red. At this point the procedure varies depending upon the alkyl halide employed.

The methyl alkylated compound was treated as follows:

After cooling, acetic acid was added until the solution was neutral. The solvents were then removed *in vacuo* and the residue taken up in benzene and water. The water layer was extracted twice with benzene, and the combined benzene solutions were washed with sodium bicarbonate and then dried with anhydrous potassium carbonate. The benzene was removed under reduced pressure. The product that remained was recrystallized from 60-70° petroleum ether acetone. Eleven grams (55%) of presumably methyl 2-methyl-α-tetralone-2-carboxylate was obtained in rectangular prisms melting at 54-56°.

The ethyl and isopropyl alkylated compounds were treated as follows:

Acetic acid was added to the yellow solution until it became neutral. The solvents were then removed *in vacuo* until about 150 ml. of material remained. The residue was taken up in benzene and water, and the water was extracted twice with more benzene. The benzene extracts were combined, washed with sodium bicarbonate and dried over anhydrous potassium carbonate. The benzene was then removed *in vacuo*, and the red oil that remained was vacuum distilled through a five-centimeter Vigreaux column.

Thirteen grams (62% yield) of presumably methyl 2-ethyl-α-tetralone-2-carboxylate distilled at 135-138°/4 mm. When the oil was scratched with petroleum ether (60-70°), it crystallized in colorless prisms melting at 55-57°.

Eight grams (35%) of presumably methyl 2-isopropyl-α-tetralone-2-carboxylate was distilled at 155-160°/5 mm. After repeated scratching of the oil with petroleum ether (30-40°), a tan crystalline material was obtained which melted at 62-63°.

The alkylated carboxylates obtained above were hydrolyzed and decarboxylated as follows:

Eleven grams (0.05 mole) of methyl 2-methyl-α-tetralone-2-carboxylate, 11 g. (0.05 mole) of methyl 2-ethyl-α-tetralone-2-carboxylate and 8 g. (0.032 mole) of methyl 2-isopropyl-α-tetralone-2-carboxylate were hydrolyzed by refluxing with 80 ml. of 20% sodium hydroxide and 20 ml. of ethanol for three hours. The reaction mixture underwent a color transition from orange to red. Acidification of the warm solution with 1:1 sulfuric acid caused a vigorous evolution of carbon dioxide. To insure complete decarboxylation, the acidified solution was warmed on a steam bath for one hour. The ketones were then extracted with benzene, and the benzene extracts were washed twice with water, once with sodium bicarbonate and again with water. The benzene extracts were dried over

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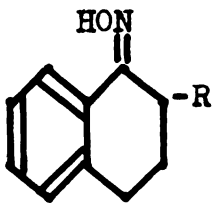
anhydrous potassium carbonate. Vacuum distillation yielded 8 g. of colorless 2-methyl-α-tetralone, b.p. 145-150°/25 mm.; 9 g. of colorless 2-ethyl-α-tetralone, b.p. 123-125°/5 mm. (the isolation of these compounds was practically quantitative); 6 g. (96%) of colorless 2-isopropyl-α-tetralone, b.p. 155-160°/5 mm.

When the alkylated α-tetralones were allowed to stand at room temperature for three to four days, they became slightly yellow in color.

Oximation of the Substituted α-Tetralones (11)



To 2 g. of the substituted α-tetralones in a 50-ml. flask was added 2.5 g. of hydroxylamine hydrochloride and 20 g. of redistilled pyridine. The flasks were fitted with condensers and placed on a steam bath for ten hours. The solution was then poured on 35 g. of ice and stirred. After standing at room temperature for two hours, the heavy oil was extracted with ethyl ether. The ether extracts were then combined, and the ether, as well as most of the pyridine, was removed by concentrating the solution on a steam bath. The remaining viscous oil was cooled and scratched until solidification occurred. The green mass was recrystallized from aqueous methanol and

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colorless plates were obtained. The yield was 2 g.

2-methyl-α-tetralone oxime melted at 96-98° (uncorrected)

Analysis for	C 75.40%	H 7.48%	N 8.00%
Calcd. for	C 75.68%	H 7.63%	N 8.03%

2-ethyl-α-tetralone oxime melted at 96-97° (uncorrected)

Analysis for	C 76.15%	H 7.99%	N 7.40%
Calcd. for	C 76.47%	H 7.98%	N 7.45%

2-isopropyl-α-tetralone oxime melted at 84-86° (uncorrected)*

Analysis for	C 76.80%	H 8.43%	N 6.89%
Calcd. for	C 75.05%	H 7.43%	N 7.97%

*The discrepancy in the analysis is discussed below.

Mixed melting point data:

2-methyl-α-tetralone oxime
α-tetralone oxime melted 82-87° (uncorrected)

2-ethyl-α-tetralone oxime
α-tetralone oxime melted 79-85° (uncorrected)

2-isopropyl-α-tetralone oxime
α-tetralone oxime melted 76-81° (uncorrected)

Beckmann Rearrangements (2,3,12,13)

I

Four grams of α-tetralone oxime was added to 15 ml. of 85% sulfuric acid. The warm solution was heated

slowly to 185°, whereupon it turned light brown. At no time was there a sudden increase in temperature which is characteristic of Beckmann rearrangements. After cooling the sulfuric acid solution to room temperature, ice was added and a precipitate formed. Upon addition of cold 20% sodium hydroxide, no oil formed, and the solid still remained. After filtration and recrystallization of the solid material from aqueous methanol, colorless plates were obtained. The plates melted at 101-103°. No depression in the melting point was noticed when these crystals were mixed with α-tetralone oxime.

II

Alpha-tetralone oxime (3 g.) was added to 10 ml. of hot (100-110°) 85% sulfuric acid. This temperature was maintained for fifteen minutes, and then the solution was allowed to cool. Upon cooling, by addition of ice, a precipitate formed. After neutralizing with cold dilute sodium hydroxide and filtering, the solution was extracted with ethyl ether, and the ether extracts were concentrated. A minute quantity of a black tarry material was recovered. The precipitate (above) gave a melting point of 100-101°. When it was mixed with α-tetralone oxime, it caused no depression in the melting point.

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III

In a 500-ml. round-bottomed flask fitted with an efficient condenser was placed 3 g. of α-tetralone oxime in 100 ml. of anhydrous ethyl ether. Three grams of phosphorus pentachloride was added. The solution was allowed to stand at room temperature for three hours. Upon distilling the ether, a yellowish white solid which consisted in part of some unreacted phosphorus pentachloride remained. Water was added to dissolve the phosphorus pentachloride, and a white flaky precipitate remained. The precipitate was filtered and recrystallized from aqueous methanol. The melting point of 101-103° indicated that the recovered material was α-tetralone oxime.

IV

2-Methyl-α-tetralone oxime (1 g.) was added to 5 ml. of hot (130°) 85% sulfuric acid. No temperature rise was noted during the addition. The temperature was maintained at 130° for ten minutes. Upon dilution with ice water, pink crystals formed. The crystals were filtered, and the filtrate was neutralized with cold 2 N sodium hydroxide and then extracted with benzene. The benzene extracts were concentrated, and only a minute quantity of black tarry material remained. The pink crystals were recrystallized from aqueous methanol and melted at 96-98° (the melting point of 2-methyl-α-tetralone oxime).

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V

Schroeter's technique was attempted in the "Beckmann rearrangement" using gaseous hydrogen chloride, glacial acetic acid and acetic anhydride. Alpha-tetralone oxime (5 g.) was treated with 40 ml. of glacial acetic acid and 4 g. of acetic anhydride. While the above solution was heated on a steam bath for three hours, a stream of hydrogen chloride gas was bubbled through it. During the course of this treatment, the solvents evaporated and left a brown crystalline mass on the bottom of the open beaker. Dilute hydrochloric acid (1:1) was used for recrystallization and 4-5 g. of colorless needles were obtained. The needles were placed in 200 ml. of hot water and dissolved. As soon as the solution cooled to 40-50°, sodium bicarbonate was added until the evolution of carbon dioxide was no longer apparent. The neutralized solution was warmed on a steam bath for thirty minutes. After cooling, ethyl ether was added, and the oil that formed following the bicarbonate treatment was extracted. Upon removal of the ethyl ether, a brown viscous liquid remained. A sample of the liquid gave a positive coupling reaction with β-naphthol. It also reacted with acetic anhydride and glacial acetic acid to give colorless plates melting at 155-157°. The acetate of α-naphthylamine was reported as melting at 159° (14).

Preparation of Semicarbazones (3)

The semicarbazones of the substituted tetralones were prepared by refluxing one gram of the ketone with one gram of semicarbazide hydrochloride in 5 ml. of pyridine and 10 ml. of absolute ethanol. The refluxing required from twelve to fifteen hours. At the end of this time, the solutions containing the semicarbazones were poured on 50 g. of ice and the semicarbazones crystallized out as colorless needles. 2-Methyl-α-tetralone semicarbazone melted at 203-205°. 2-Ethyl-α-tetralone semicarbazone melted at 200-201°.

Mixed melting point data:

2-methyl-α-tetralone semicarbazone
α-tetralone semicarbazone
melted 164-173° (uncorrected)

2-ethyl-α-tetralone semicarbazone
α-tetralone semicarbazone
melted 167-177° (uncorrected)

Table 1

Compound	B.P. °C	B.P. °C (Lit.)	Specific Gravity	Density 29°	Density 4° (Lit.)	Melting Point of Derivatives: Oxime	Melting Point of Derivatives: Semi carbazone	Melting Point of Derivatives: Semi-carbazone (Lit.)
2-Methyl-α -tetralone	145-150°/25 mm.	132°/15 mm.(15) 79-80°/2 mm.(16)	1.072	1.065	1.060(15)	96-98°	203-205°	193-195(16) 199-201°(15)
2-Ethyl-α -tetralone	116-117°/3 mm.	112-113°/1 mm.(16)	1.047	1.043	---	96-97°	200-201°	194-196°(10) 207°(21)

DISCUSSION OF RESULTS

A. Preparation of 2-Alkyl-α-tetralones and Their Oximes

The two principal methods for the preparation of 2-alkyl-α-tetralones are cyclization of γ-phenyl-α-alkylbutyric acids and the direct alkylation of α-tetralone-2-glyoxylate. Krollpfeiffer (15) and Alexander (16) employed the method of cyclization for 2-methyl-α-tetralone as indicated in Fig. 5. The over-all yield of 47% was reported by Alexander.

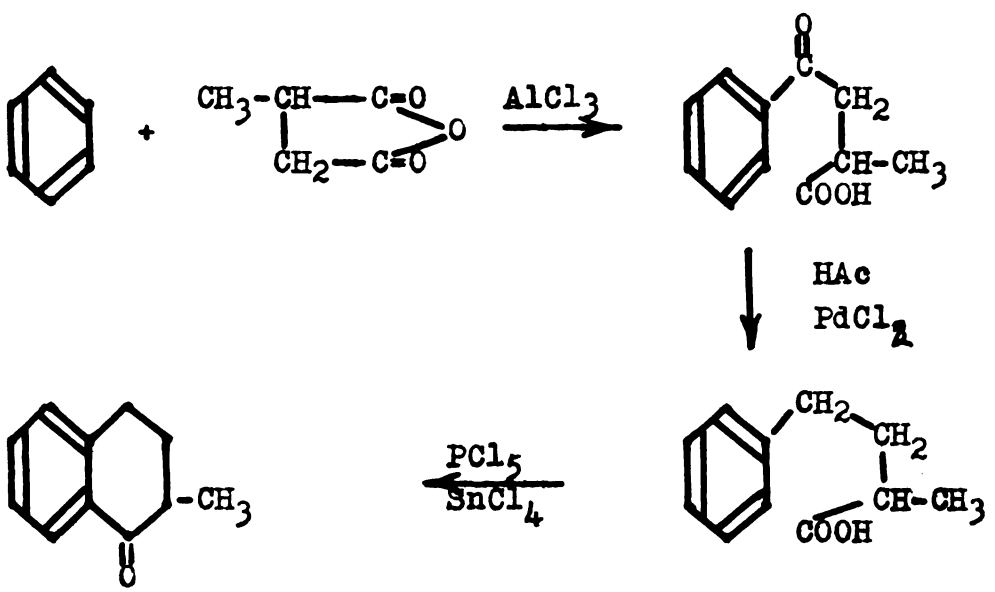

Fig. 5

The second method, developed by Bachmann (9), Kloetzel (10) and co-workers, involved the preparation of 2-methyl-2-carbomethoxy-α-tetralone followed by the

Fig. 3

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hydrolysis of the keto ester and subsequent decarboxylation (Fig. 6). The over-all yield of 75% was reported by Kloetzel and Close.

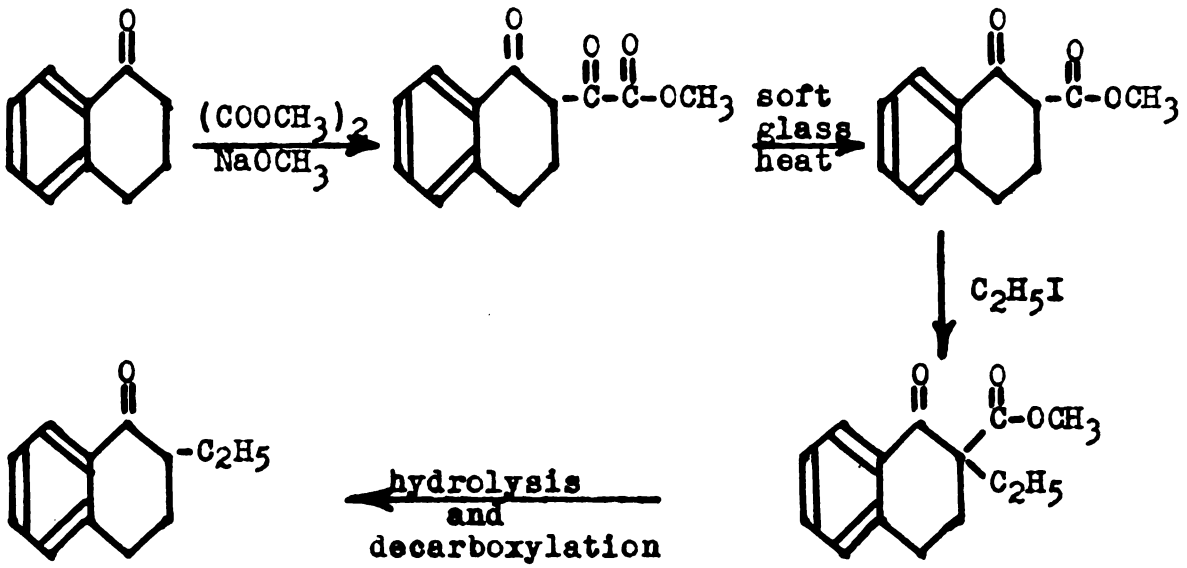
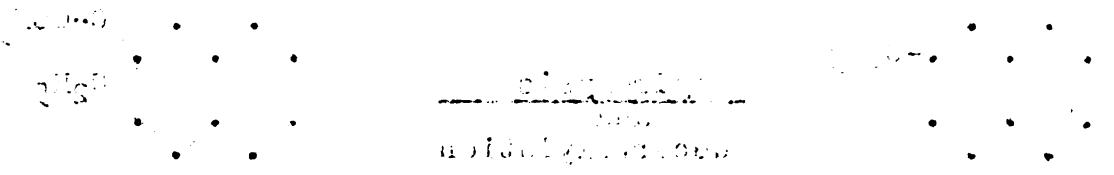


Fig. 6

Cole, in a personal communication, indicated that the first step in the above reaction is a very critical one. The yield of the glyoxylate is dependent upon the amount of starting material used. In all cases, where the amount of α-tetralone exceeded 5.84 g., the yield of the glyoxylate was lowered. Since this occurred, Cole suggested that in preparing a large quantity of the glyoxylate, a series of small runs, using α-tetralone and dimethyl oxalate, should be employed.

In the experimental portion describing the synthesis of methyl-α-tetralone-2-glyoxylate, the amount of α-tetralone used was four times the quantity suggested



by Bachmann. Bachmann's yield was 91%, whereas the maximum yield in this work was 82%. It is possible that the extent of obtaining an intimate mixture with large amounts of starting material could be facilitated by continuous stirring throughout the glyoxylation, thus improving the yield.

The ethyl α-tetralone-2-glyoxylate was prepared by using a combination of the procedures described by Bachmann (9) and Snyder (17). In an attempt to eliminate carbon monoxide by heating the compound with ground glass, only decomposition took place. The methyl ester was, therefore, employed in the remaining experiments.

The alkylation of methyl-α-tetralone-2-carboxylate was accompanied by color changes. At the beginning of the alkylation, using methyl and ethyl iodide, the color of the reaction mixture was red and later changed to yellow toward the end of the refluxing period. In the instance where isopropyl iodide, isopropyl bromide, or isopropyl chloride was used, this color change was not evident. This was probably an indication of a small amount of alkylation or no alkylation at all. The carbon-hydrogen-nitrogen values for the oxime of the isopropyl alkylated α-tetralone suggests that the oxime may have been a mixture of the isopropyl substituted and unsubstituted α-tetralone. Nevertheless, repeated recrystallizations and subsequent analysis showed no change in the melting point or percentage composition.

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The oximation technique presented in this report follows the procedure described by Siggia (18) and Sengupta (11). Normal methods of preparing oximes were not applicable to 2-alkyl cyclic ketones, since steric hindrance prevents oximation. Specifically, Sengupta found that the best conditions for converting 2,2-dimethyl-α-tetralone into the oxime was by treating the ketone with hydroxylamine hydrochloride and pyridine at 100° from ten to twelve hours. This procedure was followed and the yields were practically quantitative.

B. Attempted Beckmann Rearrangements of the Oximes

The Beckmann rearrangements attempted in this report followed the methods described by Marvel (12), Hildebrand (3) and Blatt (13). It was noticed that when sulfuric acid was used, a definite temperature rise was effected upon the addition of the oxime. It has been reported that this rise in temperature is not due to a rearrangement but to a salt-like complex that is formed between the oxime and the rearranging agent (Step 1 in Fig. 7) (19).

The steps in Fig. 7 illustrate the mechanism of the rearrangement as reported by Chapman and Kuhara and verified by Pearson (19).

In Step 2 of the reaction we find the formation of an ester that is potentially capable of ionizing (this

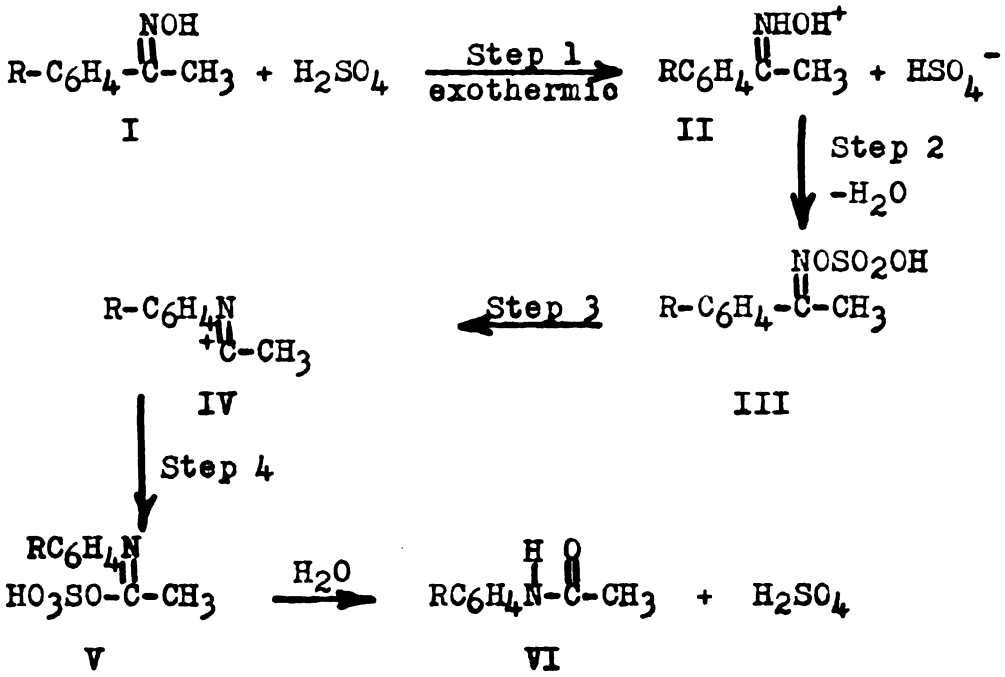
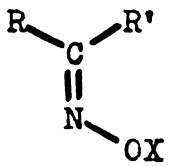


Fig. 7

can be seen in Step 3). Step 3 is the rate determining step. The ease of the ionization of the ester partially determines the rate and ease of rearrangement. The polarity of the solvents also determines the rate of rearrangement (20). The migrating group which attaches itself to the nitrogen atom is anti to the hydroxyl group in the original oxime (Step 3).

Jones (20), in reviewing the work of Chapman and Kuhara, indicated that Step 3 (Fig. 7) determines whether a rearrangement will or will not occur. Specifically, if the ionization cannot occur, in the case of the α-tetralone oxime-O-sulfonate, then the Beckmann rearrangement cannot take place. There are a number of factors which may influence ionization of this ester,

including the effect of groups which exert a dipole moment.



The group OX is the ester part of the oxime, and according to Chapmann and Kuhara, a rearrangement will occur when OX exerts a sufficient attraction for electrons to cause the electrons at the R-C bond to be displaced and thereby set up a state of stress within the molecule. If, however, group R has associated with it a dipole in the opposite direction of OX, electron displacement cannot occur, and the rearrangement will either by retarded or stopped completely.

To warrant the lack of a rearrangement in the α-tetralone oxime series, any combination of the factors discussed could conceivably prevent a rearrangement. The reason for lack of rearrangement in this series is not yet understood.

SUMMARY

1. 2-Methyl-α-tetralone and 2-ethyl-α-tetralone were prepared from α-tetralone in 40% over-all yield.

The steps included glyoxylation of α-tetralone (82%); decarbonylation (74%); alkylation (methyl 55%, ethyl 62%); hydrolysis and decarboxylation.

2. The 2-methyl and 2-ethyl-α-tetralones were characterized through semicarbazone formation.

3. Alkylation using isopropyl halides was not complete under the conditions employed and 2-isopropyl-α-tetralone oxime was not isolated in pure form.

4. The oximes of α-tetralone, 2-methyl-α-tetralone and 2-ethyl-α-tetralone did not undergo the Beckmann rearrangement under a variety of conditions. The oximes were in all cases recovered.

5. The conversion of α-tetralone oxime to α-naphthylamine reported by Schroeter (2) was verified.

6. The following new compounds were prepared:

2-methyl-α-tetralone oxime

2-ethyl-α-tetralone oxime.

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