A STUDY OF THE JACOBSEN REARRANGEMENT OF 6-n-PROPYL-7-METHYLTETRALIN

by

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A STUDY OF THE JACOBSEN REARRANGEMENT OF 6-n-PROPYL-7-METHYLTETRALIN

INTRODUCTION

Rearrangements involving polyalkybenzenes, halogenated polyalkybenzenes and polyhalogenated benzenes, which occur when these substances are sulfonated and their sulfonic acids are allowed to remain in contact with sulfuric acid, are classified as Jacobsen rearrangements.

Although this rearrangement was discovered in 1886, it was not till 1944 that a plausible mechanism for the rearrangement was proposed by Arnold and Barnes (1, p. 961). While this mechanism accounted for the necessity of having sulfuric acid present, a fact which previous mechanisms had completely ignored, it will nevertheless require further refinement if it is to be applicable to all cases.

In 1948 Smith and Lo set out to test the validity of the proposed mechanism. Arnold and Barnes regarded the migrating alkyl group as being split off as a cation. This cation in turn displaced the more hindered sulfonic acid group of the resulting disulfonic acid and thus gave rise to the rearranged sulfonic acid. Smith and Lo (18, p. 2210) concluded that if the migrating group was n-propyl, it would rearrange to an isopropyl group under the rearrangement conditions.

On choosing 6-propyl-7-methyltetralin as the compound undergoing rearrangement, Smith and Lo (18, p. 2210) found the product to be 5-propyl-6-methyltetralin.

The formation of this product necessitated the migration of a propyl group unaltered or alternatively, the migration of the non-aromatic ring. The present work was undertaken to obtain more conclusive evidence about the identity of this migratory group.

HISTORICAL

The present work concerns only that part of the Jacobsen rearrangement involving polyalkybenzenes so this section will review only directly related material.

In 1886 Jacobsen had noted that durene underwent rearrangement in sulfuric acid (5, p. 1209-1212). During the process, the liquid darkened and sulfur dioxide was liberated. The products obtained were 1,2,3,4-tetramethylbenzene-5-sulfonic acid, 1,2,4-trimethylbenzene-6-sulfonic acid and hexamethylbenzene. The main product was 1,2,3,4-tetramethylbenzene-5-sulfonic acid.

Pentamethylbenzene when subjected to the same conditions gave rise to hexamethylbenzene and 1,2,3,4-tetramethylbenzene-5-sulfonic acid (6, p. 896-898). Since hexasubstituted benzenes are found in these reactions they may be regarded as end products of the reaction and must be stable to sulfuric acid. On the other hand, trimethylated benzenes do not rearrange but are merely sulfonated (15, p. 1614). It can, therefore, be concluded that rearrangement is possible only in the case of tetra-and-penta-alkylbenzenes.

On investigating the reaction of sulfuric acid on durene, Smith and Cass (15, p. 1614-1615) found that whilst durene underwent rearrangement on heating with sulfuric acid, no rearrangement occurred on refluxing with phosphorus pentoxide. Durenesulfonic acid, however, rearranged in the presence of sulfuric acid or phosphorus pentoxide. Pentamethylbenzenesulfonic acid when placed in a dessicator over sulfuric acid underwent rearrangement whereas pentamethylbenzene

under the same conditions did not. It is, therefore, evident that it is the sulfonic acid which undergoes rearrangement.

The products resulting from the treatment of durene with sulfuric acid indicate that an intermolecular rearrangement must occur. Thus, 1,2,4,5-tetramethylbenzene gives rise to tri-, penta- and hexamethylbenzenes. In the case of the conversion from 1,2,4,5-tetramethylbenzene to 1,2,3,4-tetramethylbenzene the mode of migration is not obvious. That an intramolecular rearrangement does occur at least in some cases is clearly demonstrated in the conversion of octahydroanthracene to octahydrophenanthrene (13, p. 2036).

By-products of Jacobsen rearrangements, except those involving tetraethylbenzene, are sulfur dioxide and polymeric materials ranging from tars to insoluble infusible solids. It has been concluded that the liberation of sulfur dioxide is not an integral part of the rearrangement process. Hence, it need not be accounted for in a rearrangement mechanism.

Based on the foregoing chemical evidence, any mechanism proposed for the Jacobsen rearrangement must be able to account for the following factors:-

(1) The fact that tetralkylbenzenes and pentalkylbenzenes undergo rearrangement whereas the trialkylbenzenes, 1,2,3,4-tetralkylbenzenes and hexalkylbenzenes do not.

(2) That it is not the hydrocarbon but the sulfonic acid derivative of that hydrocarbon which undergoes rearrangement.

(3) That intra as well as intermolecular migration occurs.

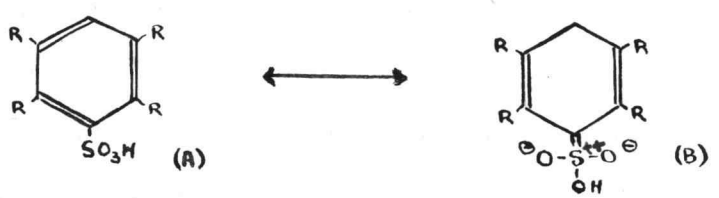
Jacobsen and later Smith and Cass proposed mechanisms for the rearrangement but neither was able to meet all the above requirements.

In 1944 Arnold and Barnes (1, p. 961) proposed a mechanism which had certain similarities to the previous mechanisms but which had a more satisfactory theoretical basis. It was based on two generalizations which immediately accounted for many of the differences in behavior of the various polyalkylbenzenes:-

(1) It is necessary to be able to sulfonate the hydrocarbon by entry of the sulfonic acid group into an unsubstituted position on the ring.

(2) Rearrangement is only possible when that sulfonic acid group is flanked by two ortho alkyl groups.

The key to the rearrangement, therefore, lies in the fact that the sulfonic acid group must be flanked by two alkyl groups. The presence of the two ortho substituents reduces the co-planarity of the ring with the sulfonic acid group. As a result, the contribution of the quinoid structure (B) to resonance is reduced.

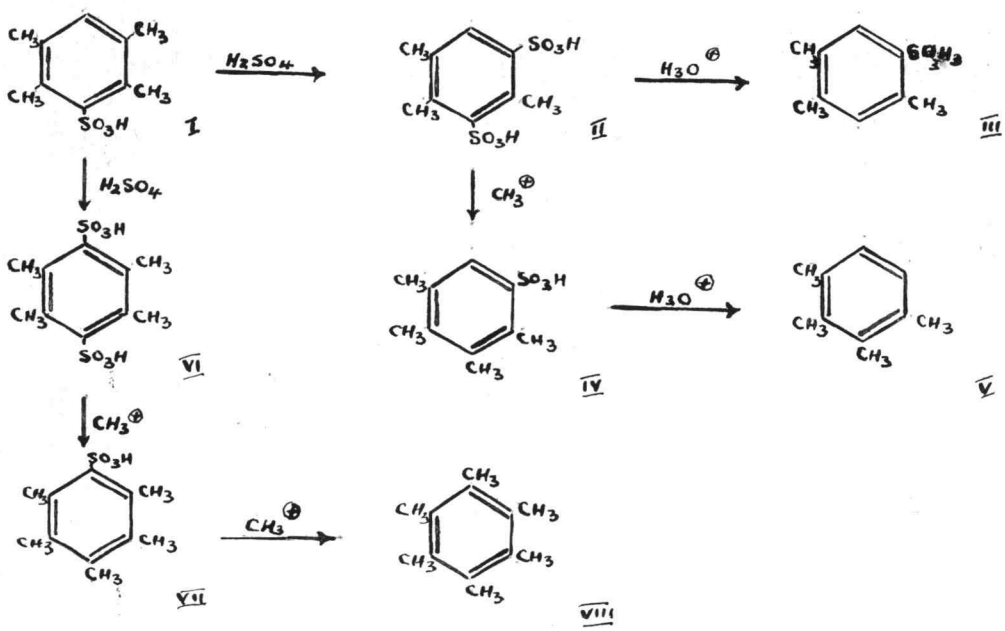


The tetralkylbenzenesulfonic acids which are subject to steric inhibition of resonance are, therefore, less deactivating but are nevertheless meta-directing. Consequently, such sulfonic acids may be converted to disulfonic acids, the entry of the second sulfonic acid group occurring meta to the first. Also, as a result of reduction in the contribution of the quinoid structure it is possible for

some of the p-disulfonic acid to be found which accounts for an intermolecular displacement occurring.

Smith showed that the most hindered sulfonic acid group was most readily hydrolyzed. Similarly, it might be expected that the most hindered sulfonic acid group would also be the most readily replaced by cationic reagents.

Thus, Arnold and Barnes (1, p. 969) essentially proposed the following mechanism:-



Since the more hindered sulfonic acid group is considered to undergo preferential displacement by a methyl carbonium ion, the formation of 2,3,4,5-tetramethylbenzenesulfonic acid (IV), which experimental data indicate is the preferred pathway, is accounted for.

Utilizing 6-propyl-7-methyltetralin as the substrate, Smith and Lo (18, p. 2210) set out to test the validity of the mechanism proposed by Arnold and Barnes. Since the migrating group in the proposed mechanism was a free cation a n-propyl group undergoing migration would be expected to isomerize to an isopropyl carbonium ion. This isopropyl carbonium ion would then be expected to displace the more hindered sulfonic acid group from the disulfonic acid to complete the rearrangement. Thus, Smith and Lo postulated that if the rearrangement proceeded through a free carbonium ion the product obtained from the rearrangement of 6-propyl-7-methyltetralin should involve the formation of 5-isopropyl-6-methyltetralin.

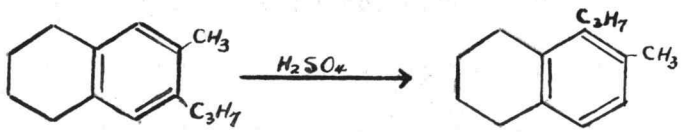
6-propyl-7-methyltetralin was subjected to the conditions necessary to bring about rearrangement. A portion of the rearranged material was oxidized and yielded as expected 1,2,3,4-benzenetetracarboxylic acid.

The other portion was dehydrogenated over palladium on charcoal yielding 1-n-propyl-2-methylnaphthalene. Smith and Lo (18, p. 2210) considered the migration of the propyl group as unlikely. On the assumption that Arnold and Barnes' mechanism was correct, this would result in the formation of 1-isopropyl-2-methylnaphthalene. Furthermore, they showed that 6-isopropyl-7-methyltetralin on rearrangement formed 6-methyltetralin. Thus, the isopropyl group became detached but did not re-enter the molecule. Due to the bulkiness of the isopropyl group it may be impossible for it to displace the sulfonic acid group. This experimental evidence makes the migration of a

propyl group seem highly improbable. Thus, the only alternative was to assume an opening of the ring followed by its closing ortho to the propyl group.

DISCUSSION

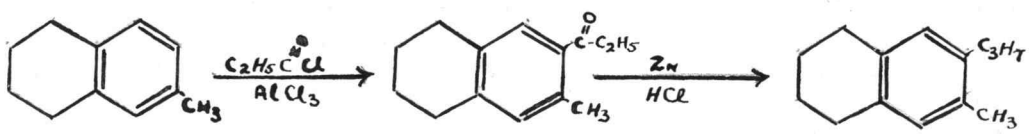
It is the intent of this discussion to consider in some detail the influence of hot concentrated sulfuric acid on 6-propyl-7-methyltetralin. As noted previously, this reaction has been reported by Smith and Lo (18, p. 2210) to give 5-propyl-6-methyltetralin in 25% yield. In the study of any reaction mechanism it is important that



the nature of the starting material be proven both as to identity and purity. This is particularly important with reactions giving a low yield for should the impurity be carried through the rearrangement without loss it would contribute very significantly to the product isolated. Furthermore, it is important to extend the same careful survey to the product in order to ascertain the nature of the main reaction and the important side processes. Accordingly, the discussion here will be divided into two sections, one devoted to each aspect of the reaction process.

I. THE NATURE OF THE STARTING MATERIAL.

In their study of this process Smith and Lo (18, p. 2213) report the preparation of 6-methyl-7-propyltetralin by the following scheme:-



The 6-methyl-7-propyltetralin was collected over the range 130°-135° (11 mm.) and had a refractive index $n^{20}D$ = 1.5250.

Repetition of this synthesis in these laboratories gave results indicating that the product was impure. The product was redistilled, therefore, using a Podbielniak Heli-Grid packed Mini-cal column at an estimated efficiency of 75-100 theoretical plates and seventeen fractions were collected. The refractive index of each fraction was determined, and apparent breaks in the boiling points and refractive indices served to indicate the presence of at least three compounds. The first boiled over the range 75°-107.3° C (6.5 mm.), $n^{25}D$ = 1.4832-1.4972, the second 107.3-124° C (6.5 mm.), $n^{25}D$ 1.5105-1.5250, and the last had a constant boiling point at 124° C (6.5 mm.), $n^{25}D$ 1.5260-1.5280. The various fractions of the last group were combined and the combined mixture had a refractive index of $n^{21}D$ 1.5290. A gas chromatogram obtained from this mixture gave one sharp symmetrical peak indicating a high probability that only a single component was present. The oxidation of a sample of this fraction with nitric acid in a sealed tube resulted in the formation of 1,2,4,5-benzenetetracarboxylic acid indicating the reactant to be 6-methyl-7-propyltetralin.

Although the latter fractions were shown to be 6-methyl-7-propyltetralin, there were still at least two unidentified components present. It was of some importance to determine the identity and the source of these contaminants.

One possible explanation for the low refractive index obtained for the first three fractions, $n^{25}D$ 1.4832-1.4972 was the formation

of 2-methyldecalin in the reduction of 2-methylnaphthalene to 6-methyltetralin. There exists, also, the possibility that the substituted ring was reduced giving rise to 2-methyltetralin.

A further source of contamination lies in the substitution process involving 6-methyltetralin. Since 6-methyltetralin and pseudocumene may be regarded as 1,2,4-trialkylbenzenes, the substitution patterns of the former might be expected to give some insight into those of the latter, which have not yet received adequate study.

In the bromination of pseudocumene, O. Wallach and E. Heusler (21, p. 233) reported the formation of 5-bromopseudocumene. Jacobsen, however, found 3-bromopseudocumene was formed as a by-product. Smith and Moyle (17, p. 8) showed that the chlorination of pseudocumene gave 5-chloropseudocumene in 34% yield. The filtrate was reported to be made up largely of 3-chloropseudocumene. In the treatment of 6-methyltetralin with phthalic anhydride, the only case reported, the same workers noted that substitution took place at the 7-position. However, the yield was low (42%) and the crude acid was reported to contain a considerable amount of other acidic materials.

It may be concluded that in the substitution of 1,2,4-trialkylbenzenes, there exists a distinct probability of 3- and 5-substituted isomers being produced simultaneously.

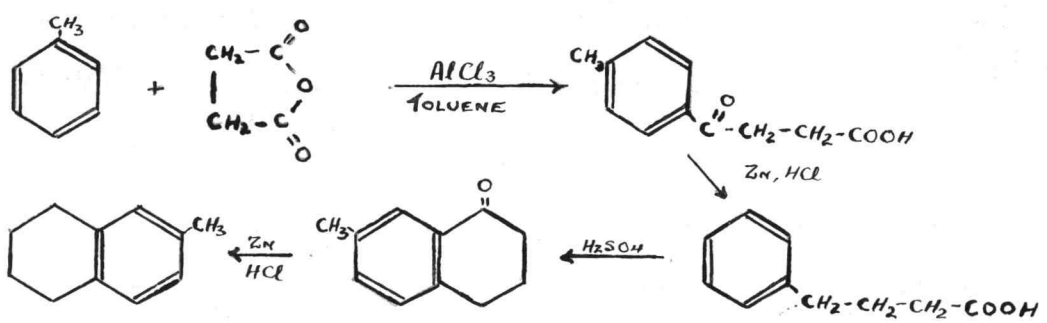
Smith and Lo (18, p. 2213) proved by oxidation to the tetra-acid, that the main product obtained by the propionylation of 6-methyltetralin was the 7-propionyl derivative. They did not prove, however, the absence of the 5-propionyl derivative. This point

must be given serious consideration since the reduction of this ketone would give rise to 5-propyl-6-methyltetralin, the compound reported by Smith and Lo (18, p. 2210) to be the product of the Jacobsen Rearrangement. Since the yield on rearrangement was reported at 25% and since any 1-propyl-2-methyltetralin might be expected to pass through the rearrangement process unchanged, a small percentage of the 5-propionyl-6-methyltetralin derivative produced in the acylation step could have great significance in the composition of the final product.

A third spot at which complications might occur is the Clemmensen reduction of the ketone. Steinkopf and Wolfam (19, p. 125) found that styrene, styrene polymers and the pinacolone of acetophenone were by-products of the conversion of acetophenone to ethylbenzene. Consequently, in the reduction of propionylmethyltetralin some propenylmethyltetralin might be formed.

In view of the possibilities for side reactions, it was deemed essential to investigate each step of the synthesis of 6-propyl-7-methyltetralin in order to determine the source of trouble.

To insure the absence of any naphthalenic material in the 6-methyltetralin, the latter was synthesized from toluene according to the following route:-



The 6-methyltetralin obtained in this manner was examined by means of gas chromatography. One sharp peak was obtained, indicating the probability of a pure compound having been obtained. The resulting product was then propionylated and a sample of this product was introduced into the vapor fractometer. There was again only one peak but in this case it was unsymmetrical and too broad to be trustworthy evidence for the presence of a single component. Thus, a sample of the 2,4-dinitrophenylhydrazone was prepared and a chromatographic separation was carried out on aluminum oxide. One main band was obtained with one minor band and two trace bands. It was concluded that propionylation gives rise to isomeric ketones.

The propionyl derivative was reduced to the corresponding methylpropyltetralin by a Clemmensen reduction. The product was found by gas chromatography to contain two components. Fractionation of the mixture followed by gas chromatographic analysis showed the minor component was concentrated in the early fractions so that a single component was obtained in the later fractions. That this compound was 6-methyl-7-propyltetralin and not 5-methyl-6-propyltetralin was proved by oxidizing a sample of the last fraction to the corresponding acid. It was shown to be the 1,2,4,5-benzenetetracarboxylic acid which was obtained. Furthermore, the minor component could not have been an isomeric propylmethyltetralin because its peak was too far from that of the major fraction. This material has not been identified. Based on the above evidence it was concluded that a pure sample of 6-propyl-7-methyltetralin was now available. Furthermore, the substitution of

6-methyltetralin has been shown to give a mixture, and since the amount of isomeric ketone present seems less than the amount of contaminant after the Clemmensen reduction, further difficulty may be arising in that step as well.

II. PRODUCTS OF THE REACTION

A sample of 5-C^{14}-6-Propyl-7-methyltetralin had been synthesized previously from 2-methyl-4-C^{14}-naphthalene (10, p. 38-39) in the same manner as the nonactive compound was prepared from 2-methylnaphthalene. Hence, any by-products which were inherent in the synthesis of the cold material were also present in the active material. The product was not fractionated on the Podbielniak column due to its activity.

In a preliminary test carried out to study the extent of the problems arising from the use of the contaminated active compound, the specific activity of the diluted material was determined by a wet combustion (3, p. 376), the compound rearranged and the specific activity again determined. It was found that the specific activity had almost doubled during the rearrangement. This result made it evident that the percent of impurity carried through the Jacobsen was high, while the yield of rearranged product from the cold starting material was substantially lower. Consequently, the percentage of active impurity in the product was very significantly increased over that originally present in the reactant.

As previously pointed out there was reason to believe that 5-propyl-6-methyltetralin might be the main impurity in the sample

of 6-propyl-7-methyltetralin prepared by Smith and Lo (18, p. 2213). Consequently, a pure sample of 6-propyl-7-methyltetralin was run through the rearrangement step. The product was then dehydrogenated to give the corresponding aromatic compound from which a picrate was formed. This picrate melted between 109.5-111° C, and the melting point was depressed when the picrate formed from the aromatized starting material was added. On the other hand, when a picrate was prepared from the rearrangement product of 6-propyl-7-methyltetralin which had been prepared in the manner of Smith and Lo, it was found to melt at 118° C. A mixed melting point with the picrate from 5-propyl-6-methyltetralin showed no depression in the melting point. This tends to confirm the belief that 5-propyl-6-methyltetralin was the probable impurity.

The fact that a possible impurity was identical with one of the expected products posed the problem of determining how much of this product was due to rearrangement and how much was due to impurity. It is, of course, possible to determine the amount of contamination in the active reactant by vicinal tetrasubstituted compounds via oxidation and isotopic dilution analysis. This can only set an upper limit on the amount of 5-propyl-6-methyltetralin in the product arising as a result of prior contamination.

In order to ascertain how Smith and Lo could have missed reasonably large amounts of isomeric contaminants a study of the fractional crystallization of the mixed tetracarboxylic esters was made. The pure tetracarboxylic acids were prepared and converted to their corresponding esters. A mixture of the three

tetramethylesters was compounded in the ratio 8:1:1. It was found that the ester present initially in the larger amount was isolated in pure form after three recrystallizations. The results of this experiment showed that Smith and Lo could have overlooked the presence of 5-propyl-6-methyltetralin in what they believed to be pure 6-propyl-7-methyltetralin.

In order to study the nature of the rearrangement product in semiquantitative fashion recourse was had to gas chromotography. This showed that the rearrangement product consisted of three major components and four minor ones.

In an attempt to identify these substances some of the more probable rearrangement products were synthesized. These, in turn, were compared chromatographically with the Jacobsen product. In this manner peaks corresponding to those of 6-methyltetralin, 6-propyltetralin and 6-propyl-7-methyltetralin were identified as minor peaks in the rearrangement product.

In an attempt to prepare possible major components, 5-propyl-6-methylnaphthalene was obtained by the reduction of 5-allyl-6-methylnaphthalene. Attempts to reduce this compound to the corresponding tetralin met with no success. For comparison purposes, therefore, a sample of the Jacobsen rearrangement product was aromatized and a gas chromatogram obtained. This showed that 1-propyl-2-methylnaphthalene was a possible component of the mixture, since addition of authentic 1-propyl-2-methylnaphthalene to the aromatized rearranged material showed that the major peak in the chromatogram of the latter had been enlarged.

Another possible rearrangement product 5-methyl-6-propyltetralin was prepared via the chloromethylation of 6-propyltetralin, followed by hydrogenolysis. A 50-50 mixture of this product and the Jacobsen rearrangement product was subjected to gas chromatography. It was found that the main peak was altered as in the previous case. Hence, it is at present impossible to ascertain experimentally whether 1-methyl-2-propylnaphthalene or 1-propyl-2-methylnaphthalene is the major component of the aromatized rearrangement product. A number of observations, however, point to the former as the most likely. Thus, whereas Smith and Lo obtained the latter as identified via the picrate, the use of purified material failed to give such a picrate. Furthermore, since propyl groups may be assumed to be lost during the Jacobsen reaction it is logical to expect the product to be formed via ring migration. The latter product above could be formed then only from, 6-propyl-7-methyltetralin-5-sulfonic acid, but this necessitates sulfonation at the more hindered position, an unlikely occurrence.

EXPERIMENTAL

P-Tolyl-β-propionic acid was prepared by the action of succinic anhydride on toluene in the presence of aluminum chloride as described by Limpricht (7, p. 110-111). After crystallization from hot water it melted at 127° C.

P-Tolylbutyric acid:- p-Tolyl-β-propionic acid (20 g.) was refluxed with amalgamated zinc (60 g.), water (75 ml.) and hydrochloric acid (4 ml.) for twelve hours (8, p. 164). The product obtained in 80% yield boiled at 180-182° C. Crystallization from heptane gave solid melting at 55-59° C.

7-Methyltetralone was prepared by the action of sulfuric acid (80%, 100 cc.) on p-tolylbutyric acid (20 g.) according to the method of Barnett and Sanders (2, p. 436). The product, obtained in 75.6% yield boiled at 136.5-138.5° C. (10 mm.) with $n^{20}D$ 1.5625 and had a m.p. of 32-33° C. The reported m.p. was 35° C. (2, p. 436).

6-Methyltetralin was prepared from the above ketone (110 g.) by refluxing with amalgamated zinc (390 g.), conc. hydrochloric acid (20 ml.), glacial acetic acid (270 ml.) and water (270 ml.) for 56 hours. The product was fractionated.

Fraction 1. b.p. 97° C. (11 mm.) $n^{25.7}D$ 1.5330

Fraction 2. b.p. 86.7° C. (8 mm.) $n^{23.8}D$ 1.5340

Fraction 3. b.p. 97° C. (11 mm.) $n^{24.0}D$ 1.5340

The product (72 g.) was obtained in 72% yield.

6-Methyltetralin was also obtained by catalytic reduction of 2-methylnaphthalene. The product obtained in 90% yield, boiled at 96-97.5° C. (12 mm.) and had $n^{20}D$ 1.5387.

6-Propionyl-7-Methyltetralin was prepared by the treatment of 6-methyltetralin (62 g.) with propionyl chloride (40 g.) in the presence of aluminum chloride (80 g.). The directions of Smith and Lo (18, p. 2213) were followed with the exception that thiophenefree benzene was used as solvent in place of nitrobenzene. The following fractions were obtained.

Fraction 1. b.p. 62-84° C. (1.4 mm.) $n^{22.8}D$ 1.5341.

Fraction 2. b.p. 84-126° C. (1.5 mm.) $n^{22.8}D$ 1.5372.

Fraction 3. b.p. 126° C. (1.5 mm.) $n^{21-2}D$ 1.5498.

Fraction 4. b.p. 126° C. (1.5 mm.) $n^{21-2}D$ 1.5503.

The last two fractions were combined (42 g.) giving a yield of 70%. A gas chromatogram, obtained on a column of Apiezon on Celite at 201° C. with helium as the carrier gas, showed one broad peak.

2,4-Dinitrophenylhydrazone of 6-Methyl-7-Propionyltetralin was prepared from the ketone in the usual manner (14, p. 111). It was placed on an alumina column with petroleum ether and eluted first with petrolumn ether-benzene (1-1) and finally with benzene. Practically all the product appeared in a single band which was eluted and the solvent evaporated in vacuo. The sample was recrystallized from ethanol-ethyl acetate and melted at 170.5-171.5° C. The reported m.p. was 153-154° C. (17, p. 2213). Anal. Calcd. for $C_{20}H_{22}N_4O_4$: C, 62.81; H, 5.80; Found: C, 62.64: H, 5.96. A

second band gave too little material to identify and was followed by two even fainter bands.

6-Propyl-7-Methyltetralin was obtained by a Clemmensen reduction of 6-propionyl-7-methyltetralin (18, p. 2213). The product was isolated by distillation.

Fraction 1. b.p. 104-109° C. (2.3 mm.) $n^{28.2}D$ 1.5148

Fraction 2. b.p. 109.2-110° C. (2.3 mm.) $n^{27.8}D$ 1.5194

Fraction 3. b.p. 108-110° C. (2.0 mm.) $n^{23.8}D$ 1.5253

Fraction 4. b.p. 111-113° C. (2.2 mm.) $n^{23.8}D$ 1.5290

The fractions were combined (total 77% yield) and distilled on a Podbielniak Hili Grid packed Mini-Cal column. Seventeen fractions were obtained but the properties of these fell into three groups.

	b.p.	$n^{24}D$	Pressure	Reflux Ratio
1.	96-100° C.	1.4840-1.4880	6.5	25/1
2.	111-115° C.	1.5150-1.5210	6.5	25/1
3.	124° C.	1.5260-1.5290	6.5	25/1

Fractions 11-17 which constituted the third group were combined. A sample (.25 g.) and nitric acid (3-1, 4 ml.) were heated together in a Carius tube for 8 hours at 165-175° C. The solution was evaporated to dryness and the residue taken up in ether. An ether solution of diazomethane was added till a yellow color persisted. The excess was destroyed with acetic acid and the solvent evaporated. The residue was recrystallized twice from methanol. The product melted at 145.5-146.5° C. The literature records m.p. 141-144° C. (11, p. 119), for tetramethyl-1,2,4,5-benzenetetracarboxylate.

2-Propyl-3-methylnaphthalene was prepared by dehydrogenation of 6-propyl-7-methyltetralin over 10% polladium on charcoal at 180° C. in a stream of carbon dioxide until no further hydrogen was liberated. The catalyst was removed and the resulting oil treated with a saturated solution of picric acid in methanol. After crystallizing three times from alcohol the picrate melted at 112° C. in agreement with literature value of 110-112° C. (18, p. 2214).

The Jacobsen Reaction:- 6-Propyl-7-methyltetralin was treated with sulfuric acid according to the procedure of Smith and Lo (18, p. 2210). The product was dehydrogenated to the corresponding naphthalenic compound which was treated with a saturated solution of picric acid in methanol. The solid on recrystallization from methanol was found to melt at 109.5-111° C. The melting point of a mixture with picrate of starting material was 90° C. The picrate of 1-propyl-2-methyl naphthalene melts at 118-119° C. (18, p. 2210).

1-Allyl-2-methylnaphthalene was obtained by treating the Grignard reagent obtained from 1-bromo-2-methylnaphthalene with allyl bromide (12, p. 23-24). The product distilled at 130° C. (5 mm.).

1-Propyl-2-methylnaphthalene:- The above hydrocarbon was reduced by shaking a solution in alcohol with Raney nickel and hydrogen at two atomospheres for two hours. The catalyst was removed by filtration and the product distilled after evaporation of the solvent.

Fraction 1. b.p. 117-119° C. (3.5 mm.) $n^{26.5}D$ 1.5923

Fraction 2. b.p. 119-121° C. (3.5 mm.) $n^{26.5}D$ 1.5899

Fraction 3. b.p. 7 121° C. (3.5 mm.) $n^{26.5}D$ 1.5888

Fraction 2 was dissolved in methanolic picric acid, the orange crystals were separated and crystallized from methanol. The picrate was found to melt at 118° C. The literature value is 118° C. (18, p. 2214).

1,2,3,5-Benzenetetracarboxylic acid:- Mesitoic acid (5 g.) was oxidized by alkaline permanganate (11, p. 118). The manganese dioxide was removed and washed by centrifugation. The solution after being passed through Dowex 50 was evaporated to dryness and the residue was boiled in concentrated nitric acid for about one hour. The hot solution was filtered and on cooling, white crystals (5.24 g.) precipitated. The m.p. was 252-257° C. and the yield 68%. The corresponding literature values were 243-247° C. and 78% (11, p. 118).

Tetramethyl-1,2,3,5-benzenetetracarboxylate was prepared by treatment of an anhydrous methanol solution of the above acid with an ether solution of diazomethane till a yellow color persisted. The excess diazomethane was destroyed with acetic acid and the solvent evaporated. The residue was crystallized twice from methanol and once from hexane. The m.p. was 111-116.2° C. in agreement with the literature value (11, p. 119).

1,2,3,4-Benzenetetracarboxylic Acid:- This acid was prepared from 2-methylnaphthoic acid (5 g.) in an identical manner to that used in the preparation of the 1,2,3,5-tetracarboxylic acid. After crystallizing from nitric acid the m.p. was 241-243° C. and the

yield 67%. Reported yield (11, p. 118) 22% and m.p. 241-244° C. The crystals did not turn purple on standing, as reported.

Tetramethyl-1,2,3,4-benzenetetracarboxylate:- This tetramethyl ester was prepared from the above acid as described for the preparation of the 1,2,3,5-tetramethyl ester. After two recrystallizations from methanol and one from hexane the m.p. was 132-133° C., while the reported m.p. was 130-131° C. (11, p. 119).

Tetramethyl 1,2,4,5-benzenetetracarboxylate:- This compound was prepared as above, from the 1,2,4,5-tetracarboxylic acid.* After recrystallizing as in previous case, the m.p. was 144.5-145.6° C. The reported m.p. 143-144° C. (11, p. 119).

Fractional Crystallization of Tetramethyl-Esters:- A mixture of the 1,2,4,5-tetramethyl ester (56 mg.), the 1,2,3,5-tetramethyl ester (7 mg.) and the 1,2,3,4-tetramethyl ester (7 mg.) was compounded. After three recrystallizations from methanol the m.p. was 144.5-145.6° C. showing the presence of pure 1,2,4,5-tetramethyl ester.

5-C^{14}-6-propyl-7-methyltetralin was prepared# from 1-C^{14}-3-methylnaphthalene in the identical manner to 6-propyl-7-methyltetralin. The specific activity after dilution with 6-propyl-7-methyltetralin was determined by the Van Slyke Foch method (3, p. 376), and found on two runs to be 641,060 and 630,000 cpm/m. mole of methylpropyltetralin.

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* This acid was generously donated by L. I. Smith.
\# This sample prepared by N. R. Odell.

Jacobsen Reaction:- The above active compound was subjected to the conditions of Jacobsen reaction (18, p. 2210). The specific activity was determined as in the previous case. The results on two runs gave values of 1,014,090 and 1,016,850 cpm/m. mole of rearrangement product.

6-Propionyltetralin was prepared by propionylation of tetralin according to the method of Smith and Lo (18, p. 2212) with the exception that thiophane-free benzene was used in place of nitrobenzene. The product was fractionated.

Fraction 1. b.p. 118-135° C. (5.3 mm.) $n^{23.6}D$ 1.5458

Fraction 2. b.p. 135-144° C. (5.3 mm.) $n^{24.8}D$ 1.5517

Fraction 3. b.p. 144.5-145° C. (5.3 mm.) $n^{24.8}D$ 1.5511

Fraction 4. b.p. 145-148° C. (5.3 mm.) $n^{26.0}D$ 1.5508

Fraction 5. b.p. 148° C. (5.3 mm.) $n^{26.6}D$ 1.5507

The yield based on the last four fractions was 76%. Physical properties previously recorded are b.p. 169° C. (17 mm.) and $n^{23}D$ 1.5500 (18, p. 2212).

6-Propyltetralin resulted from a Clemmensen reduction (18, p. 2212) of the above compound. The product was purified by fractional distillation.

Fraction 1. b.p. 118-123° C. (14 mm.) $n^{20}D$ 1.5026

Fraction 2. b.p. 126.7-127° C. (14 mm.) $n^{20}D$ 1.5198

Fraction 3. b.p. 125.2° C. (11 mm.) $n^{20}D$ 1.5256

Fraction 4. b.p. 125.2° C. (11 mm.) $n^{20}D$ 1.5262

Fractions 3 and 4 were combined, giving a 93% yield. Smith and Lo report, b.p. 123-125° C. (10 mm.) and $n^{29}D$ 1.5253 (18, p. 2212). A gas chromatogram of each fraction was obtained utilizing helium and an Apiezon-L Celite column at 202° C. The impurities, which were preferentially removed in the first two fractions, had apparent retention volumes of 250 and 270 ml. The third and fourth fractions had only the main peak at 480 ml.

2-Propylnaphthalene was prepared by dehydrogenation of the above compound at 220-250° C. in a current of nitrogen in the presence of palladium on charcoal (10%) for about three hours. The reaction product was taken up in ether, the catalyst removed and the product distilled.

Fraction 1. b.p. 121° C. (4 mm.) $n^{24.2}D$ 1.5671

Fraction 2. b.p. 118° C. (3.5 mm.) $n^{24}D$ 1.5732

Fraction 3. b.p. 119° C. (4.2 mm.) $n^{24}D$ 1.5780

A gas chromatogram of fraction 1 on a 6 ft. column of Apiezon-L on Celite at 203° C. showed two peaks with retention volumes of 725 ml. and 948 ml. The impurity at 725 ml. was reduced to a trace amount in fraction three.

Picrate:- The 2-propylnaphthalene was dissolved in methanolic picric acid and the solution cooled. The yellow crystals which deposited were removed and crystallized from methanol. The picrate melted at 91° C. in agreement with the literature (18, p. 2212).

Chloromethylation of 2-propylnaphthalene:- 2-Propylnaphthalene (9.4 g.) was dissolved in acetic acid (25 ml.) followed by the addition of paraformaldehyde (3.3 g.) (4, p. 299). The mixture was cooled on an ice-bath and hydrogen chloride bubbled through until the paraformaldehyde had dissolved. The flask was stoppered and left at room temperature for eighteen hours, whereupon the solution separated into two layers. The oil was separated and the water layer extracted three times with benzene. The combined oil and benzene fractions were washed three times with water, twice with sodium carbonate solution (5%) and finally twice with water. Three fractions were collected during distillation.

Fraction 1. b.p. 115-127° C. (2.5 mm.) $n^{20}D$ 1.5818

Fraction 2. b.p. 127-137° C. (2.2 mm.) $n^{20}D$ 1.5862

Fraction 3. b.p. 132-135° C. (1.0 mm.) $n^{20}D$ 1.6011

The yellow oil, comprising the last fraction, on cooling overnight gave white crystals. The solid was separated and crystallized from alcohol. It melted sharply at 52° C. The yield was (.625 g.) 11%. Anal. Calcd. for $C_{14}H_{15}Cl$: C, 76.87; H, 6.91; Found: C, 76.25: H, 7.21.

Hydrogenolysis of Chloromethylnaphthalenes:- The above solid was dissolved in acetone and subjected to hydrogenolysis in the presence of palladium on charcoal. A yellow oil was obtained having $n^{23}D$ 1.5713 and giving a negative Beilstein test.

Chloromethylation of 6-propyltetralin:- 6-propyltetralin (32 g.) was chloromethylated as in the same manner as used in the case of

2-propylnaphthalene. The product was purified by fractional distillation.

Fraction 1. b.p. 136-137° C. (2.5 mm.) $n^{17.5}D$ 1.5502

Fraction 2. b.p. 137-138° C. (2.0 mm.) $n^{18}D$ 1.5527

Fraction 3. b.p. 138-140° C. (1.85 mm.) $n^{18}D$ 1.5530

Fractions 2 and 3 were combined giving a 45% yield.

5-Methyl-6-propyltetralin:- The above product (12 g.) was dissolved in acetone and palladium on charcoal (.5 g.) was added. Hydrogen was introduced to a pressure of 34 lbs. and the mixture was shaken for five hours. The resulting solution was yellow in color. The acetone was evaporated and the resulting liquid was distilled under reduced pressure.

Fraction 1. b.p. 134° C. (1.5 mm.) $n^{22.3}D$ 1.5488

Fraction 2. b.p. 134° C. (1.5 mm.) $n^{22.5}D$ 1.5490

Fraction 3. b.p. 135° C. (1.2 mm.) $n^{22.5}D$ 1.5494

The yield was 9.7 grams (96%). A gas chromatogram of the product utilizing helium and a column of Apiezon-L on Celite at 220° C. showed two peaks. The major product (80%) had a retention volume of 800 ml. and was identified as 6-propyl-7-methyltetralin. The minor product (20%) having a retention volume of 940 ml. was probably 5-methyl-6-propyltetralin.

Another sample of chloromethylated 6-propylnaphthalene, having $n^{25.8}D$ 1.5990, was dissolved in tetrahydronaphthalene and heated under reflux with lithium aluminum hydride (16, p. 75) for eight hours. The excess lithium aluminum hydride was destroyed with

ethyl acetate and the aluminum salts taken up in hydrochloric acid. The solution was extracted with petroleum ether and the solvent removed by evaporation. Distillation of the product gave an oil having $n^{24.8}D$ 1.5801 and giving a negative Beilstein test. The yield was 82%. The gas chromatogram of this oil obtained on a three-foot column of Apiezon-L on Celite at 219° C. showed three peaks. The major one had an apparent retention volume of 507 ml. while the minor ones were 413 ml. and 281 ml. The major product was identified by gas chromatography as 6-propyl-7-methyltetralin. Similarly, the peak at 281 ml. was shown to be 2-propylnaphthalene. The other peak was deduced to be due to 1-methyl-2-propylnaphthalene.

The Gas Chromatogram of the Product from Jacobsen Rearrangement of 6-propyl-7-methyltetralin - was obtained on a column composed of Apiezon-L on Celite at 201 C. Seven peaks were obtained having the following apparent retention volumes and percentage composition.

	Apparent retention volume	% present	
1.	1079 ml.	76.4%	
2.	813 ml.	12.9%	(6-propyl-7-methyltetralin)
3.	1270 ml.	5.0%	
4.	282 ml.	2.9%	(6-methyltetralin)
5.	613 ml.	1.3%	
6.	491 ml.	.8%	(6-propyltetralin)
7.	239 ml.	.5%	

Aromatized Jacobsen Products:- The possible aromatized Jacobsen products were purified via their picrates. The picrates were decomposed by passing them through a column of alumina using hexane as eluant. The solvent was evaporated in vacuo. The hydrocarbons were then subjected to gas chromatography on a 3 ft. column of Apiezon-L on Celite at 220° C. The apparent retention volumes of the compounds examined were as follows:-

	apparent retention volume
1-methylnaphthalene	146 ml.
2-methylnaphthalene	156 ml.
2-propylnaphthalene	312 ml.
1-propyl-2-methylnaphthalene	468 ml.
1-methyl-2-propylnaphthalene	484 ml.
2-methyl-3-propylnaphthalene	503 ml.
Aromatized Jacobsen	429 ml., 499 ml., 351 ml.
Aromatized Jacobsen	429 ml., 488 ml., 343 ml.
Mixture of 1-methyl-2-propyl and 2-methyl-3-propylnaphthalene	1st trial: 546 ml., 355 ml. 2nd trial: 538 ml., 355 ml.
Mixture of 1-propyl-2-methyl and 2-methyl-3-propylnaphthalenes	1st trial: 515 ml., 343 ml., 156 ml. 2nd trial: 484 ml., 335 ml., 156 ml.

CONCLUSION

A rather detailed reinvestigation of the Jacobsen rearrangement of 6-propyl-7-methyltetralin has been carried out. The results of this work showed that the conclusions of Smith and Lo, who previously studied this reaction, are erroneous, probably as a result of impure starting material. In this reinvestigation, a sample of 6-methyl-7-propyltetralin was prepared which was uniform in refractive index and to gas chromatography. Rearrangement of this material gave rise to a product which gas chromatography showed to be made up of three major and four minor components. Contrary to the results of Smith and Lo, we have been unable to confirm the presence of 5-propyl-6-methyltetralin in that product, but we have identified three of the components as, 6-methyltetralin, 6-propyltetralin and 6-methyl-7-propyltetralin.

Tracer experiments indicated that the divergence between our results and those of Smith and Lo was due to an impurity which was more stable to sulfuric acid than was 6-methyl-7-propyltetralin. A step-by-step investigation of the synthesis was carried out in an attempt to confirm this deduction, but was not completely successful. It was shown that the propionylation of 6-methyltetralin leads to trace amounts of isomeric ketones and that the Clemmensen reduction of the ketone gives a product in which is present considerable amounts of lower boiling substances. Structures for these contaminants were not established. The oxidation procedure employed by Smith and Lo to identify 6-methyl-7-propyltetralin was found on

examination of synthetic mixtures to be incapable of detecting impurities composing 10-20% of the mixture.

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