The ring structure of N-acetyl-D-glucofuranosylamine has been determined by its behavior when oxidized by lead tetraacetate. The new reactions give further insight into the mechanism of the Wohl degradation of sugars.

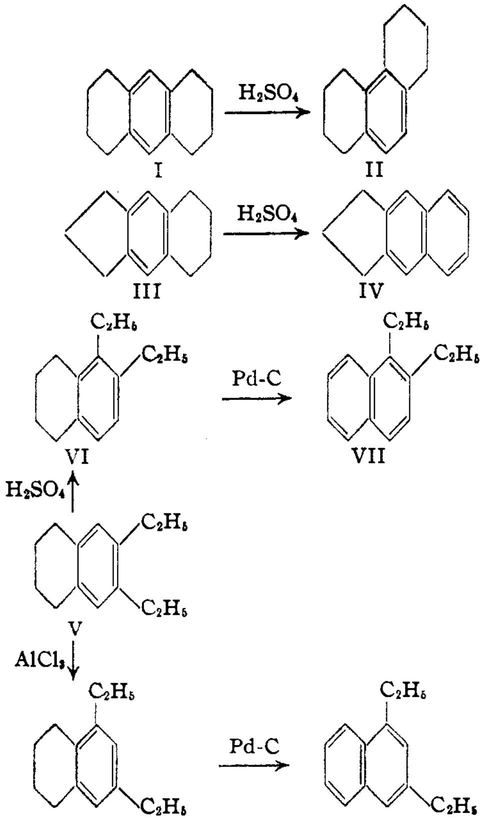
CAMBRIDGE, MASS. RECEIVED FEBRUARY 23, 1944

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

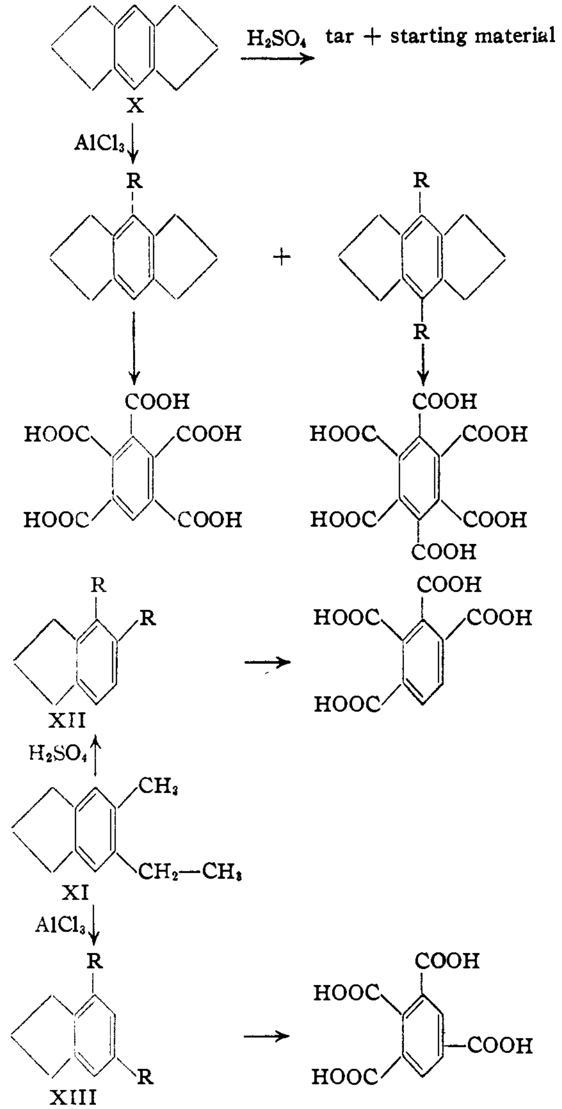
The Jacobsen Rearrangement. VIII.[1] Cyclic Systems; Mechanism

BY RICHARD T. ARNOLD AND RODERICK A. BARNES[2]

For many purposes it is convenient to regard hydrindene and tetralin as *o*-dialkylbenzenes. If this view is accepted, then one might suppose that the tri- and tetramethylene rings in these substances would undergo rearrangement when the molecule is subjected to conditions which bring about a migration of simple alkyl groups. Therefore it was of interest to study the Jacobsen rearrangement of hydrocarbons derived from tetralin and hydrindene. During the course of this investigation octahydroanthracene (I), 5,6,7,8-tetrahydrobenz[f]indan (III),[3] 6,7-diethyltetralin (V), 5-ethyl-6-methylhydrindene (XI), and *s*-hydrindacene (X) (Ring Index 1459) have been prepared and their reactions with sulfuric acid and aluminum chloride (in three cases) investigated.



R = oxidizable side chain of unknown structure



(R = CH_3 or C_2H_5)

The only example of a Jacobsen rearrangement involving a cyclic system which so far has been

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[1] VII, THIS JOURNAL, **62**, 2631 (1940). The Authors desire to thank Dr. Lee Irvin Smith for his interest in this work and for the authentic samples of benzene tetracarboxylic acids used as reference compounds.

[2] Abstracted from a thesis by Roderick A. Barnes, presented to the Graduate Faculty of the University of Minnesota in partial fulfillment of the requirements for the Ph.D. degree, November, 1943.

[3] Sen-Gupta, *J. Ind. Chem. Soc.*, **16**, 89 (1939).

reported is the conversion of octahydroanthracene into octahydrophenanthrene.[4] The results obtained in our work are in charts.

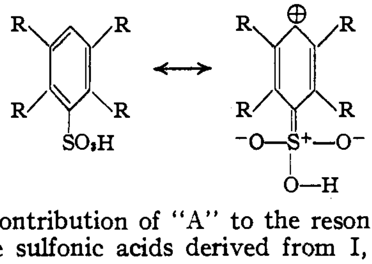
Discussion

No satisfactory and adequate explanation has yet been proposed for the mechanism of the Jacobsen rearrangement.[5]

In their original paper, Mills and Nixon[6] pointed out that in hydrindene the two bonds linking the trimethylene group to the benzenoid ring are probably distorted toward one another and that such a distortion should affect the aromatic character of the benzenoid ring. A very important result which must accompany such a deflection of these valence bonds is the reduction in the steric influence of the methylene groups adjacent to the benzene ring.[7]

As the chart of reactions shows, successful Jacobsen rearrangements have been effected with compounds I, V and XI to give products with the expected orientations (*i. e.*, 1, 2, 4, 5- to 1, 2, 3, 4-). Compound III was not rearranged but was dehydrogenated by the action of sulfuric acid. No products from the rearrangement of X could be detected. In every case where possible (V and XI), aluminum chloride brought about a change in the orientation of the alkyl groups from the 1, 2, 4, 5-position to the 1, 2, 3, 5-position in a manner identical to that observed with simple tetraalkylbenzenes.

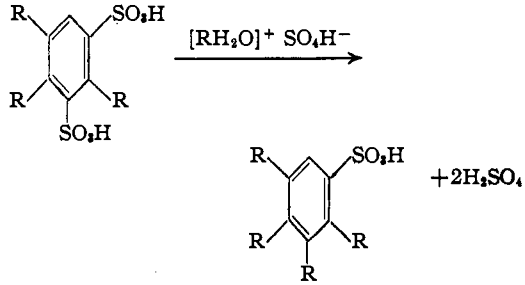
The evidence so far accumulated indicates that the Jacobsen rearrangement proceeds via an initial sulfonation and that it is the sulfonic acid which undergoes the rearrangement.[5] If the statement at the close of the footnote[7] is accepted, then it becomes apparent that in the sulfonic acids derived from I, V and XI, the sulfonic acid group is sterically more hindered than it is in the sulfonic acids from III and X. This steric factor is important because it controls in part the contribution of structure "A" to the resonance.[8,9]



(A)

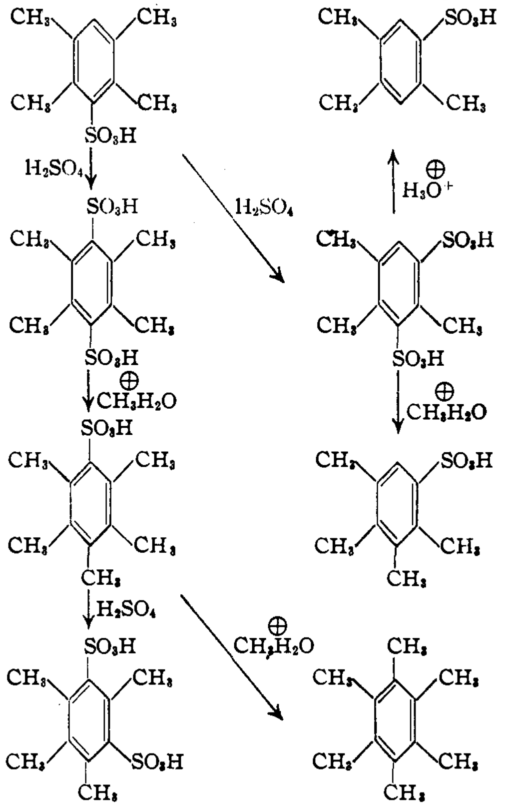
The contribution of "A" to the resonance is less in the sulfonic acids derived from I, V and XI than it is in the sulfonic acids derived from III and X. As a result the benzene rings in the former compounds are more susceptible to attack by cationoid reagents than are those in the latter compounds. Furthermore, it has been shown[10] that the most hindered sulfonic acid groups are those most readily hydrolyzed by acid solutions. It follows, therefore, that in a disulfonic acid of type "B" the sulfonic acid grouping subject to the greatest hindrance will be the one to be preferentially replaced by cationic reagents.

(B)



The entrance of a second sulfonic acid group and the replacement of the original sulfonic acid group by an alkyl cation is an essential feature of the Jacobsen rearrangement. This conclusion together with the other considerations mentioned above lead to the following generalizations with regard to the mechanism of the Jacobsen reaction:

(1) The rearrangement of alkyl groups can occur only if the initial sulfonic acid group is



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[4] Schroeter and Gotzsky, *Ber.*, **60**, 2035 (1927).

[5] Smith, "Organic Reactions," J. Wiley and Sons, New York, N. Y., 1943, pp. 370–384.

[6] Mills and Nixon, *J. Chem. Soc.*, 2510 (1930).

[7] A systematic investigation of the relative steric influence of the methylene group when present in a methyl group, a six-membered ring (as in tetralin), and a five-membered ring (as in hydrindene) has been under way for some time in this Laboratory and will be continued as conditions permit. This work has already indicated that the steric effect of these groups decreases in the order in which they are mentioned above.

[8] Kumler and Daniels, THIS JOURNAL, **65**, 2190 (1943).

[9] Kumler and Halverstadt, *ibid.*, **63**, 2182 (1941).

[10] Smith and Guss, *ibid.*, **62**, 2634 (1940).

sufficiently hindered sterically by two ortho substituents so that the contribution of form "A" to the resonance is diminished.

(2) The resulting steric inhibition of resonance allows for the formation of a disulfonic acid.

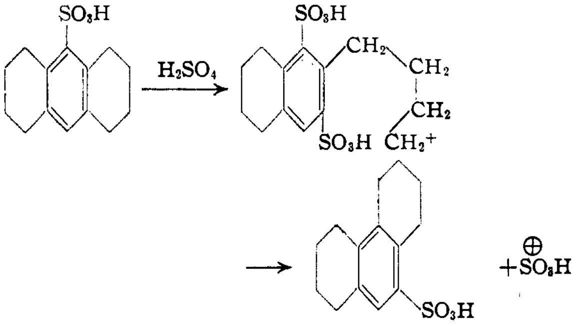
(3) This latter reaction takes place preferentially in the meta position to the first sulfonic acid group and leads to the elimination of an alkyl cation or the opening of a saturated ring to form an intermediate having a cationic terminal carbon atom.

(4) The cationic alkyl group preferentially replaces the most hindered sulfonic acid group.

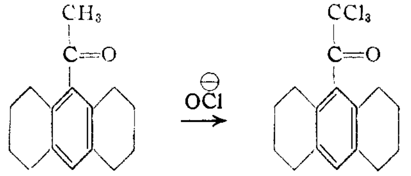
(5) Because of a diminution in the contribution of the resonance structure "A," some para disulfonic acid is formed. This gives rise to the intermolecular Jacobsen reaction (disproportionation).

These generalizations are well illustrated by their application to the Jacobsen rearrangement of durene already shown.

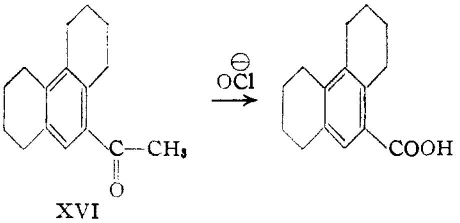
When applied to the specific case of octahydroanthracene, the rearrangement can be written as follows



There can be little doubt that the 9-position in octahydroanthracene is hindered to a rather considerable degree since 9-acetyloctahydroanthracene XIV when subjected to the haloform reaction yields a trichloromethyl ketone XV. As expected such is not the case with 9-acetyloctahydrophenanthrene XVI.

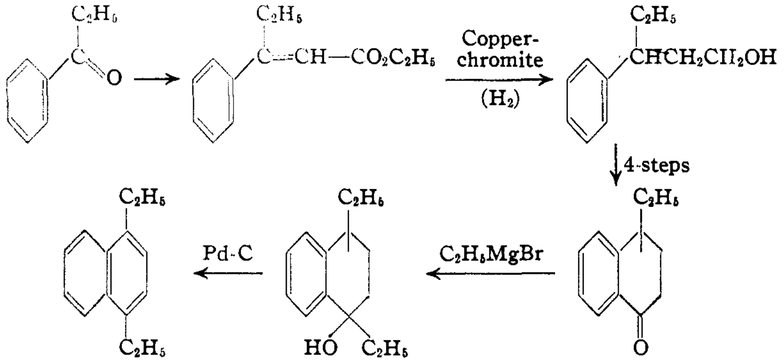


XIV XV



XVI

Incidental to this study, all of the possible diethylnaphthalenes having the two alkyl groups in a single ring have been synthesized. The 1,2-, 2,3- and 1,3-diethylnaphthalenes resulted from the catalytic dehydrogenation of the corresponding tetralins (VI, V and VIII) by means of palladium–charcoal catalyst. The structures of the tetralins employed were established by nitric acid oxidation to the known benzenetetracarboxylic acids; these were identified as their tetramethyl esters. 1,4-Diethylnaphthalene was prepared via the following sequence of reactions



XVII

The resulting hydrocarbon XVII (m. p. 16.5–17°) formed a picrate melting at 91–93°. These physical properties are quite different from those reported for 1,4-diethylnaphthalene by Frösche and Harlass.[11]

Experimental

5-Methylhydrindene.—A mixture of freshly distilled 5-chloromethylhydrindene (50 g.), absolute alcohol (200 cc.) and palladium on barium sulfate catalyst (1.5 g.) was shaken with hydrogen (45–50 lb. pressure) at room temperature. When the reaction was complete (twenty minutes), the catalyst was removed by filtration. From four such runs there was obtained on fractionation 154 g. of hydrocarbon (96%); b. p. 86–88° (19 mm.). Platinum oxide also is an effective catalyst.[12]

5-Ethyl-6-methylhydrindene.—Acetic anhydride (102 g.) was slowly added (one hour) to a cooled, stirred mixture of aluminum chloride (223 g.), nitrobenzene (500 cc.) and 5-methylhydrindene (100 g.). The mixture was stirred for ninety minutes at 30° after the addition was completed. The reaction mixture was worked up in the usual manner to give 106.8 g. of 5-acetyl-6-methylhydrindene; b. p. 152–158° (11 mm.). Nitric acid oxidation of the ketone gave only pyromellitic acid (identified as its methyl ester; m. p. and mixed m. p. 139–141°).

A mixture of amalgamated zinc (450 g.), water (450 cc.), concentrated hydrochloric acid (900 cc.), acetic acid (450 cc.) and the ketone (100 g.) was refluxed for fifty hours during which time 800 cc. of hydrochloric acid was added in portions. There was obtained 70.7 g. of hydrocarbon; b. p. 112–116° (11 mm.).

Anal. Calcd. for $C_{12}H_{16}$: C, 89.93; H, 10.07. Found: C, 89.70; H, 10.25.

5-Propionylhydrindene.—Propionic anhydride (130 g.) was added to a cooled, stirred mixture of aluminum chloride (292 g.), nitrobenzene (500 cc.) and hydrindene (118 g.). The mixture was worked up as described above for 5-acetyl-6-methylhydrindene. There was obtained 139 g. of ketone; b. p. 159° (12 mm.).

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[11] Frösche and Harlass, *Monatsh.*, **59**, 282 (1932).

[12] Plattner and Roniger, *Helv. Chim. Acta*, **25**, 593 (1942).

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.97; H, 8.33.

The oxime melted at 95–96°.

Anal. Calcd. for $C_{12}H_{15}ON$: C, 76.15; H, 7.99. Found: C, 76.26; H, 7.78.

Diethyl 5-Hydrindenylmethylmalonate.—Sodium (46 g.) was dissolved in one liter of absolute ethanol. Malonic ester (320 g.) was added and this was followed by the slow addition (two hours) of 5-chloromethylhydrindene (200 g.). The mixture was gently refluxed for five hours, made acidic (litmus) with 1:1 hydrochloric acid, and then the alcohol was removed by distillation. The residue was poured into water, separated, and distilled; b. p. 158–165° (3 mm.); weight 225 g.

Anal. Calcd. for $C_{17}H_{22}O_4$: C, 70.30; H, 7.65. Found: C, 70.28; H, 7.77.

β-5-Hydrindenylpropionic Acid.—(a) A mixture of 5-propionylhydrindene (35 g.), dioxane (110 cc.), sulfur (14 g.) and concentrated ammonia saturated with hydrogen sulfide (140 cc.) was heated in a closed iron pipe at 150–155° for twenty-four hours. The residue after removing the solvents was refluxed for two hours with potassium hydroxide (200 cc., 15%). The alkaline solution was treated with norite, filtered, and acidified. The liberated acid was extracted with benzene. Distillation in a sausage flask at 4 mm. pressure followed by recrystallization from dilute acetic acid gave 26 g. of acid; m. p. 85–86°.

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.41. Found: C, 75.64; H, 7.45.

(b) Saponification of diethyl 5-hydrindenylmethylmalonic ester followed by decarboxylation gave the same acid in a more impure condition; yield 91%; m. p. 78–80°. It was impossible to raise this melting point appreciably by recrystallization. A mixed melting point determination of the two samples gave m. p. 82–84°.

5-Hydrindacene-1-one.—Phosphorus pentachloride (5.21 g.) was added in portions to a solution of pure β-5-hydrindenylpropionic acid (4.76 g.) in dry benzene (50 cc.). Upon cooling to room temperature stannic chloride (3.7 cc.) dissolved in benzene (6 cc.) was added dropwise during an interval of forty-five minutes. Decomposition with dilute hydrochloric acid gave the ketone; yield 3.84 g.

Anal. Calcd. for $C_{12}H_{12}O$: C, 83.68; H, 7.03. Found: C, 83.36; H, 7.18.

***s*-Hydrindacene.**—A mixture of amalgamated zinc (140 g.), water (115 cc.), hydrochloric acid (230 cc.), acetic acid (86 cc.), toluene (115 cc.) and 5,6-cyclopenteno-1-indanone (20 g.) was refluxed for thirty-six hours during which time an additional 200 cc. of hydrochloric acid was added. There was obtained on distillation of the toluene layer 15.1 g. of hydrocarbon; b. p. 116–120° (9 mm.). Recrystallization from ethanol gave long prisms; m. p. 52–54°.

Anal. Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.92; H, 8.59.

This hydrocarbon on nitric acid oxidation gave only pyromellitic acid (methyl ester; m. p. 139–141°).

6,7-Diethyltetralin.—This hydrocarbon was prepared essentially by the method of Fleischer and Siefert.[13] Proof of its structure was established by nitric acid oxidation to pyromellitic acid.[14]

5,6,7,8-Tetrahydrobenz[f]indan.—This hydrocarbon was prepared according to the directions published by Sen-Gupta.[15]

4,9-Dibromo-5,6,7,8-tetrahydrobenz[f]indan.—The hydrocarbon (1.0 g.) was dissolved in acetic acid and a solution of bromine in acetic acid was added dropwise until a permanent reddish solution resulted. After a few minutes sodium bisulfite (0.2 g.) in 50 cc. of water was added. The white precipitate was collected and recrystallized from ethanol; m. p. 141.5–142.5°.

Anal. Calcd. for $C_{13}H_{14}Br_2$: C, 47.3; H, 4.27. Found: C, 47.5; H, 4.36.

3-Phenylpentanol-1.—Ethyl β-ethylcinnamate (200 g.) was hydrogenated at 250° with an initial pressure of 2800 pounds in the presence of 35 g. of copper chromite (37 KAF). The reduction was complete in six hours. Fractionation gave 137.4 g. of 3-phenylpentanol-1; b. p. 145–148° (26 mm.).[16]

1-Ethyltetralone-4.—This cyclic ketone was prepared from 3-phenylpentanol-1 by use of the method of Levy.[16]

1,4-Diethylnaphthalene.—A solution of the above ketone (5.6 g.) dissolved in dry ether (25 cc.) was slowly added to a solution of ethylmagnesium bromide prepared from 5.5 g. of ethyl bromide. After thirty minutes the mixture was decomposed with dilute hydrochloric acid. The ether layer, after removal of the ether, left a residue of crude carbinol (6.4 g.). This carbinol was heated for two hours at 225° with palladium-charcoal (0.2 g., 10%) in a current of carbon dioxide. After cooling, the product was taken up in ethanol (50 cc.), filtered, and treated with 5 g. of picric acid while the solution was warm. On cooling, the picrate separated; m. p. 91–93°. The hydrocarbon was regenerated by shaking the picrate with ether and ammonia. Evaporation of the ether layer and distillation gave 4.1 g. of hydrocarbon; b. p. 165° (25 mm.); m. p. 16.5–17°.

Anal. Calcd. for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.70; H, 9.04.

9-Acetyl-1,2,3,4,5,6,7,8-octahydrophenanthrene.—In the preparation of 6-acetyltetralin from tetralin (132 g.) acetic anhydride (82 g.), aluminum chloride (300 g.) and dry carbon bisulfide (400 cc.) there were obtained 69.2 g. of 6-acetyltetralin and 11 g. of 9-acetyloctahydrophenanthrene (m. p. 50.5–51.5).[17] The structure of the latter was established by conversion to the corresponding 9-octahydrophenanthrene carboxylic acid; m. p. 236–238°. Schroeter[18] reports 239–240°.

9-Acetyloctahydroanthracene.—A solution of acetic anhydride (11.3 g.) in tetrachloroethane (25 cc.) was added slowly to a cooled solution of aluminum chloride (30 g.) and octahydroanthracene (9.3 g.) in tetrachloroethane (100 cc.). The solution was stirred in an ice-bath for two hours after the addition was completed, and the mixture was decomposed with dilute hydrochloric acid. Fractionation gave 7.8 g. of ketone; b. p. 169° (3 mm.). Crystallization from methanol gave a white solid; m. p. 72–72.5°.

Anal. Calcd. for $C_{16}H_{20}O$: C, 84.16; H, 8.83. Found: C, 84.09; H, 8.86.

9-Trichloroacetyloctahydroanthracene.—An aqueous solution of potassium hypochlorite from 15 g. of bleaching powder (H. T. H.) was shaken vigorously with 1.0 g. of acetyloctahydroanthracene. The solution became warm and, on cooling, a precipitate (1.4 g.) melting at 123.5–124.5° was isolated. The trichloro ketone crystallized with one molecule of water.

Anal. Calcd. for $C_{16}H_{17}OCl_3 \cdot H_2O$: C, 57.59; H, 5.14. Found: C, 57.61; H, 5.17.

2,3-Diethylnaphthalene.—One gram of 6,7-diethyltetralin was heated with palladium-charcoal (0.1 g., 10%) at 200–240° for three hours. The product was taken up in a small quantity of ethanol, filtered, and treated with a saturated solution of picric acid in ethanol. The precipitated picrate melted at 126–128°. The regenerated hydrocarbon was liquid at room temperature.

Action of Sulfuric Acid on the Hydrocarbons

(A) **Octahydroanthracene.**—The reported rearrangement to octahydrophenanthrene[4] was confirmed.

(B) **5,6,7,8-Tetrahydrobenz[f]indan.**—The hydrocarbon (11.8 g.) and concentrated sulfuric acid (47 g.) were heated at 118°. Sulfur dioxide was continuously evolved.

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(13) Fleischer and Siefert, *Ber.*, **53**, 1255 (1920).

(14) Campbell, Soffer and Steadman, THIS JOURNAL, **64**, 425 (1942).

(15) Sen-Gupta, *J. Ind. Chem. Soc.*, **16**, 89 (1939).

(16) Levy, *Compt. rend.*, **197**, 772 (1933).

(17) Bergmann and Bergmann, *J. Chem. Soc.*, 1364 (1939).

(18) Schroeter, *Ber.*, **57**, 2003 (1924).

On cooling the mixture was poured into 250 cc. of water and treated with calcium oxide (27 g.). After filtering, the filtrate was treated with sodium carbonate to remove the excess calcium ion. Evaporation of the aqueous filtrate gave a semicrystalline mass. This was steam distilled at 145–150° in the presence of dilute sulfuric acid. One gram of starting hydrocarbon and one gram of benz[f]-indan (m. p. 92–93°) were recovered. The latter formed its well known picrate, m. p. and mixed m. p. 116–118°.

(C) **6,7-Diethyltetralin.**—Eighteen grams of the hydrocarbon in sulfuric acid (80 cc.) was heated gradually while being stirred. At 60° complete solution was effected. The mixture was then heated at 95° for fifteen minutes and allowed to cool. Steam distillation at 150° gave 4.9 g. of liquid hydrocarbon. Oxidation of a portion of this material with nitric acid gave only mellophanic acid (methyl ester—m. p. and mixed m. p. 129–131°). Dehydrogenation of the hydrocarbon with palladium-charcoal gave 1,2-diethylnaphthalene a liquid hydrocarbon whose picrate melted at 105.5–107°.

(D) **5-Ethyl-6-methylhydrindene.**—Ten grams of the hydrocarbon was heated with 40 cc. of sulfuric acid at 90° for thirty minutes. Steam distillation as described above gave 1.4 g. of volatile hydrocarbon. Nitric acid oxidation gave only mellophanic acid (methyl ester—m. p. and mixed m. p. 129–131°).

(E) ***s*-Hydrindacene.**—Three grams of the hydrocarbon and 20 g. of sulfuric acid were heated at 70° for three minutes. More drastic conditions (*i. e.*, higher temperatures, etc.) gave only unidentifiable tarry materials. The solution was cooled and a solid sulfonic acid separated. To the total contents of the flask acetic acid (2 cc.) and sulfuric acid (5 cc.) were added and the temperature was raised to 98° and held there for one hour. Steam distillation gave the starting hydrocarbon (m. p. 52–53°) as the sole product. Considerable tarry residue remained in the distilling flask.

Action of Aluminum Chloride on the Hydrocarbons

(A) **6,7-Diethyltetralin.**—Thirteen grams of hydrocarbon and aluminum chloride (1 g.) was heated on the steam-bath for two and one-half hours and then allowed to stand several days at room temperature. After decomposition with water followed by ether extraction there was obtained on fractionation at 11 mm. three cuts boiling at 124–140°, 142–152°, and 155–168°. The first cut on oxidation with nitric acid gave impure prehnitic acid (identified as its methyl ester—m. p. and mixed m. p. 109–110°). Fraction II (b. p. 142–152°) gave fairly pure prehnitic acid. Dehydrogenation of this fraction with palladium-charcoal gave a naphthalenic hydrocarbon whose picrate melted at 100–101°. This hydrocarbon must be 1,3-diethylnaphthalene.

(B) **5-Ethyl-6-methylhydrindene.**—Treatment of 20 g. of hydrocarbon with aluminum chloride (2.0 g.) as described above gave on fractionation at 15 mm. the following cuts: I, 80–100° (1 g.), II, 100–120° (7 g.), III, 120–140° (10 g.), IV, 140–180° (0.5 g.) and V, 215–230° (0.8 g.). Fraction III gave prehnitic acid on nitric acid oxidation (identified as its methyl ester) and fraction V gave benzenepentacarboxylic acid (pentamethyl ester—m. p. and mixed m. p. 146–148°).

(C) ***s*-Hydrindacene.**—The hydrocarbon (1.5 g.) was treated with aluminum chloride (0.5 g.) as described above. The reaction product was oxidized with nitric acid and the resulting carboxylic acid mixture was esterified with diazomethane. Penta- and hexacarbomethoxybenzenes were isolated; m. p. 146–148° and 184–186°, respectively.

Summary

1. The Jacobsen rearrangement has been studied with cyclic hydrocarbons related to hydrindene and tetralin.

2. The action of aluminum chloride on 6,7-diethyltetralin, 5-ethyl-6-methylhydrindene, and *s*-hydrindacene is reported.

3. A new and convenient synthesis of pure 1,4-diethylnaphthalene is described.

4. A mechanism for the Jacobsen rearrangement is proposed and discussed.

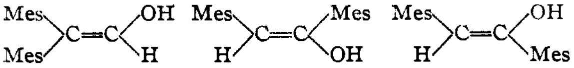
MINNEAPOLIS, MINNESOTA RECEIVED FEBRUARY 14, 1944

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Vinyl Alcohols. IX.[1] Esters of 1,2-Dimesitylvinyl Alcohols

BY REYNOLD C. FUSON, L. J. ARMSTRONG[2] AND W. J. SHENK, JR.

For the dimesitylvinyl alcohol produced by the dehydration of hydromesitoin or isohydromesitoin[1] three structures are possible—1,1-dimesitylvinyl alcohol (I) and the *cis* (II) and *trans* (III) forms of 1,2-dimesitylvinyl alcohol. The present paper is concerned with the last two of these. Although it has not been possible to prepare these enols, evidence has been accumulated which shows both to be unstable and thus entirely different from the dehydration product. The structure, 1,1-dimesitylvinyl alcohol, (I), previously assigned to this product is thereby confirmed.



I II III

One of the methods employed in attempts to make enols II and III consisted in the condensation of mesitylmagnesium bromide with mesitylketene (IV). The possibility of preparing enols from ketenes was suggested by the work of Gilman and Heckert,[3] who found that the enolate formed by the addition of the Grignard reagent to diphenylketene was converted by the action of benzoyl chloride to the corresponding enol benzoate. Hydrolysis of this ester produced the enol, which immediately ketonized. It seemed possible that a more stable enol could be made by the condensation of a Grignard reagent with mesitylketene. Although this ketene could not be isolated it was prepared in solution and to the solution was added mesitylmagnesium bromide. The enolate (V) reacted with benzoyl chloride to yield a benzoate (VI) of desoxymesitoin (VII). The structure of the benzoate was established by

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(1) For the preceding communication in this series see Fuson and Rowland, THIS JOURNAL, 65, 992 (1943).

(2) Present address, Rohm and Haas Company, Philadelphia, Pennsylvania.

(3) Gilman and Heckert, THIS JOURNAL, 42, 1010 (1920).