Anal. Calcd. for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 83.10; H, 8.55.

The **oxime**, sublimed at 105° (0.1 mm.), formed short thick prisms, m.p. 146–150° (inserted at 140°).

Anal. Calcd. for $C_{13}H_{17}ON$: C, 76.81; H, 8.43. Found: C, 77.06; H, 8.45.

2,3-Dimethylbenzosuber-5-ene-5-ol-6-glyoxylic Acid Lactone (IIId).—As before,[2] 2.82 g. (0.015 mole) of the suberone IIe was treated with dimethyl oxalate. In contrast to the previous case,[2] pale yellow silky crystals began to separate in the reaction mixture after 10 minutes. The usual treatment[2] gave 1.3 g. (5.37 mmoles, 36%) of golden yellow broad prisms from ethyl acetate, m.p. 168–168.5° dec., becoming orange at 146°. The compound was insoluble in 5% sodium bicarbonate and gave a slowly developing red brown color with ferric chloride. After four crystallizations from ethyl acetate the yellow long thin prisms melted at 167.5–168 5° dec., turning orange at *ca.* 140°.

Anal. Calcd. for $C_{15}H_{14}O_3$: C, 74.36; H, 5.82. Found: C, 74.27; H, 5.82.

Methyl 2,3-Dimethylbenzosuberone-6-glyoxylate (Ie).—The solution of 0.500 g. (2.06 mmoles) of IIId in 3 cc. of methanol was complete after warming for 5 minutes. After 10 minutes the solution was concentrated and cooled to −20°. The methanol washed product weighed 0.54 g. (1.97 mmoles, 96%), melted at 94–94.5° and gave an immediate dark red ferric chloride test. Four crystallizations from methanol gave nearly colorless short thick prisms, m.p. 94–96°.

Anal. Calcd. for $C_{16}H_{18}O_4$: C, 70.05; H, 6.61. Found: C, 70.06; H, 6.58.

1,4-Dimethylbenzosuberone[5] (IIf).—The acylation of *p*-xylene as described[3] gave γ-2,5-dimethylbenzoylbutyric acid, b.p. 165–170° (0.23 mm.). From petroleum ether (60–90°) material, m.p. 54–68° (72%), was obtained; reported[5] m.p. 72–73°. Reduction[12] gave δ-2,5-dimethylphenylvaleric acid[5] (87.7%) which was cyclized by polyphosphoric acid at 95° for 35 minutes to yield (67%) 1,4-dimethylbenzosuberone, b.p. 110–112° (1.2 mm.); reported[5] b.p. 121–131° (1 mm.).

Methyl 1,4-Dimethylbenzosuberone-6-glyoxylate (If).—The described treatment[2] with 6.3 g. (0.033 mole) of IIf and dimethyl oxalate gave a precipitate in the benzene solution. After 20 hours at room temperature the dark red solution contained only a few crystals. The usual treatment produced an orange red oil (9.0 g., 0.033 mole, 98%) unchanged by heating 1 hour on the steam-bath at 0.6–0.25 mm. It gave an immediate wine red color with ferric chloride.

On heating the orange red oil at 180° decarbonylation occurred and the residue then distilled as a colorless oil, b.p. 109–121° (0.35 mm.). Redistillation gave a faintly yellow middle portion b.p. 110–114° (0.15 mm.) which gave a deep purple color with alcoholic ferric chloride. Repeated distillation with analysis of the center cut gave consistently high results for **methyl 1,4-dimethylbenzosuberone-6-carboxylate** indicating partial decomposition to the suberone.

Anal. Calcd. for $C_{15}H_{18}O_3$: C, 73.15; H, 7.37. Found: C, 77.23; H, 7.79.

SALT LAKE CITY 1, UTAH

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Reaction of Aromatic Nitro Compounds with Polynuclear Hydrocarbons at Elevated Temperatures

BY CHARLES D. HURD AND LESLIE H. JUEL

RECEIVED JULY 19, 1954

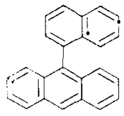
Anthracene and 1-nitronaphthalene react at about 300° to give as the principal product 7,12-dihydro-7,12-*o*-benzenobenz[a]anthracene. Its structure is established by independent synthesis. The mechanism by which it is formed is thought to involve a diene synthesis. followed by elimination of the elements of nitrous acid, the latter undergoing reduction to nitric oxide. Several derivatives of the hydrocarbon have been prepared which include a mononitro derivative, an acetyl derivative, and adducts with picric acid, *sym*-trinitrobenzene and 2.4.7-trinitrofluorene. Naphthacene has been condensed with 1-nitronaphthalene to give 7,14-dihydro-7,14-*o*-benzenobenz[a]naphthacene, the reaction being analogous to that between anthracene and 1-nitronaphthalene. Anthracene and 2-methylanthracene were condensed with 1,4-dihydronaphthalene, and the resulting adducts were dehydrogenated to yield 5,12-dihydro-5,12-*o*-benzenonaphthacene and its 2-methyl derivative, respectively. A new synthesis of 1,2-dihydronaphthalene has been developed involving the reduction of 1-naphthol to 1,2,3,4-tetrahydro-1-naphthol in alkaline media and in the presence of nickel catalyst followed by dehydrogenation of the secondary alcohol in the presence of hydrochloric acid.

This investigation grew out of an observation made at Great Lakes Carbon Corporation and communicated to us by Charles L. Thomas, namely, that the softening point and viscosity of coal tar pitch or pitch fractions could be raised by heating a mixture of the pitch and 1-nitronaphthalene to about 175° for an extended period of time, whereas admixture at lower temperatures merely caused lowering of melting point and viscosity. The high temperature effect pointed to a chemical reaction.

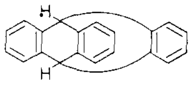
As a starting point for the elucidation of this problem we selected anthracene as a component in coal tar which might be expected to undergo this type of thermal reaction with 1-nitronaphthalene and, indeed, such a reaction was observed on heating the mixture at about 300° for 10–15 hours. The principal product was a white, crystalline hydrocarbon, $C_{24}H_{16}$, melting at 209°. It underwent Friedel–Crafts acetylation to yield a ketone $C_{24}H_{15}COCH_3$, nitration to yield $C_{24}H_{15}NO_2$, and oxidation by chromic anhydride in acetic acid to produce both anthraquinone and carbon dioxide. Picric acid, *sym*-trinitrobenzene and 2,4,7-trinitrofluorenone all formed adducts with this hydrocarbon, the first two on a 1:1 basis and the last 2:1. Hydrogen at 265° and 100 atm., in the presence of a copper-on-alumina catalyst promoted cleavage into naphthalene and dihydroanthracene, although yields were small. A boiling chloroform solution of the hydrocarbon was not changed by bromine and iron, conditions which are known to cause nuclear bromination of toluene.

Of the three most plausible structures (I, II, III), 9-α-naphthylanthracene (I) seemed unlikely because of the evolution of carbon dioxide on oxidation and the non-bromination. To decide between 5,12-dihydro-5,12-*o*-benzenonaphthacene (II) and 7,12-dihydro-7,12-*o*-benzenobenz[a]anthracene (III), their syntheses were planned. The lower analog, 9,10-dihydro-9,10-*o*-benzenoanthracene

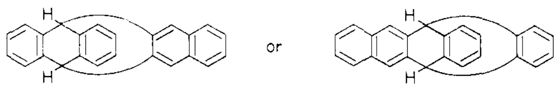
(IV), was prepared by Bartlett.[1] The chemical properties which he listed were very similar to those of our hydrocarbon, including evolution of carbon dioxide on oxidation.



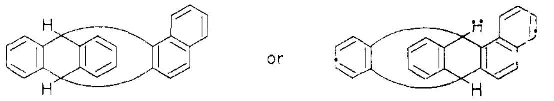
I



IV

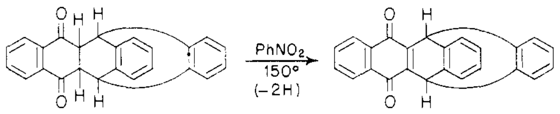


II



III

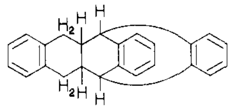
Of the two approaches used for the synthesis of II the first failed at the last step. In this approach, the adduct V of anthracene and 1,4-naphthoquinone was converted into the quinone VI as indicated.



V VI

The dioxime of VI was reduced by stannous chloride to the diamine, but tetrazotization and reduction with hypophosphorous acid was unsuccessful. Reduction of the monoxime to the monoamine, then oxidation with nitrous acid, regenerated quinone VI.

In the next approach, 1,4-dihydronaphthalene and anthracene were heated together at 250° to form an adduct, VII.



VII

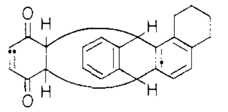
Dehydrogenation of VII at 350° over palladium-on-carbon yielded a hydrocarbon of structure II, m.p. 257°, obviously not the substance of m.p. 209° formed from 1-nitronaphthalene and anthracene.

The first attempt to synthesize III was through the addition of anthracene to 1,2-dihydronaphthalene, but no addition occurred at 250°. The second approach which started with benz[a]anthracene and 1,4-benzoquinone also was fruitless. From 70 to 80% of the benzanthracene was recovered at 140° or 250°.

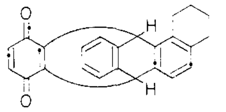
1,2,3,4-Tetrahydrobenz[a]anthracene was next selected, the idea being to lessen the resonance stabilization over that of benzanthracene with the hope that the increased reactivity would be sufficient for reaction with benzoquinone. Fieser[2] reported preparation of this compound starting with 1-bromonaphthalene. In our first approach we used the Elbs reaction, involving pyrolysis of 5,6,7,8-tetrahydro-2-naphthyl *o*-tolyl ketone. Two compounds were isolated, but neither was the desired tetrahydrobenzanthracene. One compound appeared to contain oxygen while the other corresponded to a dihydrobenzanthracene. These results are similar to those of Fieser and Seligman[3] on the pyrolysis of 5,6,7,8-tetrahydro-1-naphthyl ketones. While condensation occurs readily, considerable aromatization occurs along with migration of hydrogen to different parts of the molecule.

A successful synthesis involved condensing phthalic anhydride with tetralin, cyclizing the resulting *o*-(5,6,7,8-tetrahydro-2-naphthyl)-benzoic acid to 1,2,3,4-tetrahydrobenz[a]anthraquinone and finally reducing the latter directly to the hydrocarbon.

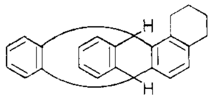
This compound added benzoquinone readily and the yellow adduct VIII was tautomerized quantitatively by use of hydrogen bromide in acetic acid. Oxidation of the colorless diol by peracetic acid gave rise to the red quinone IX. The dioxime of IX was reduced to the diamine which was tetrazotized and reduced by hypophosphorous acid to colorless hydrocarbon X, m.p. 194–195°.



VIII



IX

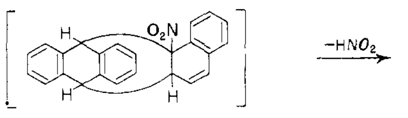


X

It is interesting to point out that tetrazotization was possible in this compound which contained the *p*-phenylenediamine moiety, whereas it was impossible to tetrazotize the diamine related to VI, which contained the 1,4-naphthylenediamine moiety.

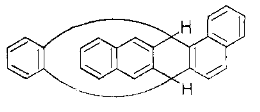
Dehydrogenation of X at 300° with palladium-on-carbon gave rise to a hydrocarbon in 85% yield, melting at 209–210° and indistinguishable from the one prepared from anthracene and 1-nitronaphthalene. Structure III is thus confirmed for this substance. Its mode of formation is believed to involve a diene synthesis with ultimate loss of the elements of nitrous acid from the angular positions

$C_{14}H_{10} + C_{10}H_7NO_2 \longrightarrow$

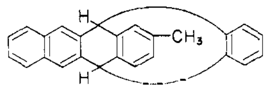


III

Just as 1-nitronaphthalene condenses with anthracene so also it condenses with naphthacene. The compound formed is 7,14-dihydro-7,14-*o*-benzenobenz[a]naphthacene (XI). Its properties resembled those of III.



XI



XII

---

[1] P. D. Bartlett and co-workers, THIS JOURNAL, **64**, 2649 (1942); **72**, 1003, 1005 (1950).

[2] L. Fieser and E. Hershberg, *ibid.*, **59**, 1028, 2331, 3502 (1937).

[3] L. Fieser and A. Seligman, *ibid.*, **58**, 478 (1936).

1,4-Dihydronaphthalene also added successfully to 2-methylanthracene and dehydrogenation of this adduct produced 2-methyl-5,12-dihydro-5,12-*o*-benzenonaphthacene (XII).

The following experiments did not yield condensation products of this type: a. Anthracene and 2-nitronaphthalene at 300°. Considerable gas evolution occurred during 18 hours, but no nitric oxide was found and only anthracene was recoverable from the black, pitchy solid. b. Anthracene and nitrobenzene. At 270–285° (20 hours) there was obtained a 20% yield of pinkish crystalline solid (after chromatographic separation on alumina and crystallizations from benzene and hexane), m.p. 251–253°: C, 91.2, 91.4; H, 5.10, 5.25. At 350° (27 hours) unreacted anthracene (21%) and anthraquinone (10%) were the only isolable products. At 305–310° (48 hours), 13% of the anthracene was recoverable, and about 1% of white solid, m.p. 260–276°: C, 93.1; H, 5.53. c. Phenanthrene and 1-nitronaphthalene. Much unreacted phenanthrene was found after 17 hours at 340°, but no oxides of nitrogen were detectable. d. 1-Chloroanthracene and 1-nitronaphthalene. There was evidence for liberation of both nitric oxide and hydrogen chloride during 18 hours at 350°. The only crystalline product that was isolated was dichloroparaanthracene $(C_{14}H_9Cl)_2$, m.p. 235°: C, 79.0; H, 4.21. e. 2-Methylanthracene and 1-nitronaphthalene. There was no evolution of nitric oxide but the mixture did turn black. No pure product was identified.

Experiments a and b bear witness to the fact that 1-nitronaphthalene is more reactive than either 2-nitronaphthalene or nitrobenzene in these diene syntheses.

Experimental[4]

7,12-Dihydro-7,12-*o*-benzobenz[a]anthracene (III) from Anthracene and 1-Nitronaphthalene.—Recrystallized 1-nitronaphthalene (8.8 g.) and recrystallized anthracene (8.8 g.) were placed in a tared, 250-ml. round-bottom flask, provided with a means for continually sweeping the flask with nitrogen. To the exit tube was connected a tared calcium chloride tube to collect water of decomposition. With nitrogen passing slowly through the apparatus, the reaction flask was heated by means of a salt-bath to 300° and there maintained for about 15 hours. During this period nitric oxide was evolved as evidenced by the formation of brown nitrogen dioxide fumes on contact with air. The final loss in weight of the contents of the flask was 1.0 g., of which 0.35 g. was collected in the calcium chloride tube.

On distilling the reaction mixture at 12–14 mm., 7.62 g. of distillate was obtained (fraction A) up to 177°. The residue was dissolved in benzene, transferred to a 125-ml. flask and distilled further up to 250° at 1 mm. There was collected 3.82 g. of distillate (fraction B). The residue from this distillation was taken up in benzene and transferred to a sublimation apparatus. At a bath temperature of 250° and a pressure of 1 mm. 2.7 g. of material was sublimed onto the cold finger. The final residue weighed 1.78 g. The material appeared carbonaceous but it still retained considerable solubility in benzene.

Fraction A was crystallized from benzene and 2.74 g. of anthracene was isolated. The mother liquor was evaporated and the residue taken up in ligroin. Cooling caused the separation of light yellow needles of unreacted nitronaphthalene.

Fraction B together with the sublimate was worked up by solvent fractionation from benzene and petroleum hexane. The crude product was purified by passing a hexane solution over activated alumina, and 4.5 g. (44.3% based on the anthracene reacting) of the white crystalline hydrocarbon of m.p. 207–208° was isolated. Fractional crystallization from ligroin, b.p. 85–100°, raised the m.p. to 208–209°. A mixture of this substance with anthracene melted at 180–200°.

Anal. Calcd. for $C_{24}H_{16}$: C, 94.65; H, 5.30; mol. wt., 304. Found: C, 94.88; H, 5.30; mol. wt. (Rast), 301.

Derivatives.—The picrate was formed on slow evaporation of a solution of the hydrocarbon and picric acid in ethyl acetate; m.p. 147–147.5°.

Anal. Calcd. for $C_{24}H_{16}\cdot C_6H_3N_3O_7$: N, 7.88. Found: N, 7.52.

An addition compound with *sym*-trinitrobenzene crystallized from a 1:1 alcohol–benzene solution of the hydrocarbon and *sym*-trinitrobenzene. It melted at 173–174°.

Anal. Calcd. for $C_{24}H_{16}\cdot C_6H_3N_3O_6$: C, 69.70; H, 3.68; N, 8.13. Found: C, 69.93; H, 4.11; N, 8.12.

Crystallization of a benzene–alcohol solution of 2,4,7-trinitrofluorenone and the hydrocarbon yielded a deep red complex, m.p. 189.5–190.5°, containing two molecules of trinitrofluorenone per molecule of hydrocarbon.

Anal. Calcd. for $C_{24}H_{16}\cdot 2C_{13}H_5N_3O_7$: C, 64.30; H, 2.79; N, 9.00. Found: C, 64.19; H, 2.87; N, 9.18.

Nitration.—A solution of 2.0 g. of the hydrocarbon III in 30 ml. of acetic anhydride and 30 ml. of glacial acetic acid was cooled to around 10°. To this was added with stirring a solution of 0.6 ml. of fuming nitric acid (d. 1.50) in 15 ml. of acetic acid. After 0.5 hour at 0–2° the solution, which had turned light yellow in color, was allowed to warm to 25° and to stand for 2 hours. A yellow crystalline material (1.3 g.) separated, was filtered off, washed with glacial acetic acid and dried. The mother liquor was diluted with ice water to precipitate more yellow material which was collected. Digestion with hexane caused a portion to go into solution. The remaining 0.2 g. was collected. Recrystallization of the combined solids from acetic anhydride gave 1.4 g. of yellow plates, m.p. 308–309°.

Anal. Calcd. for $C_{24}H_{15}NO_2$: C, 82.48; H, 4.33; N, 4.01. Found: C, 82.67; H, 4.22; N, 4.07.

Attempted Bromination.—To 10 ml. of chloroform was added 0.1 g. of hydrocarbon III. The mixture was shaken to effect solution and a small amount of acid-washed iron powder was added. A solution of bromine in chloroform was added dropwise, a few drops sufficing to color the solution a light yellow. No decolorization took place even after refluxing for 1.5 hours. The starting material was recovered unchanged, m.p. 206–207.5°.

Acetylation.—Anhydrous aluminum chloride (2.4 g.) was dissolved in 15 ml. of nitrobenzene. A solution of 3 g. of hydrocarbon III in 15 ml. of nitrobenzene was then added to it, causing the entire solution to become red-brown in color. After cooling the solution to around 10°, 0.96 ml. of acetic anhydride was added with swirling. Cooling was continued for 25 minutes after which the solution was kept at 20° for 3.5 hours. The mixture was then poured onto cracked ice acidulated with 15 ml. of concentrated hydrochloric acid. The resulting mixture was steam distilled to remove the nitrobenzene, leaving a brown residue which solidified on cooling. After filtration, the product was dissolved in ligroin and the solution was treated with Norit A. After filtration, the solution was cooled and 1.34 g. (43%) of a white microcrystalline material was collected. Recrystallization from a mixture of chloroform and petroleum hexane (1:1) gave a white crystalline methyl ketone, m.p. 264–265.3°.

Anal. Calcd. for $C_{26}H_{18}O$: C, 90.25; H, 5.24. Found: C, 90.12; H, 5.22.

Oxime of the Ketone.—A solution of 0.1 g. of the crude ketone and 0.1 g. of hydroxylammonium chloride in 5 ml. each of pyridine and alcohol was heated under reflux for two hours. The solvent was removed and the residue digested with water causing a solid to separate. This crude material (0.1 g. or 96%) was collected, dried and recrystallized from benzene. A second recrystallization from benzene–alcohol (2:1) yielded a white, microcrystalline material, m.p. 273–275°.

Anal. Calcd. for $C_{26}H_{19}NO$: N, 3.88. Found: N, 3.85.

Oxidation.—One gram of hydrocarbon III was dissolved in 40 ml. of glacial acetic acid in a flask equipped with a

---

(4) Microanalytical determinations for carbon and hydrogen were performed by J. Anderson, P. Craig, J. Gibbs, V. Hobbs and M. Hines.

rubber stopper carrying a dropping funnel and delivery tube. The delivery tube was connected to a sulfuric acid scrubber and thence to an absorption tube for carbon dioxide. The flask was placed on a steam-bath, and a solution of 2.64 g. of chromic anhydride in 25 ml. of glacial acetic acid was added dropwise during 30 minutes. The flask was swept slowly with nitrogen for ten hours. The carbon dioxide absorbed was 0.315 g. The theory for $2CO_2$ for each $C_{24}H_{16}$ is 0.290 g. Dilution of the solution with two volumes of ice-water precipitated 0.5 g. of yellow flocculent solid. Recrystallization from alcohol–benzene (2:1) gave light greenish-yellow needles, m.p. 275–276°. A mixed melting point with anthraquinone was at 274–276°.

Destructive Hydrogenation.—Three grams of hydrocarbon III and 1.5 g. of a 2:1 copper–alumina catalyst (supplied by Universal Oil Products Company, Riverside, Ill.) were placed in a 250-ml. bomb and put under an initial hydrogen pressure of 106 atmospheres. After 5.5 hours of heating to a maximum temperature of 275°, the bomb was cooled to room temperature. Pressure in the bomb had dropped to 95 atmospheres. The contents were removed with the aid of benzene, which when evaporated off left a residue of 2.87 g. (95.7% recovered). This material was steam distilled and two fractions were collected. The first was 0.72 g. of colorless oil lighter than water. The second was 0.44 g. of light yellow oil, heavier than water. The residue, a greenish-yellow viscous material, weighed 1.19 g. Fraction one partially crystallized on standing. Fractional precipitation of the picrates from this fraction yielded a small amount of a picrate (m.p. 135–145°) which could not be purified further. Decomposition of this picrate with water yielded an amount of white crystalline material which, when recrystallized from aqueous methanol, was sufficient for melting point determinations only. The melting point was 78–79°. A mixed melting point with pure naphthalene showed no depression. No single pure substance was obtainable from the other fractions.

In a second similar hydrogenation experiment on a 0.2-g. sample of the hydrocarbon the reaction product was distilled under diminished pressure. The first fraction (naphthalene) solidified in the condenser. The second fraction, a liquid with a blue-green fluorescence, gradually solidified on standing. Recrystallization from alcohol gave 0.04 g. of white material, fusing at 85–105°. Dehydrogenation with palladium-on-charcoal at 350° gave anthracene, m.p. 212°.

Synthetical Experiments Leading to II. Quinone, VI.—This was prepared by the method of Collins,[5] by heating 10.4 g. of anthracene, 8.76 g. of 1,4-naphthoquinone and 80 ml. of nitrobenzene for 24 hours at 140–150°, then precipitating with 400 ml. of methanol; yield 12.9 g. (70%). A duplicate experiment gave a 78% yield. The yellow solid melted at 275–277° after crystallization from dioxane.

Oximes of VI.—This mixture was heated under reflux for 3 hours: 3.2 g. of VI, 4 g. of hydroxylammonium chloride, 25 ml. of pyridine and 25 ml. of ethanol. Then the solvent was removed and the residue triturated with water. The solid (3.1 g.) which separated was filtered off, washed with water and then dissolved in 30 ml. of glacial acetic acid. On cooling, 1.1 g. (31.6%) of a yellow crystalline monoxime, m.p. 233–236° dec., was obtained as a first fraction.

Anal. Calcd. for $C_{24}H_{15}NO_2$: C, 82.60; H, 4.33; N, 4.02. Found: C, 82.33; H, 4.27; N, 4.02.

The dioxime, which remained in solution, was thrown out with water, filtered off and dried; weight 1.46 g. (41.8%). A portion on recrystallization from aqueous alcohol melted about 178° dec.

Anal. Calcd. for $C_{24}H_{16}N_2O_2$: C, 79.09; H, 4.43. Found: C, 79.25; H, 4.73.

Reduction of the Monoxime.—A solution of 0.5 g. of the yellow monoxime in 20 ml. of alcohol was heated to 60° on a steam-bath and to it was added a solution of 2.2 g. of stannous chloride in 10 ml. of concentrated hydrochloric acid with swirling. The yellow color became completely discharged. Heating was continued for an additional three minutes, then the solution was cooled and 10 ml. of concentrated hydrochloric acid was added. After cooling to 0° a white crystalline precipitate formed. After desiccation in an oven for one hour at 105° the product darkened to a grayish color; weight, 0.66 g. which is a quantitative yield of crude amine hydrochloride. This crude hydrochloride was acetylated to 6-acetamido-11-acetoxy-5,12-dihydro-5,12-*o*-benzenonaphthacene by heating 0.1 g. of it with 3 ml. each of acetic anhydride and glacial acetic acid. After 30 min. the clear solution was diluted with two volumes of water to form 0.12 g. of pure white precipitate. The yield was quantitative. Recrystallization of a portion from aqueous acetic acid gave a white microcrystalline material, m.p. 344–349°, dec.

Anal. Calcd. for $C_{28}H_{21}NO_3$: N, 3.34. Found: N, 3.18.

Behavior of Monoamine Hydrochloride toward Nitrous Acid.—Half a gram of the crude hydrochloride was suspended in 15 ml. of glacial acetic acid at 10°, and to it was added a cooled solution of 10 ml. of concentrated sulfuric acid, 10 ml. of acetic acid and 6 ml. of water. With vigorous stirring and cooling 0.6 g. of potassium nitrite was dusted in gradually, causing the solution to turn orange. Stirring was continued for one hour in the cold; then 1 g. of urea was added followed by a filtered solution of 1.2 g. of sodium hypophosphite in 30 ml. of concentrated hydrochloric acid. After standing overnight in the ice-box, a flocculent, deep-pink precipitate separated. The suspension was diluted with 100 ml. of water and the solid collected on a filter, washed with water and dried. The crude material was taken up in a benzene–alcohol mixture, treated with Norit A, filtered and cooled. Yellow needle-like crystals, m.p. 272–276°, separated; weight 0.34 g. A mixed melting point with the original quinone VI showed no depression.

5,5a,6,11,11a,12-Hexahydro-5,12-*o*-benzenonaphthacene (VII).—A sample of 1,4-dihydronaphthalene of 85% purity was kindly supplied by V. L. Hansley of Electrochemical Department, du Pont and Co., Niagara Falls, N. Y. A mixture of 12 g. of it and 13.8 g. of pure anthracene was heated in a sealed tube overnight at 242°. Fractional crystallization from benzene, petroleum hexane, and methyl and ethyl alcohols yielded 8.1 g. (33.7%) of adduct, VII, m.p. 189–190°. From a methanol solution upon evaporation and steam distillation was obtained 0.96 g. of a light-brown oil and 4.36 g. of a white solid from which 4.54 g. of naphthalene picrate was isolated, m.p. 145–147°.

Anal. of VII. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54. *Found:* C, 93.63; H, 6.49.

5,12-Dihydro-5,12-*o*-benzenonaphthacene (II).—A mixture of 0.3 g. of VII and 0.1 g. of palladium-on-charcoal was heated in a test-tube immersed in a salt-bath to a temperature of 350° over a period of 2 hours. The hydrogen evolved was 28.5 cc. (theory 50 cc.). There was isolated 0.21 g. (70%) of pure hydrocarbon, m.p. 256–257°.

Anal. Calcd. for $C_{24}H_{16}$: C, 94.77; H, 5.23. Found: C, 94.91; H, 5.54.

No dehydrogenation of VII occurred when it was heated with palladium-on-charcoal at 160°, and no II was isolable from 0.2 g. of VII heated with 0.33 g. of chloranil at 140°.

Synthetical Experiments Leading to III. 1,2-Dihydronaphthalene *via* 1,2,3,4-Tetrahydro-1-naphthol.[6]—One ml. of 50% potassium hydroxide was added to a mixture of 22 g. of 1-naphthol and enough 95% alcohol to make 140 ml. Reduction was carried out at 82° in a 300-ml. hydrogenation bomb containing about 2 g. of Raney nickel catalyst. The initial pressure was 1700 p.s.i.g. Time required for absorption of theoretical hydrogen was one hour. The alcohol solution from the hydrogenation was bluish in color and on acidification with hydrochloric acid turned light brownish-red. Removal of the alcohol by distillation followed by solution in ether and extraction with 2% sodium hydroxide solution yielded a brown colored ether solution which was dried over calcium chloride and then evaporated. Distillation of the residual liquid gave 12.3 g. (66.1%) of 1,2-dihydronaphthalene, b.p. 87–89° at 15 mm. The residue in the flask was a high boiling material which set solid on cooling.

Preparation of the dibromide of the dihydronaphthalene was made in carbon disulfide. The crude dibromide was recrystallized from petroleum hexane in the form of white prisms, m.p. 69–71°. The dibromide of 1,4-dihydronaphthalene was prepared in a similar manner and crystallized in the form of white needles, m.p. 71–74°. A mixed melting point of the two dibromides melted 41–60°.

Non-reaction of 1,2-Dihydronaphthalene and Anthracene.—Most of the anthracene was recovered from a mixture of

---

[5] C. J. Collins, doctoral dissertation, Northwestern University, 1944, p. 29.

[6] This procedure follows that described by G. Stork, THIS JOURNAL, 69, 576 (1947), for the reduction of 2-naphthol.

these hydrocarbons after heating for 16 hours in a sealed tube at 230° or 18 hours at 250°.

5,6,7,8-Tetrahydro-2-naphthyl *o*-Tolyl Ketone.—To a mixture of 104 g. of tetralin, 400 ml. of dry benzene and 77.3 g. of *o*-toluyl chloride was gradually added 119 g. of anhydrous aluminum chloride in such a way as to exclude moisture. Hydrogen chloride was evolved vigorously for about a half-hour, but addition of the last 25 g. failed to cause any further visible evolution of gas. Heating and stirring was continued for one-half hour, and the mixture was then poured onto cracked ice containing 125 ml. of concentrated hydrochloric acid. The benzene layer was separated and steam distilled to remove the benzene and unused tetralin. The residual oil was vacuum distilled and a fraction boiling in the range 180–186° at 3–4 mm. pressure was collected. This product was a yellow-green oil at room temperature; weight 98 g. or 78% yield.

A 2,4-dinitrophenylhydrazone of the ketone was prepared in the usual manner. Recrystallization from alcohol gave bright red needles, m.p. 180–181°.

Anal. Calcd. for $C_{24}H_{22}N_4O_4$: N, 13.01. Found: N, 12.80.

Pyrolysis of 5,6,7,8-Tetrahydro-2-naphthyl *o*-Tolyl Ketone.—Thirty grams of the ketone was refluxed for three hours at 275°. Approximately 2 ml. of water of decomposition was collected. The product which solidified upon cooling was distilled under reduced pressure. Two fractions were collected. The first fraction, 12.6 g., distilled below 250° at 29 mm. From this fraction 8.6 g. of unchanged ketone was recovered by partial solution in alcohol. Recrystallization of the alcohol insoluble material from ligroin gave 3.5 g. of an unidentified yellow-green, fluorescent compound, m.p. 153–154°. A picrate prepared in the usual manner melted 136–138°.

Anal. Calcd. for $C_{18}H_{14}O_2$: C, 82.50; H, 5.38. Found: C, 82.11; H, 5.53.

The second fraction, 11.3 g., distilled in the range 190–208° at 3 mm. From this fraction 1.2 g. of a white hydrocarbon, m.p. 208–209°, was obtained by tedious fractional crystallization from benzene and petroleum hexane.

Anal. Calcd. for $C_{19}H_{14}$: C, 93.88; H, 6.12. Found: C, 93.78; H, 5.90.

Adduct of *p*-Benzoquinone and 1,2,3,4-Tetrahydrobenz[a]anthracene. Quinone VIII.—To make this compound the starting point was a quinone of m.p. 135° described by Schroeter and by Mikhailov and Chernova,[7] which is actually an addition compound between the two isomeric 1,2,3,4-tetrahydrobenz[a and b]anthraquinones. This material was reduced by zinc and sodium hydroxide solution (refluxed 48 hours) in essentially the manner used by Fieser and Hershberg[2,8] on the corresponding anthrone. Two products were isolated, namely, 1,2,3,4-tetrahydronaphthacene, m.p. 219–225°, in 10% yield, and the desired hydrocarbon (white plates, m.p. 102–104°; lit. 104.5–105°) in 49% yield. The two were separated from each other readily by crystallization from hexane in which the latter is more soluble.

Two grams of the tetrahydrobenz[a]anthracene and 1.5 g. of *p*-benzoquinone were refluxed for 5 hours in 35 ml. of alcohol. The yellow solid which had separated weighed 2.1 g. (66%). Crystallization from glacial acetic acid gave yellow crystals melting at 215–216°. Somewhat lower yields were realized when the reaction was conducted in boiling benzene or xylene instead of alcohol. Exposure to light and the atmosphere for extended periods of time caused this yellow material to undergo transformation into a white, amorphous solid which was insoluble in alkali and melted above 300°.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.66; H, 5.92. Found: C, 84.22; H, 6.04.

Isomerization of Quinone VIII to the Hydroquinone.—A solution of 2.0 g. of quinone VIII in 80 ml. of acetic acid was heated to boiling and one drop of 40% hydrobromic acid in acetic acid added. The yellow color disappeared almost immediately. Heating at the boiling point was continued for one-half hour. When the solution was diluted with several volumes of water a white product separated; weight 2.0 g. After one recrystallization from aqueous acetic acid (90%) the hydroquinone melted 256–260° dec.

Anal. Calcd. for $C_{24}H_{20}O_2$: C, 84.68; H, 5.92. Found: C, 84.23; H, 5.89.

1,2,3,4,7,12-Hexahydro-7,12-*o*-benzeno-8,11-benz[a]anthraquinone (IX).—To a boiling solution of 2.0 g. of the crude hydroquinone in 75 ml. of acetic acid was added dropwise a solution of 0.43 g. of potassium bromate in 10 ml. of water. With the first drop, the solution developed a light orange color which gradually deepened with addition of more bromate. When all had been added, the solution was cooled and diluted with 100 ml. of water to precipitate the crude quinone (IX); weight 2.0 g. Attempts to crystallize this material from alcohol–benzene mixtures or ligroin were unsuccessful, so the crude quinone was used as such in subsequent work.

Monoxime.—A solution of 0.33 g. of the crude quinone IX and 1.0 g. of hydroxylammonium chloride in 10 ml. of alcohol was refluxed for one hour. At the end of this time, 1.5 ml. of pyridine was added. Refluxing was continued for an additional hour. The solution was diluted with water. The yellow solid which separated was filtered off, washed with water and digested with 4 *N* sodium hydroxide solution. The alkaline solution was filtered and then acidified with hydrochloric acid precipitating a yellow flocculent solid which was collected on a filter, washed and dried; weight 0.26 g. Upon recrystallization from glacial acetic acid, the monoxime separated as yellow rosettes which decomposed at temperatures above 230°. A qualitative test for bromine was negative.

Anal. Calcd. for $C_{24}H_{19}NO_2$: N, 3.96. Found: N, 3.61.

1,2,3,4,7,12-Hexahydro-7,12-*o*-benzenobenz[a]anthracene (X).—Two grams of crude quinone IX was refluxed for 2 hours in solution with 25 ml. of alcohol and 2.0 g. of hydroxylammonium chloride, after which 3 ml. of pyridine was added and refluxing was continued for an additional 2.5 hours. The dark green reaction mixture was poured into water precipitating a greenish-brown material which was filtered off, washed with water and digested in 4 *N* sodium hydroxide solution. The resulting solution was filtered and then acidified with hydrochloric acid to precipitate a mixture of mono- and dioximes as a light brown material. After collecting the solid and washing with water, it was dissolved in 20 ml. of ethyl alcohol, warmed on a steam-bath and to it was added 6.6 g. of stannous chloride in 30 ml. of hydrochloric acid. The color lightened considerably after five minutes of heating. The entire mixture was poured into three volumes of water causing separation of a small amount of a brown solid. The filtrate from this was made strongly alkaline with potassium hydroxide to keep the tin compounds in solution. The insoluble pinkish-white solid was collected, washed with water and redissolved in dilute hydrochloric acid. Treatment of the acid solution with hydrogen sulfide gas caused precipitation of black sulfides of tin. Upon filtration, a clear white solution was obtained. Neutralization of this solution with sodium hydroxide caused a white flocculent precipitate of the diamine to form. The latter was separated, washed with water until free from chloride ion and then dried; weight 0.54 g. (27%).

A solution of 0.3 g. of this crude diamine in 25 ml. of acetic acid was added dropwise with stirring into a solution of 0.4 g. of sodium nitrite in 40 ml. of concentrated sulfuric acid and 40 ml. of 50% hypophosphorous acid maintained between 0–5°. The solution turned blood red. Stirring was continued for three hours at 0°, after which time the mixture was kept at 5° for 48 hours, at which time the color was light yellow. After addition of 100 g. of cracked ice the mixture was extracted thrice with 25-ml. portions of benzene. The extracts were combined and washed with water, twice with sodium hydroxide solution, twice with water again and dried. The solution was evaporated in a sublimation apparatus. Sublimation at a bath temperature of 160–210° and a presssure of 2 mm. gave a yellow-white, slightly gummy material. This material was dissolved in 5 ml. of benzene and the solution passed through a column (10 × 0.8 cm.) of alumina. An additional 8 ml. of fresh benzene was used for elution. The clear-white slightly fluorescent effluent was evaporated to dryness, and the residue was recrystallized from petroleum hexane to yield 0.030 g. (11%) of the hydrocarbon (X) as small white crystals in the form of rosettes, m.p. 194–195°. A 12.5%

---

(7) G. Schroeter, *Ber.*, **54**, 2242 (1921); B. M. Mikhailov and N. G. Chernova, *J. Gen. Chem.* (*U.S.S.R.*), **12**, 288 (1942).

(8) See also H. J. Backer and J. R. van der Bij, *Rec. trav. chim.*, **62**, 561 (1943).

yield was obtained in a duplicate deamination of the crude diamine.

Anal. Calcd. for $C_{24}H_{20}$: C, 93.46; H, 6.54. Found: C, 92.97; H, 6.45.

Synthesis of 7,12-Dihydro-7,12-*o*-benzenobenz[a]anthracene (III).—A mixture of 28 mg. of X and 12 mg. of palladium-on-charcoal was placed in an 8-cm. side-arm test-tube. The tube was flooded with nitrogen and immersed in a salt-bath, the temperature of which was raised from 160 to 300° during 30 minutes. About 5 cc. of gas was collected. The product was dissolved in benzene, filtered and evaporated to dryness. The residue was dissolved in 1 ml. of hexane at 60°. Upon cooling, white plates of III separated. The mother liquor was decanted. The crystals were washed twice with hexane and then dried; weight 23 mg. or 83%, m.p. 208–210°. A mixed melting point with the hydrocarbon prepared from anthracene and 1-nitronaphthalene showed no depression. A mixture of this material with anthracene melted at 170–196°.

A 2,4,7-trinitrofluorenone derivative of the hydrocarbon was prepared, m.p. 185–186°. A mixed melting point with the corresponding derivative of the hydrocarbon obtained from the reaction of anthracene with 1-nitronaphthalene showed no depression. A mixed melting point with the 2,4,7-trinitrofluorenone derivative of anthracene gave a depression of 30°.

Ultraviolet absorption spectra for hydrocarbon III from the two sources were identical. A Beckman quartz spectrophotometer with hydrogen lamp was used. Absorption maxima were noted as follows: (mμ, log ϵ): 245, 4.3; 263–265, 3.6; 272, 3.7; 280, 3.8; 295, 3.6.

7,14-Dihydro-7,14-*o*-benzenobenz[a]naphthacene (XI).—Naphthacene, m.p. 228–230°, was prepared from 1,2,3,4-tetrahydro-6,11-naphthacenequinone heated to 260° in an intimate mixture with zinc dust, sodium chloride and anhydrous zinc chloride by Clar's method.[9]

A mixture of 1.44 g. of naphthacene and 1.5 g. of 1-nitronaphthalene was heated for 10 hours at 275° in an open flask. Nitric oxide was evolved, and the reaction product was a black, pitch-like material partially soluble in benzene. Passage of the benzene solution over a column of alumina yielded 0.28 g. of white substance, which when recrystallized from hexane melted at 214–215°.

Anal. Calcd. for $C_{28}H_{18}$: C, 94.88; H, 5.12. Found: C, 95.08; H, 5.16.

A 2,4,7-trinitrofluorenone addition compound of XI was prepared in 80% yield by adding 5 ml. of a hot saturated solution of 2,4,7-trinitrofluorenone in alcohol to a solution of 0.1 g. of the hydrocarbon in 5 ml. of benzene. A portion was recrystallized from alcohol and melted 191–192.5°.

Anal. Calcd. for $C_{24}H_{28}N_6O_{14}$: C, 65.85; H, 2.86. Found: C, 65.85; H, 3.09.

2-Methyl-5,5a,6,11,11a,12-hexahydro-5,12-*o*-benzenonaphthacene.—2-Methylanthracene, m.p. 205–207°, was prepared by prolonged hot alkaline zinc dust reduction of 2-methylanthraquinone (in toluene) by adapting Martin's directions[10] for anthraquinone. The yield was 25%.

A mixture of 2.6 g. of 85% 1,4-dihydronaphthalene and 2.7 g. of 2-methylanthracene was sealed into a glass tube and heated for 12 hours at 245°. After opening the tube, the product was removed with the aid of benzene. Evaporation of the benzene solution left a residue which was fractionally crystallized from ligroin (b.p. 60–71°) and alcohol to give 0.75 g. (16.7%) of a white crystalline compound, m.p. 165–167°.

Anal. Calcd. for $C_{25}H_{22}$: C, 93.14; H, 6.88. Found: C, 92.91; H, 6.71.

2-Methyl-5,12-dihydro-5,12-*o*-benzenonaphthacene (XII).—Dehydrogenation of the above hydrocarbon was accomplished by heating 0.25 g. of it with palladium-on-charcoal for an hour to a maximum temperature of 255°. Hydrogen (30 cc.) was evolved. The product was recrystallized from absolute alcohol to give 0.2 g. (81%) of a white crystalline compound (XII), m.p. 174–176°. A mixed melting point determination with the starting material was 140–165°.

Anal. Calcd. for $C_{25}H_{18}$: C, 94.32; H, 5.70. Found: C, 94.05; H, 5.73.

Acknowledgment.—We are grateful to Great Lakes Carbon Corporation for generous financial support to one of us (L. J.) during the period of this work.

EVANSTON, ILLINOIS

---

[9] E. Clar, *Ber.*, **72**, 1645 (1939).

[10] E. L. Martin, THIS JOURNAL, **58**, 1438 (1936).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA, BERKELEY]

The Structure of ψ-Santonin

BY WILLIAM G. DAUBEN AND PAUL D. HANCE[1]

RECEIVED AUGUST 20, 1954

The relative positions of the hydroxyl group, the lactone and the olefinic double bond in ψ-santonin have been determined. It was found that both the free hydroxyl group and the lactonic hydroxyl group are gamma to the carboxyl group of the side-chain and that the hydroxyl grouping is secondary. The carbon–carbon double bond was shown to be tetrasubstituted and in the ring opposite but allylic to the lactonic hydroxyl group. It was demonstrated that in the dihydrogenation of ψ-santonin, hydrogenolysis of the lactone ring occurred. A new structure for this sesquiterpene has been postulated and preliminary results with regard to the stereochemistry of the molecule have been discussed.

ψ-Santonin is one of the sesquiterpenic lactones isolated from various species of the plant family Artemisia[2] and the structure of this compound has received considerable attention.[3,4] Degradation studies by Clemo and Cocker[5] and Cocker and his co-workers[3] have established that ψ-santonin has a normal isoprenoid structure of the eudalene group, a carbon skeleton also possessed by santonin, β-santonin and artemisin which occur in the same plant family.[6] In addition to the lactonic function, the presence of a carbonyl group, a free hydroxyl and a carbon–carbon double bond also have been demonstrated, but of the latter groupings only the carbonyl group has been established fairly firmly as being located at C_1.[7] Recently, Dauben and Hance[4] reported an extensive study with

---

[1] Recipient of the Dow Fellowship in Chemistry, Univ. of Calif., 1953–1954.

[2] Messrs. T. and H. Smith, Ltd., *Pharm. J.*, **80**, 3 (1935).

[3] W. Cocker, B. E. Cross and D. H. Hayes, *Chemistry & Industry*, 314 (1952), and earlier papers.

[4] W. G. Dauben and P. D. Hance, THIS JOURNAL, **75**, 3352 (1953).

[5] G. R. Clemo and W. Cocker, *J. Chem. Soc.*, 30 (1946).

[6] An excellent summary of these structural studies is to be found in J. Simonsen and D. H. R. Barton, "The Terpenes," Vol. III, University Press, Cambridge, England, 1951.

[7] The ring numbering system employed in the present paper differs from that suggested by Cocker[3] in that the reactive carbonyl group is called C_1 rather than C_4. For details of the present numbering system as well as changes in nomenclature see footnote 10.