is roughly so. This is true also in the case of sodium anthraquinone β-sulfonate. With sodium anthraquinone 1,5-disulfonate IV, no runs at the same (H$^+$) with different concentrations of catalyst are available, so the dependence of rate constants on catalyst concentration is not clearly visible without a more adequate treatment of the dependence of rate on (H$^+$). However, it is clear that both k_c and κ_c rise with catalyst concentration.

Even the short survey here reported shows how differently may various catalysts of the quinone–phenazine class behave in the titanous chloride–iodine reaction. Thus we have the rate law 2 for indigo carmine II. For pyocyanine V and α-hydroxyphenazine VII, we have the rate law 1, as though reduction of the catalyst is rate-determining. Making the structural change from α-hydroxyphenazine (VII) to β-hydroxyphenazine (III) gives the rate law 5 which is also followed by the anthraquinone derivatives IV and VI. The rate law 5 corresponds to two terms in the rate, one the same as for rate law 1, the other an additional term proportional to both titanous ion and iodine. The latter third order term is especially interesting since it corresponds to a rate-determining transaction involving the reducing agent, titanous ion, the catalyst and the oxidizing agent, iodine.

The dependence of rate on hydrogen ion concentration can be involved, as is illustrated by the data in Table II. For example, while k_c for VI does not increase when (H$^+$) is decreased from 0.177 to 0.101 M, for IV it increases rapidly.

Acknowledgment.—One of us (C. E. J., Jr.) is indebted to E. I. du Pont de Nemours and Co. for a fellowship during the year 1949–1950.

LOS ANGELES, CALIF. RECEIVED JULY 13, 1951

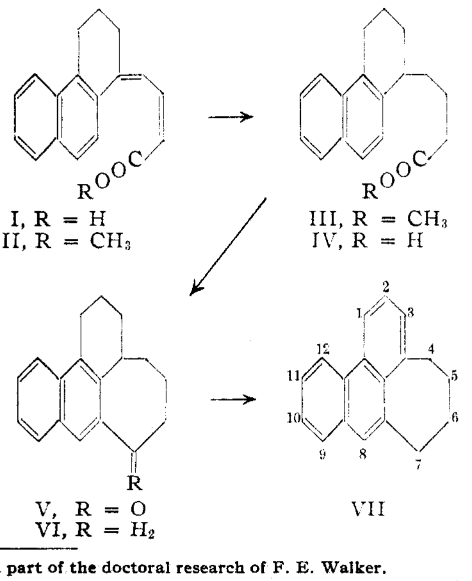
[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

Seven-membered Ring Compounds. III. 4,5,6,7-Tetrahydrocyclohepta[jk]phenanthrene

BY W. J. HORTON AND F. E. WALKER[1]

The structure of 4,5,6,7-tetrahydrocyclohepta[jk]phenanthrene has been established by two independent syntheses. The synthesis of 7,8,9,10-tetrahydrocyclohepta[de]naphthalene (VIII) from benzosuberone has been improved and it has been shown that VIII is attacked in position 2 or 3 by succinic anhydride.

In a previous investigation[2] the peri-cyclization of γ-tetrylbutyric acid was brought about in excellent yield by the use of phosphorus pentoxide in orthophosphoric acid. In a similar manner, from 1-keto-1,2,3,4-tetrahydrophenanthrene and methyl γ-bromocrotonate, γ-1-(1,2,3,4-tetrahydrophenanthryl)-butyric acid (IV) has been prepared in four steps and submitted to cyclization. This acid (IV) has been made previously[3a,b] as an intermediate in the synthesis of chrysenes and the process used here is that of Cook.[4] There appear to be no attempts to cyclize this acid using the conventional methods.



I, R = H
II, R = CH_3

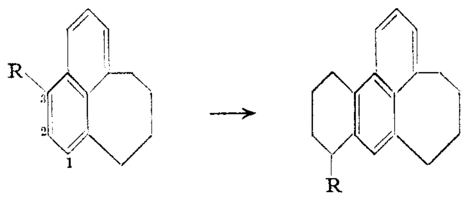
III, R = CH_3
IV, R = H

V, R = O
VI, R = H_2

VII

The phosphorus pentoxide–phosphoric acid procedure converted the acid IV to a viscous oil V which could not be crystallized. The oil, however, formed a crystalline semicarbazone in excellent yield. Decomposition of the semicarbazone (Wolff–Kishner) gave the hydrocarbon VI and dehydrogenation of VI over palladium–charcoal produced VII which crystallized with ease and formed a picrate.

By analogy with acenaphthene and α-methylnaphthalene, it might be predicted that 7,8,9,10-tetrahydrocyclohepta[de]naphthalene (VIII) would be attacked at position 3 by electrophilic reagents. The following series of reactions conclusively demonstrate that the point of attack is position 3 or 2 and position 3 is thought to be the more likely. The hydrocarbon VIII gave an aroylpropionic acid (IX) when treated with succinic anhydride and aluminum chloride in nitrobenzene. The keto acid IX was reduced to the arylbutyric acid X. Cyclization of the acid chloride of X by means of stannic chloride gave a ketone XI. The noncyclization of X to the alternate position 4 is of interest since the difficulties of such a second peri-cyclization have been noted[5] in the case of the formation of a second five-membered ring. The ketone XI was reduced to the carbinol XII by



VIII, R = H
IX, R = $CO(CH_2)_2COOH$
X, R = $(CH_2)_3COOH$

XI, R = O
XII, R = OH

---

[1] A part of the doctoral research of F. E. Walker.

[2] R. C. Gilmore and W. J. Horton, THIS JOURNAL, **73**, 1411 (1951).

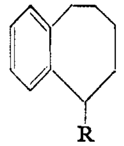
[3] (a) J. Hoch, *Compt. rend.*, **207**, 921 (1938); (b) W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **5**, 416 (1940).

[4] J. W. Cook and R. Schoental, *J. Chem. Soc.*, 288 (1945).

[5] M. C. Kloetzel and F. L. Chubb, THIS JOURNAL, **72**, 150 (1950).

means of lithium aluminum hydride and this lost water and hydrogen when heated over palladium-charcoal to produce VII with properties identical to those previously noted. The attack at position 2 by succinic anhydride is not excluded since ring closure to the 3-position would lead to the same final product.

In a previous synthesis of 7,8,9,10-tetrahydrocyclohepta[de]naphthalene (VIII) from benzosuberone,[2] a considerable amount of material proved not to be the desired β-5-benzosuberylpropionic acid XV but probably the α-5-benzosuberyl-isomer. By means of a Darzens reaction using benzosuberone and ethyl chloroacetate with sodium hydride as a condensing agent, a glycidic ester was obtained which was saponified and converted to 5-benzosuberylaldehyde (XIII). This with malonic acid in pyridine gave an unsaturated acid XIV. Catalytic reduction gave XV which was cyclized and the oxime of the ketone obtained was found to agree with the m.p. of the oxime reported.[2] A mixture of the oximes melted undepressed.



XIII, R = CHO
XIV, R = CH=CHCOOH
XV, R = $(CH_2)_2COOH$

The use of polyphosphoric acid[6] for cyclization rather than phosphorus pentoxide–phosphoric acid would greatly add to the convenience of the method.[2] It has been found[8] that δ-phenylvaleric acid is converted to benzosuberone in essentially the same yield by polyphosphoric acid (83% total phosphorus pentoxide content) as was obtained by the reported method.[2] When polyphosphoric acid was combined with a small amount of orthophosphoric acid to give a calculated total phosphorus pentoxide content of 80.5%, the yield remained unchanged. An acid mixture of 75% total phosphorus pentoxide content, however, did not cyclize phenylvaleric acid and the unreacted acid was recovered with a loss of only 4%.

This work received assistance in the form of a Frederick Gardner Cottrell Grant for which we express our great appreciation. The gift of samples of polyphosphoric acid by the Victor Chemical Company is gratefully acknowledged.

Experimental[9]

Benzosuberone.[8]—Commercial polyphosphoric acid cyclized[2] δ-phenylvaleric acid in 83.3% yield. Dilution of the polyphosphoric acid using 85% orthophosphoric acid to a phosphorus pentoxide content of 80.5% resulted in 85.5% yield. When the dilution was made to a phosphorus pentoxide content of 75%, the starting acid was recovered in 96% yield.

5-Benzosuberylaldehyde (XIII).—To a mixture of 8.8 g. of benzosuberone and 10.2 g. of ethyl chloroacetate cooled under dry nitrogen in an ice-bath there was added portionwise with mechanical stirring 1.32 g. of sodium hydride over a 1-hour period. Stirring was continued while the mixture stood overnight and warmed to room temperature. The absence of sodium hydride in the red solution was determined by the addition of a drop of methanol. Then ice and 50 cc. of 1:1 hydrochloric acid was added and the product was collected in benzene. The water washed benzene solution was evaporated and the residue was dissolved in 105 cc. of ethyl alcohol to which was added 10 g. of potassium hydroxide in 100 cc. of water. After refluxing for 1 hour the alcohol was removed *in vacuo* and the solution was acidified. A red oil separated and was collected in benzene. The benzene solution was washed, dried, filtered and evaporated. The residue lost carbon dioxide at 140° at 18 mm. Distillation of the product gave 7.0 g. of colorless aldehyde, b.p. 90–93° (0.95 mm.). The material reduced Fehling and Tollens reagents.

Anal. Calcd. for $C_{12}H_{14}O$: C, 82.72; H, 8.10. Found: C, 82.45; H, 7.72.

The semicarbazone (0.187 g.) from 0.207 g. of aldehyde was obtained as colorless plates, m.p. 205–206° after extensive recrystallization from methanol.

Anal. Calcd. for $C_{13}H_{17}ON_3$: N, 18.2. Found: N, 18.2.

β-(5-Benzosuberyl)-propionic Acid (XV).[2]—A mixture of 4.0 g. of the above aldehyde, 3.0 g. of malonic acid, 6.1 cc. of dry pyridine and 3 drops of piperidine was warmed on the water-bath for 72 hours. The reaction mixture when acidified with dilute acid gave an oil which was dissolved in benzene, transferred by washing to 10% sodium hydroxide and by acidification again transferred to benzene. Distillation of the benzene gave 3.0 g. of XIV, b.p. 135–142° (0.4 mm.).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.67; H, 7.66.

Catalytic hydrogenation of 1.12 g. of XIV in 10 cc. of glacial acetic acid over platinum at room temperature required 1.5 hours for the theoretical amount of hydrogen to be absorbed. Removal of the catalyst and the solvent gave 1.1 g. of light yellow oil XV which could not be crystallized. The acid distilled as a colorless oil, b.p. 140–147° (0.3 mm.).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.27; H, 8.69.

The amide was obtained in 51% yield as straw colored crystals, m.p. 95.5–97°, after repeated recrystallization from aqueous methanol and benzene–petroleum ether (60–70°). Mixed with the compound reported,[2] m.p. 101–102°, the mixture melted at 94–96.5°. A redetermination of the m.p. of the sample available from the previous work confirmed the m.p. reported. Cross seeding did not support the possibility of two polymorphic forms.

Cyclization of XV according to the reported procedure[2] gave a ketone whose oxime, m.p. 151–152°, did not depress the m.p. of that previously prepared.[2]

γ-1-(1,2,3,4-Tetrahydrophenanthryl)-butyric Acid (IV).—Using a procedure identical to that reported for α-tetralone,[2] 3.6 g. of 1-keto-1,2,3,4-tetrahydrophenanthrene[10] and 1.5 cc. of methyl γ-bromocrotonate after refluxing for 10 hours and standing at room temperature for 60 hours gave 5.1 g. of light yellow oil. Dehydration of 5 g. of this oil with 60 cc. of 90% formic acid over boiling water for 1 hour gave 4.5 g. of yellow viscous oil[4] II. Hydrogenation of the ester II in glacial acetic acid with 0.30 g. of platinum oxide gave 4.5 g. of yellow oil III. Absorption of 550 cc. of hydrogen was observed; calculated for two double bonds, 720 cc. On saponification by refluxing III in aqueous alcoholic potassium hydroxide for 2 hours and acidifying, 2.77 g. of solid IV was obtained. After crystallization of 100 mg. from methanol–water, and then from aqueous acetic acid, 60 mg., m.p. 93–95°, was obtained; reported[3a] m.p. 94–95°.

7-Keto-1,2,3,3a,4,5,6,7-octahydrocyclohepta[jk]phenanthrene (V).—Cyclization[2] of 1.10 g. of IV by means of 45.8 g. of a solution of 22.0 g. of phosphorus pentoxide in 14.0 cc. of orthophosphoric acid gave a neutral oil. Extraction of this non-acidic material gave 0.78 g. of alcohol soluble viscous oil V. This material gave a positive test with 2,4-dinitrophenylhydrazine.

---

[6] The work of R. N. Bell, *Ind. Eng. Chem.*, **40**, 1464 (1948), on the composition of polyphosphoric acid suggested its identity to the solution used in this and in the preceding work. Commercially available polyphosphoric acid has been recently reported[7] for the closure of several six-membered rings.

[7] H. R. Snyder and F. X. Werber, THIS JOURNAL, **72**, 2966 (1950).

[8] Work of G. Thompson.

[9] Melting points are uncorrected.

[10] R. D. Haworth, *J. Chem. Soc.*, 1125 (1932).

The semicarbazone was prepared as described above in quantitative yield and was obtained as colorless crystals after recrystallization from ethanol and from benzene–petroleum ether (60–70°), m.p. 209.5–210.5°.

Anal. Calcd. for $C_{19}H_{21}ON_3$: N, 13.7. Found: N, 13.7.

4,5,6,7-Tetrahydrocyclohepta[jk]phenanthrene (VII).—The semicarbazone of V (0.650 g.) was heated in a sealed tube with a solution of 1.5 g. of sodium in 41 cc. of absolute alcohol at 180° for 20 hours. From the reaction mixture 0.495 g. of a viscous oil VI was obtained which could not be crystallized. Dehydrogenation of 0.495 g. of VI with 0.10 g. of palladium–charcoal[11] in an atmosphere of nitrogen and a temperature of 270–280° for 3 hours gave the expected amount of hydrogen and a light yellow oil which crystallized at room temperature. Treatment with warm petroleum ether (30–60°) dissolved material which crystallized on cooling, yielding 0.398 g. of colorless crystals. Recrystallization from methanol of material which had been converted to the picrate and recovered gave colorless rosettes of prisms, m.p. 59.5–60.5°.

Anal. Calcd. for $C_{18}H_{16}$: C, 93.06; H, 6.94. Found: C, 93.23; H, 7.04.

The picrate from VII and an equivalent weight of picric acid in warm alcohol separated as red-orange needles in 85% yield and melted at 117–118° after repeated recrystallization from ethanol.

Anal. Calcd. for $C_{24}H_{19}O_7N_3$: N, 9.11. Found: N, 8.90.

β-3-(7,8,9,10-Tetrahydrocyclohepta[de]naphthoyl)-propionic Acid (IX).—To a solution of 1.333 g. of anhydrous aluminum chloride in 5 cc. of nitrobenzene at −5 to −2° was added over a 40-minute period 0.900 g. of VIII[2] and 0.450 g. of succinic anhydride in 5 cc. of nitrobenzene. After the addition of 0.100 g. of succinic anhydride and 2 cc. of nitrobenzene, the temperature was allowed to come to −2 to 4° over a 2-hour period and then slowly to room temperature while standing overnight. The reaction mixture was decomposed with aqueous acid and the nitrobenzene was removed by steam distillation. The cooled residue was extracted with benzene and the benzene was washed, dried and evaporated. Extraction of the residue with warm petroleum ether (30–60°) gave after evaporation of the solvent, 1.220 g. of brown bicarbonate soluble oil. By activated charcoal treatment of a solution of the oil in aqueous sodium bicarbonate and acidification, a solid was obtained. Repeated crystallization from methanol gave almost colorless prisms, m.p. 127.5–128°.

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.43. Found: C, 76.39; H, 6.30.

γ-3-(7,8,9,10-Tetrahydrocyclohepta[de]naphthyl)-butyric Acid (X).—Reduction of 1.247 g. of IX by the Clemmensen procedure[12] with refluxing for 33 hours gave 1.074 g. of light colored oil which crystallized at room temperature. Recrystallization from aqueous methanol gave colorless rosettes of prisms, m.p. 130.5–131°. The compound gave a negative test with 2,4-dinitrophenylhydrazine and mixed with the keto-acid IX melted at 113–123°.

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.31; H, 7.55.

9-Keto-4,5,6,7,9,10,11,12-octahydrocyclohepta[jk]phenanthrene (XI).—A solution of 0.502 g. of the acid X in 7.5 cc. of dry benzene in an ice–salt-bath was treated with 0.412 g. of phosphorus pentachloride and allowed to come to room temperature and stand for 26 hours. The cooled solution was then treated with 0.5 cc. of stannic chloride in 1.25 cc. of benzene and held at 5° for 45 minutes and at room temperature for 10 minutes with intermittent swirling. Decomposition of the complex in the usual manner[13] gave 0.413 g. of a light colored neutral oil which gave a positive test with 2,4-dinitrophenylhydrazine. The semicarbazone (87% yield) melted at 253–254° when recrystallized from glacial acetic acid containing 1 drop of water.

Anal. Calcd. for $C_{19}H_{21}ON_3$: N, 13.7. Found: N, 13.9.

4,5,6,7,9,10,11,12-Octahydrocyclohepta[jk]-9-phenanthrol (XII).—To 0.150 g. of lithium aluminum hydride in 5 cc. of anhydrous ether with cooling in an ice-bath was added in portions 0.410 g. of XI in 5 cc. of ether over a 5-minute period. An additional 5 cc. of ether was used to complete the transfer of the ketone. After standing with occasional swirling at room temperature for 10 minutes the mixture was treated cautiously with methanol, water and then 6 *N* sulfuric acid. The product collected in ether weighed 0.363 g. when the ether was removed and could not be crystallized.

4,5,6,7-Tetrahydrocyclohepta[jk]phenanthrene (VII).—As described above, 0.303 g. of XII and 80 mg. of palladium–charcoal[11] gave 85% of the expected volume of hydrogen and 0.232 g. of light brown oil. The oil was converted to 0.189 g. of red-orange picrate as described above, which melted at 117–118° after recrystallization from 95% ethyl alcohol. A mixture of the two samples of the picrate melted at the same temperature.

A benzene solution of the picrate, after thorough washing with 1% aqueous ammonia and evaporation of the benzene gave 50 mg. of light yellow oil which solidified when cooled. Recrystallization from aqueous methanol gave prisms m.p. 58.5–60° and the m.p. was identical when mixed with the sample prepared previously.

SALT LAKE CITY 1, UTAH

RECEIVED MAY 5, 1951

---

[11] N. D. Zelinski and M. B. Turowa-Pollak, *Ber.*, **58**, 1295 (1925).

[12] E. L. Martin, "Organic Reactions," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1942, p. 155.

[13] W. S. Johnson, *ibid.*, Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 114.