[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, WAYNE UNIVERSITY]

# Cyclic Dienes. II. A New Synthesis of Pentacene[1,2]

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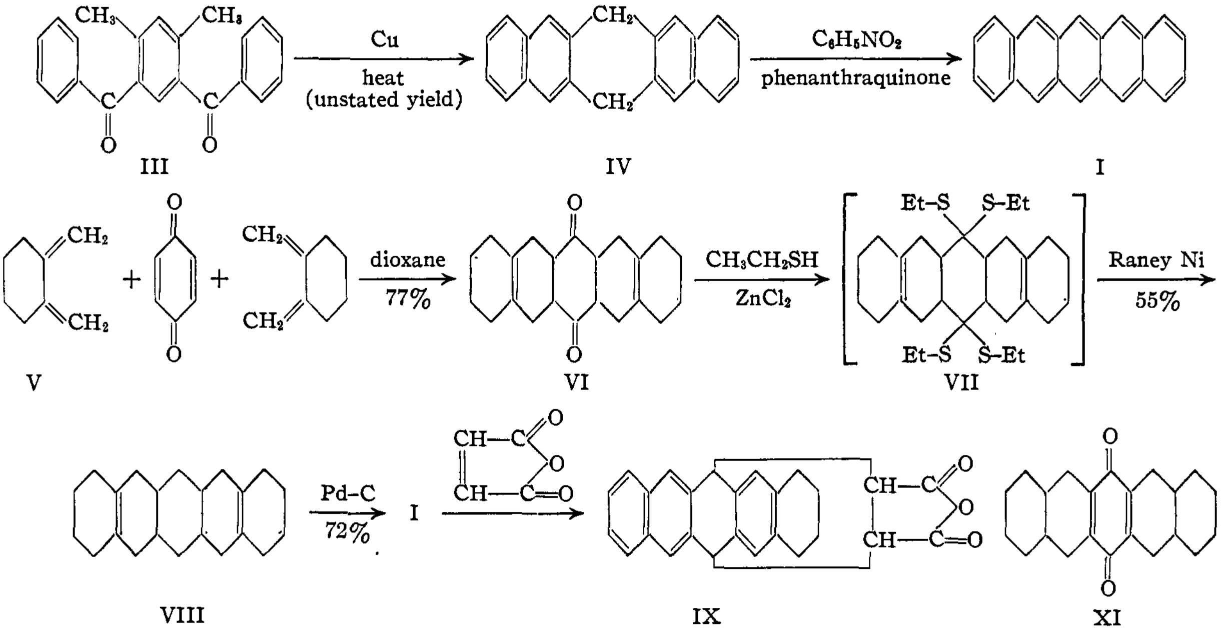
A general method for the synthesis of linear condensed polynuclear aromatic hydrocarbons is outlined. Pentacene (I) is synthesized in an over-all yield of 30% starting with 1,2-dimethylenecyclohexane (V).

Although many excellent syntheses have been developed for angular condensed aromatic hydrocarbons, no good general method has been worked out for the linear condensed ring systems.[4] This is due to the fact that most common ring closures tend to proceed in the angular position. Pentacene (I) was first synthesized by Clar and John[5] starting from *m*-xylophenone (II). A vigorous Friedel–Crafts reaction yielded 40% of 4,6-dibenzoyl-1,3-dimethylbenzene (II) from a complex mixture. Heating with copper in a modified Elbs reaction converted III into dihydropentacene (IV) in an unstated yield. Dehydrogenation of IV to I was accomplished by boiling the dihydro derivative in nitrobenzene with phenanthraquinone or by passing over copper at 350–400°.



Since Cook and Lawrence[6] were able to synthesize 1,2,5,6-dibenzanthracene from 1-vinylcyclohexene and quinone, it was considered likely that a synthesis of pentacene could be worked out using the readily available 1,2-dimethylenecyclohexane (V)[2] and quinone. Thus it was found that refluxing V with benzoquinone produced a 77% yield of 6,13-diketo-$\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene (VI). All attempts to simultaneously dehydrogenate and deoxygenate VI directly to pentacene failed. Although Cook and Lawrence[6] converted 9,10-diketoöctadecahydro-1,2,5,6-dibenzanthracene directly to 1,2,5,6-dibenzanthracene by heating over platinum at 300°, similar treatment of VI produced only partially dehydrogenated products that sublimed at a low temperature. Zinc dust distillation of VI produced a mixture of products containing 6,13-pentacenequinone (X).

Since the direct methods failed, procedures for the reduction of the two carbonyl groups were investigated. Wolff–Kishner reduction of VI yielded a mixture of products. Chromatography over alumina produced a small amount of the hydrocarbon VIII plus a yellow solid. Probably the base rearranged the double bonds to produce the quinone XI which would not be expected to produce the hydrocarbon under the Wolff–Kishner conditions.[7]

An excellent method for removing the oxygen atom was developed by applying the method of Wolfrom and Karabinos[8] for the desulfurization of the corresponding thioketal. Treatment of VI with an excess of ethyl mercaptan in the presence of zinc chloride produced the crude tetraethyltetrathiodiketal (VII), which was not purified but treated directly with Raney nickel to produce VIII

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[2] Previous paper in this series, THIS JOURNAL, **75**, 4780 (1953).

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[4] E. Clar, "Aromatische Kohlenwasserstoffe," Springer Verlag, Berlin, 1941.

[5] E. Clar and F. John, *Ber.*, **62**, 3027 (1929); **63**, 2967 (1930); **64**, 2194 (1931).

[6] J. W. Cook and C. A. Lawrence, *J. Chem. Soc.*, 58 (1938).

[7] D. Todd in R. Adams, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, 1948, p. 378; J. Thiele and P. Barlow, *Ann.*, **302**, 311 (1898).

[8] M. L. Wolfrom and J. V. Karabinos, THIS JOURNAL, **66**, 909 (1944).

in an over-all yield of 55%. The hydrocarbon VIII was smoothly dehydrogenated to pentacene (I) by heating with 5% palladium-on-carbon for 3 hours at 245°. Purification of I by sublimation at 300° (5 mm.) in a stream of carbon dioxide afforded pure pentacene in a 72% yield. The violet-blue pentacene was characterized by analysis and conversion to its maleic anhydride adduct IX. The properties of these two products agreed with those previously reported by Clar and John.[5]

Thus, this direct, easy synthesis of I in an over-all yield of 30% from 1,2-dimethylenecyclohexane (V) appears to be a considerable improvement over previous methods. Since the procedure used in the synthesis of the cyclic diene V is general, this method can be applied to other linear condensed polynuclear aromatic hydrocarbons.

## Experimental

**6,13-Diketo-$\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene (VI).**—In a 50-ml. round-bottom flask was placed a solution of 5 g. (0.048 mole) of 1,2-dimethylenecyclohexane[2] and 2.5 g. (0.024 mole) of benzoquinone in 25 ml. of dioxane (purified). The solution was heated under reflux until a precipitate formed (2 hours) and then an additional hour. The precipitated adduct was filtered, washed well with ether and recrystallized from chloroform–petroleum ether (30–60°). There was obtained 5.8 g. (77%) of fluffy white needles of 6,13-diketoöctadecahydropentacene (VI), m.p. 225–226°.

*Anal.* Calcd. for $C_{22}H_{28}O_2$: C, 81.48; H, 8.64. Found: C, 81.39; H, 8.78.

**$\Delta^{4a(14a),7a(11a)}$-Octadecahydropentacene (VIII). A. By Wolff–Kishner Reduction.**—A mixture of 2 g. (0.006 mole) of the above diketoöctadecahydropentacene (VI), 1.84 ml. of hydrazine hydrate (80% aqueous solution), 10 ml. of triethylene glycol and 1.2 g. of potassium hydroxide was heated under reflux for 1.5 hours according to the directions of Huang-Minlon.[9] The water was then drained from the condenser, the temperature was allowed to rise to 195°, and the refluxing was continued for 4 hours. The cooled solution was diluted with 20 ml. of water and poured slowly into 10 ml. of 6 *N* hydrochloric acid. The resulting yellow solid was filtered and dried (wt. 1.80 g.).

On recrystallizing from a benzene–alcohol mixture, there was obtained a light yellow-orange solid, m.p. 110–143°, which could not be purified further by recrystallization.

The colored material from several runs (2 g.) was combined, dissolved in benzene, and chromatographed on a 30 × 2 cm. alumina column. The column was eluted with 50-ml. portions of benzene until the yellow band had moved down the column and begun to appear in the eluate. These eluates (which had a slight violet-blue fluorescence) were combined, evaporated to dryness, and extracted with 100 ml. of petroleum ether. The extract was then evaporated to dryness and the residue was recrystallized from chloroform–petroleum ether. There was obtained 34 mg. of white needles, m.p. 127–128°. Mixed melting point with an authentic sample of $\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene prepared below showed no depression. The yellow substance formed during the reaction was assumed to be the quinone XI but was not characterized.

**B. By Desulfurization of the Dithioketal.**—Following the desulfurization procedure of Newman and Walborsky,[10] 1.7 g. of anhydrous zinc chloride was placed in 50-ml. flask and fused under vacuum. After adding 3 g. (0.011 mole) of the above diketone VI, 1 g. of anhydrous sodium sulfate and 35 ml. of ethyl mercaptan, the flask was well stoppered and shaken at room temperature until the zinc chloride dissolved. After standing overnight at room temperature, the reaction mixture was heated to remove the excess ethyl mercaptan. The residue was taken up in ice-water and ether. The aqueous layer and insoluble material (zinc oxychloride) were extracted thoroughly with ether. The combined ether extracts were washed with 10% aqueous sodium hydroxide solution, water and saturated sodium chloride solution. After the solution was dried over anhydrous sodium sulfate, the ether was removed by distillation leaving the crude dithioketal.

This crude dithioketal was dissolved in ethanol and added to a suspension of 50 g. of Raney nickel catalyst (W-4)[11] in a total volume of 175 ml. of ethanol. After the mixture had been refluxed for about 12 hours, the catalyst was removed by centrifuging and thoroughly washed with hot benzene. The benzene washings and alcoholic filtrate were evaporated to dryness and the resultant white solid recrystallized from a benzene–alcohol mixture to yield 1.4 g. (55%) of $\Delta^{4a(14a),7a(11a)}$-octadecahydropentacene (VIII), m.p. 131–132°.

*Anal.* Calcd. for $C_{22}H_{32}$: C, 89.19; H, 10.81. Found: C, 89.49; H, 10.74.

**Pentacene (I).**—A mixture of 75 mg. (0.00026 mole) of octadecahydropentacene (VIII) and 100 mg. of 5% palladium-on-charcoal was heated at 245° in a test-tube with two side arms and a cold finger until the calculated amount of hydrogen (96%) swept out with carbon dioxide was collected in a gas buret containing 30% potassium hydroxide solution. Some material sublimed during the dehydrogenation. This was recovered and converted to pentacene by use of a larger quantity of catalyst. The combined mixture of catalyst and pentacene was transferred to a 100-ml. three-neck round-bottom flask fitted with an inlet capillary tube, a cold finger, and an exit to the vacuum pump. The pentacene was sublimed onto the cold finger in a stream of carbon dioxide at 5–8 mm. pressure by heating the flask in a Woods metal-bath at 270–300°. The yield of the violet-blue pentacene (I) was 52 mg. (72%). In accordance with the observation of Clar and John[5] the pentacene (I) sublimed below its melting point.

*Anal.* Calcd. for $C_{22}H_{14}$: C, 94.96; H, 5.04. Found: C, 94.68; H, 4.82.

**Maleic Anhydride Adduct of Pentacene (IX).**—A mixture of palladium-on-charcoal catalyst and pentacene prior to purification [obtained from 55 mg. (0.0002 mole) of octadecahydropentacene] was suspended in 6 ml. of xylene according to the directions of Clar.[5] To this suspension was added 32 mg. (0.00032 mole) of maleic anhydride, and the solution was heated to boiling for 10 minutes. The hot solution was filtered and the adduct crystallized on cooling to yield 63 mg. (92%) of the microcrystalline needles of IX. This adduct was recrystallized from a chloroform–petroleum ether mixture to yield white crystals, m.p. 295°, decomposing to a red liquid in agreement with Clar's observations.[5]

*Anal.* Calcd. for $C_{26}H_{16}O_3$: C, 82.98; H, 4.26. Found: C, 82.78; H, 4.01.

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[9] Huang-Minlon, THIS JOURNAL, **68**, 2487 (1946).

[10] M. S. Newman and H. M. Walborsky, *ibid.*, **72**, 4296 (1950).

[11] A. A. Pavlic and H. Adkins, *ibid.*, **68**, 1471 (1946).