[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, WAYNE UNIVERSITY AND THE UNIVERSITY OF MARYLAND]

Cyclic Dienes. XI. New Syntheses of Hexacene and Heptacene[1,2]

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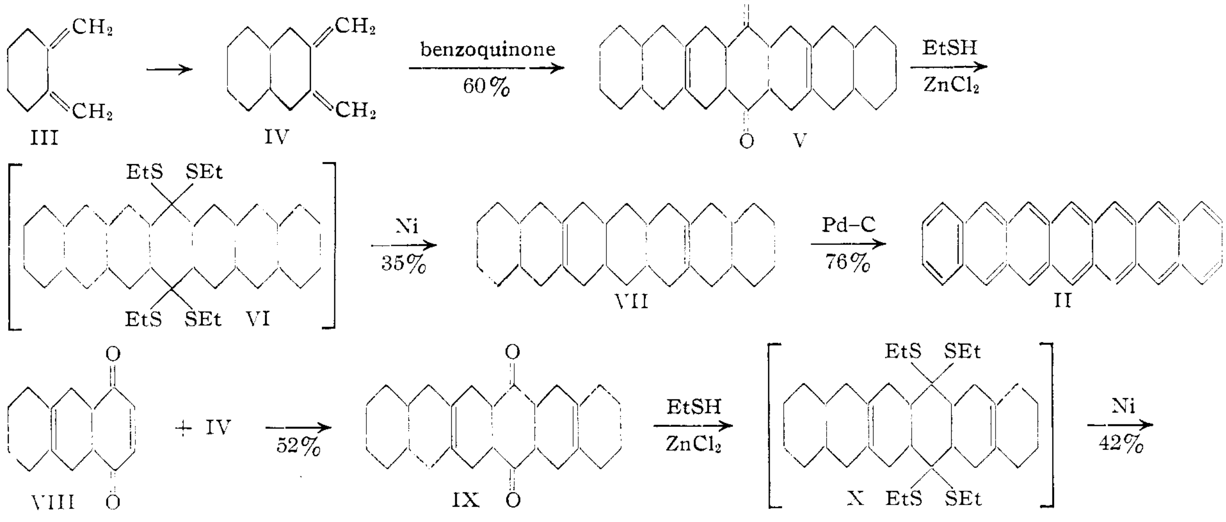
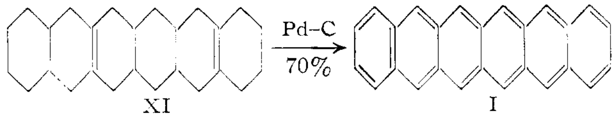
A general method for the synthesis of linear condensed polynuclear aromatic hydrocarbons has been developed. Heptacene was synthesized in three steps from 2,3-dimethylenedecalin in an over-all yield of 14%. Hexacene was synthesized from 1,2-dimethylenecyclohexane and 2,3-dimethylenedecalin in four steps in an over-all yield of 15%.

Because of the tendency of most aromatic ring closures to proceed in the angular position, no excellent general method for the synthesis of linear condensed polynuclear hydrocarbons has been described. However, Clar[5] was able to synthesize hexacene (I) in an unreported yield by taking advantage of the fact that partially hydrogenated aromatic derivatives will give some of the linear product. A laborious four-step synthesis starting from 4-(2-carboxybenzoyl)-phthalic anhydride and tetralin produced only a small amount of hexacene (I).





In a similar synthesis, Clar[6,7] synthesized heptacene (II) in an unreported yield.

Since both these syntheses are long and produce a very low yield, neither could be conveniently adapted for the syntheses of substituted linear condensed polynuclear hydrocarbons. However, it had been shown previously[8] that pentacene could be synthesized from 1,2-dimethylenecyclohexane (III) by a three-step procedure in an over-all yield of 30%. It was of interest, therefore, to extend this procedure to the syntheses of hexacene and heptacene. An approach was made possible by the fact that a general procedure for ascending a diene series by the addition of a cyclohexane ring had been developed[9] and recently applied to the synthesis of 2,3-dimethylenedecalin (IV) in five steps starting from 1,2-dimethylenecyclohexane (III).[1] When 2 moles of the diene IV was heated under reflux in dioxane with 1 mole of benzoquinone, the Diels–Alder adduct, $\Delta^{5a(17a),8a(14a)}$-hexacosahydroheptacene-7,16-dione (V), was produced in a 60% yield. V was converted to the heptacyclic tetraethyltetrathiodiketal VI by shaking for 24 hours with ethyl mercaptan and zinc chloride. The crude VI was not purified but was treated directly with Raney nickel to produce $\Delta^{5a(17a),8a(14a)}$-hexacosahydroheptacene (VII) in an over-all yield of 35%. Catalytic dehydrogenation of VII produced a 76% yield of heptacene (II). The over-all yield of II from IV was 14%.

In a previous paper[10] it was shown that unsymmetrical polycyclic Diels–Alder adducts could be prepared by treating benzoquinone with a molar equivalent of one cyclic diene, followed by a reaction of this monoadduct with a second cyclic diene. Thus, when $\Delta^{2,5a(9a)}$-decahydroanthracene-1,4-dione (VIII), the monoadduct of 1,2-dimethylenecyclohexane (III) and benzoquinone, was heated with 2,3-dimethylenedecalin (IV), a 52% yield of the unsymmetrical $\Delta^{4a(16a),7a(13a)}$-docosahydrohex-

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[1] Previous paper in this series, THIS JOURNAL, **77**, 990 (1955).

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[4] Office of Naval Research Fellow, Wayne University, 1951.

[5] E. Clar, *Ber.*, **75B**, 1283 (1942).

[6] E. Clar, *ibid.*, **75B**, 1330 (1942).

[7] C. Marschalk, *Bull. soc. chim.*, **10**, 511 (1943).

[8] W. J. Bailey and M. Madoff, THIS JOURNAL, **75**, 5603 (1953).

[9] W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **76**, 2251 (1954).

[10] W. J. Bailey, J. Rosenberg and L. J. Young, *ibid.*, **76**, 3009 (1954).

acene-6,15-dione (IX) was produced. By a procedure very similar to that described for the synthesis of heptacene, IX was converted to a crude hexacyclic tetraethyltetrathiodiketal X by means of ethyl mercaptan and zinc chloride. This crude X again was not purified but was treated directly with Raney nickel to produce $\Delta^{4a(16a),7a(13a)}$-docosahydrohexacene (XI) in an over-all yield of 42%. Catalytic dehydrogenation over palladium-on-charcoal produced hexacene (I) in a 70% yield. The over-all yield of hexacene (I), based on the 2,3-dimethylenedecalin (IV), was 15%.

Thus, a completely general method for the syntheses of linear condensed polynuclear hydrocarbons has been demonstrated. Since methods have been developed for the syntheses of cyclic dienes with a wide variety of substituents and for the addition of any number of cyclohexane rings in a linear manner to any diene, it is now possible to prepare polycyclic compounds with a large number of substituents and rings. Since the Diels–Alder reaction may be carried out stepwise, both symmetrical and non-symmetrical polycyclic derivatives can be produced. The application of this convenient method to the syntheses of other linear condensed polynuclear aromatic hydrocarbons is being studied in this Laboratory.[3]

Experimental[11]

$\Delta^{5a(17a),8a(14a)}$-Hexacosahydroheptacene-7,16-dione (V).—A mixture of 1.6 g. (0.01 mole) of 2,3-dimethylenedecalin (IV) and 0.54 g. (0.005 mole) of purified benzoquinone was heated under reflux in 20 ml. of dioxane for 3 hours. After the reaction mixture was cooled, a white solid precipitated out. The precipitate was filtered off and recrystallized from benzene to yield 1.2 g. (60%) of $\Delta^{5a(17a),8a(14a)}$-hexacosahydroheptacene-7,16-dione (V), m.p. 288° dec.

Anal. Calcd. for $C_{30}H_{40}O_2$: C, 83.28; H, 9.32. Found: C, 83.24; H, 9.64.

$\Delta^{5a(17a),8a(14a)}$-Hexacosahydroheptacene (VII).—A mixture of 0.65 g. (0.0015 mole) of $\Delta^{5a(17a),8a(14a)}$-hexacosahydroheptacene-7,16-dione (V),[10] 10 ml. (*ca.* 1.35 moles) of ethyl mercaptan, 0.5 g. of freshly fused (under vacuum) zinc chloride and 0.5 g. of anhydrous sodium sulfate was placed in a glass-stoppered flask and shaken on a mechanical shaker at room temperature for 24 hours and then was allowed to stand at room temperature for an additional 36 hours. After the flask was cooled in ice, the reaction mixture was poured into 50 ml. of ice-water in a separatory funnel. The water-insoluble layer was dissolved in ether and this solution was washed consecutively with 10% aqueous sodium hydroxide and water. After the ether solution was dried over anhydrous sodium sulfate, the ether was evaporated to produce the crude tetraethyltetrathiodiketal VI, which was not purified but was used directly for the subsequent hydrogenolysis.

This crude VI was dissolved in 25 ml. of ethyl alcohol, and the solution was added to a suspension of 50 g. of freshly prepared Raney nickel in 100 ml. of alcohol. After the mixture was heated under reflux for 24 hours, the catalyst was removed by filtration and the filtrate was concentrated to yield a waxy solid. Recrystallization of the crude material from ethyl alcohol produced 0.21 g. (35%) of the light-green waxy $\Delta^{5a(17a),8a(14a)}$-hexacosahydroheptacene (VII), m.p. 249–250°.

Anal. Calcd. for $C_{30}H_{44}$: C, 89.04; H, 10.96. Found: C, 88.74; H, 11.24.

Heptacene (II).—A mixture of 77.8 mg. (0.000192 mole) of $\Delta^{5a(17a),8a(14a)}$-hexacosahydroheptacene (VII) and 200 mg. of 5% palladium-on-carbon was placed in a small dehydrogenation apparatus,[12] which was heated in a Woods metal bath. The temperature, which was 340° at the beginning, was increased gradually to 375° at the end of the reaction. Dry carbon dioxide was passed through the system during the dehydrogenation, and the exit gases were conducted to a nitrometer, filled with 30% potassium hydroxide. The volume of hydrogen evolved in the dehydrogenation, after a period of 135 minutes of heating, was 55 ml. (98%). Isolation and purification by two consecutive vacuum sublimations produced 56 mg. (76%) of greenish-black crystalline heptacene (II), which decomposed at approximately 400°, in agreement with the work of Clar.[6]

Anal. Calcd. for $C_{30}H_{18}$: C, 95.21; H, 4.79. Found: C, 95.12; H, 4.68.

$\Delta^{4a(16a),7a(13a)}$-Docosahydrohexacene-6,15-dione (IX).—A mixture of 1.3 g. (0.008 mole) of 2,3-dimethylenedecalin (IV) and 2.5 g. (0.0116 mole) of $\Delta^{2,5a(9a)}$-decahydroanthracene-1,4-dione (VIII)[10] was heated under reflux for 3 hours in 25 ml. of purified dioxane. After the reaction mixture was cooled, a white solid precipitated out. The precipitate was then filtered off and recrystallized from benzene to produce 1.5 g. (52%) of $\Delta^{4a(16a),7a(13a)}$-docosahydrohexacene-6,15-dione (IX), m.p. 213–214°.

Anal. Calcd. for $C_{26}H_{34}O_2$: C, 82.52; H, 9.05. Found: C, 82.79; H, 9.04.

$\Delta^{4a(16a),7a(13a)}$-Docosahydrohexacene (XI).—A mixture of 0.82 g. (0.0021 mole) of $\Delta^{4a(16a),7a(13a)}$-docosahydrohexacene-6,15-dione (IX), 10 ml. (*ca.* 1.35 moles) of ethyl mercaptan, 0.5 g. of freshly fused (under vacuum) zinc chloride and 0.5 g. of anhydrous sodium sulfate was placed in a glass-stoppered flask and shaken on a mechanical shaker at room temperature for 24 hours and then was allowed to stand at room temperature for an additional 36 hours. After the mixture was thoroughly cooled it was poured into 50 ml. of ice-water in a separatory funnel. The water-insoluble layer was dissolved in ether and the solution was washed consecutively with 10% aqueous sodium hydroxide and water. After the solution was dried over anhydrous sodium sulfate, the ether was evaporated to produce the crude tetraethyltetrathiodiketal X, which was not purified but was used directly for the following hydrogenolysis.

The crude X was dissolved in 25 ml. of ether alcohol and added to a suspension of 50 g. of freshly prepared Raney nickel in 100 ml. of alcohol. After the mixture was heated under reflux for 24 hours, the catalyst was removed by filtration, and the filtrate was concentrated to yield a waxy solid. Recrystallization from ethyl alcohol produced 0.31 g. (42%) of a grayish waxy $\Delta^{4a(16a),7a(13a)}$-docosahydrohexacene (XI), m.p. 225–230° dec.

Anal. Calcd. for $C_{26}H_{38}$: C, 89.07; H, 10.93. Found: C, 88.78; H, 10.87.

Hexacene (I).—A mixture of 43.9 mg. (0.000128 mole) of $\Delta^{4a(16a),7a(13a)}$-docosahydrohexacene (XI) and 20 mg. of 5% palladium-on-carbon was placed in a small dehydrogenation apparatus immersed in a Woods metal bath. The temperature of the mixture was increased from 250° at the beginning to 330° at the end of the reaction. The volume of hydrogen evolved, after 80 minutes of heating, was 31 ml. (98%). Sublimation of the reaction mixture in vacuum produced 30 mg. (70%) of the dark bluish-green crystalline hexacene (I), which decomposed approximately at 380°, in accordance with the observation of Clar.[5]

Anal. Calcd. for $C_{26}H_{16}$: C, 95.09; H, 4.91. Found: C, 94.86; H, 4.69.

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[11] All melting points are corrected. The authors are indebted to Vivian Kapuscinski for the analyses.

[12] L. F. Fieser, "Experiments in Organic Chemistry," 2nd ed., D. C. Heath and Co., Boston, Mass., 1941, pp. 368–369.