[Contribution from the Department of Chemistry, University of Glasgow]

Aromatic Hydrocarbons. LXVII. Heptaphene and 2,3,8,9-Dibenzopicene

By E. Clar and W. Kelly

Received October 29, 1953

Phenanthrene condensed under drastic conditions with two molecules of phthalic anhydride. Ring closure of the resulting dicarboxylic acid gave heptaphene diquinone which was reduced to heptaphene, the structure of which was proved by the absorption spectrum. Pyrolysis of a mixture of di-*o*-toluoylphenanthrenes yielded mostly 2,3,8,9-dibenzopicene, which was also obtained as a by-product in the above synthesis. An orange hydrocarbon, probably anthracenotetracene, was another by-product in both syntheses.

Phenanthrene condensed with excess phthalic anhydride, in the presence of aluminum chloride in tetrachlorethane at 95° to form a mixture of dicarboxylic acids. Crystallization gave a uniform dicarboxylic acid with the probable structure I. Ring closure with sulfuric acid gave a homogeneous diquinone (II), from which heptaphene was prepared by reduction with pyridine, acetic acid and zinc dust. The constitution of heptaphene was established by a comparison of its absorption spectrum with those of benzene, phenanthrene and pentaphene (Fig. 1); the relationships are in complete agreement with those which can be predicted from the annulation principle.[1] There are two types of absorption spectra in the phene series. The "whole-numbered" series: naphthalene, tetraphene, hexaphene and the "half-numbered" series: benzene, phenanthrene, pentaphene and the newly synthesized heptaphene. The corresponding α- and β-bands can be calculated from the equations

$$\nu_\alpha = R_\alpha/K^2 \qquad \nu_\beta = R_\beta/K^2$$

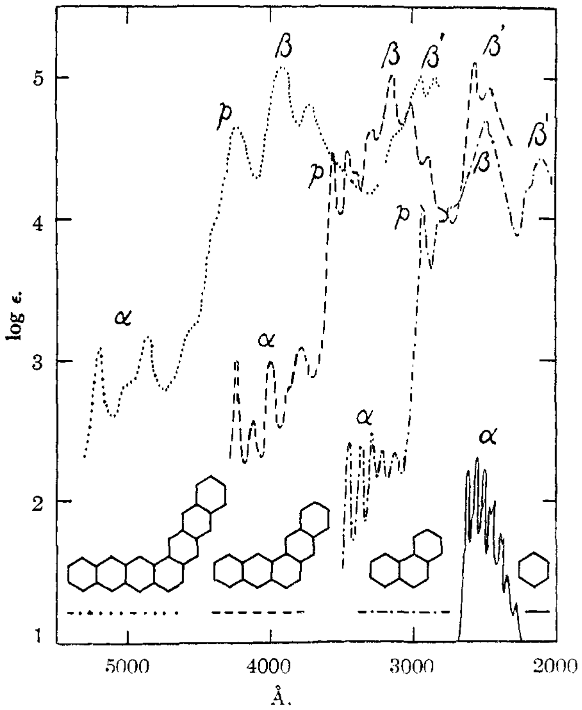


Fig. 1.—Absorption spectrum of heptaphene (III) in trichlorobenzene, from 3200 Å. in benzene, maxima in Å. with log ε in parentheses: α, 5190 (3.08), 5030 (2.83), 4870 (3.16), 4570 (3.25); ρ, 4230 (4.65); β, 3910 (5.06), 3720 (4.80); β', 2935 (5.00), 2835 (5.00). - - - - -, pentaphene in alcohol (E. Clar and D. G. Stewart, *J. Chem. Soc.*, 3215 (1951)). —-—-—, phenanthrene in alcohol (E. Clar, "Aromatische Kohlenwasserstoffe," 2nd Edition, Springer-Verlag, 1952, p. 142); ———, benzene in alcohol.

In the half-numbered series heptaphene must have the order number 10.5. With the constant R_α = 2194600 cm.$^{-1}$, the first α-band for the gaseous state, is calculated to be at 19905 cm.$^{-1}$. A correction of −350 cm.$^{-1}$ must be made for solution in benzene. Therefore, the first α-band of heptaphene in benzene solution should be at 19555 cm.$^{-1}$ 5114 Å., the observed value is 5160 Å.

With the constant R = 2962700 cm.$^{-1}$ the first β-band for the gaseous state is calculated to be at 26873 cm.$^{-1}$. A correction of 1200 cm.$^{-1}$ is made for the solution in benzene. The first β-band should be at 25673 cm.$^{-1}$ = 3895 Å.; the observed value is 3850 Å.

The β'-bands shift toward the red with extension of the linear part of the molecule. Their position is roughly the same as in naphthalene, anthracene and tetracene systems which form the linear parts of phenanthrene, pentaphene and heptaphene, respectively. This might indicate that the β'-bands originate from the π-electrons the orbitals of which are restricted to the linear part of the molecule. The same observation can be made for numerous other angular hydrocarbons.[1] As would be expected the *p*-bands do not follow the simple rules of the acene series.

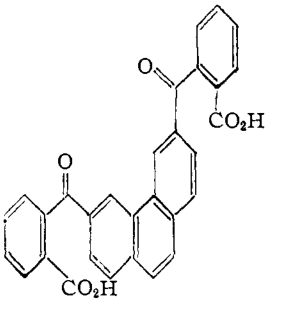
Heptaphene reacted with two molecules of maleic anhydride, forming the dianhydride IV which shows the expected absorption spectrum of a phenanthrene derivative, Fig. 2.

Phenanthrene also reacted with two molecules of benzoyl chloride in the presence of aluminum chloride without a solvent; a homogeneous dibenzoylphenanthrene was obtained by crystallization.

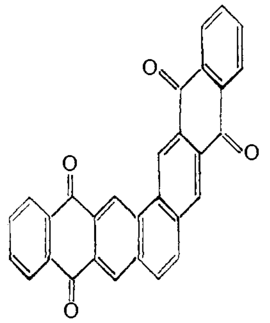
When the benzoyl chloride was replaced by *o*-toluoyl chloride and the crude diketone pyrolyzed at 400–420°, a mixture of hydrocarbons was obtained; an homogeneous pale yellow substance was prepared by treatment of the mixture in 1-methylnaphthalene solution with small portions of maleic anhydride until the first absorption bands of III and VI disappeared. From the absorption spectrum (Fig. 2) it can be deduced that the pale yellow hydrocarbon contains not more than 3 linearly condensed rings and has, therefore, structure V. Oxidation with chromic acid in acetic acid yielded a diquinone which did not show the char-

---

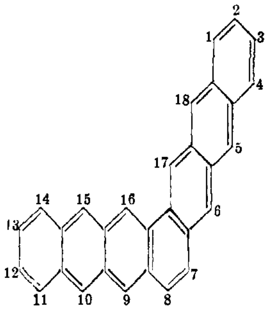
[1] E. Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, 2nd Edition, 1952, pp. 28, 29, 79.



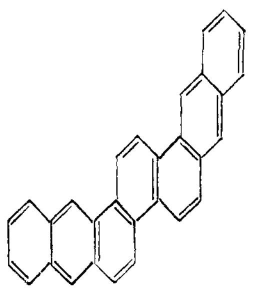
I



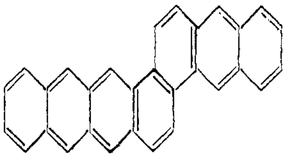
II



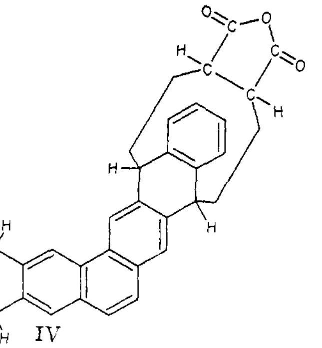
III



V



VI



IV

acteristics of an *o*-quinone; it is probably the 1,4,-7,10-diquinone.

2,3,8,9-Dibenzopicene (V) also was obtained when the isomeric dicarboxylic acids from the mother liquor of I were submitted to ring closure and reduction as described for I. V could be separated from heptaphene and VI by chromatography. The orange hydrocarbon VI, the most reactive of the isomers, was shown to be a by-product of both syntheses by its absorption bands at 4870 and 4570 Å. in benzene solution. Anthracenotetracene (VI) has the expected absorption bands for this last member of the annulation series: chrysene, 3,4-benzotetraphene, anthracenoanthracene.[2] Owing to its high reactivity and difficulties in the chromatographic separation, it could not be purified. The fact that all three hydrocarbons have the expected absorption spectra serves to confirm the structures assigned to them.

Experimental[3]

3,6-Di-*o*-carboxybenzoylphenanthrene (I) and Isomeric Acids.—Finely powdered phenanthrene (90 g.) was added to a mixture of phthalic anhydride (222 g.) and powdered aluminum chloride (400 g.) in tetrachloroethane (300 ml.) at 95°. This temperature was maintained with frequent shaking for 75 minutes. After decomposition of the reaction mixture, the tetrachloroethane layer was separated and washed thoroughly with hot dilute hydrochloric acid and hot water. On standing overnight, the mixture yielded light brown crystals (35 g.) (A) which were recrystallized from nitrobenzene to give colorless crystals of the dicarboxylic acid (I), m.p. 299–301°. The crystals dissolved in concentrated sulfuric acid to produce a red color. The tetrachloroethane mother liquor was extracted with hot ammonia solution. The extract, on acidification, yielded a brown solid (180 g.) (B) consisting of mixed isomeric acids.

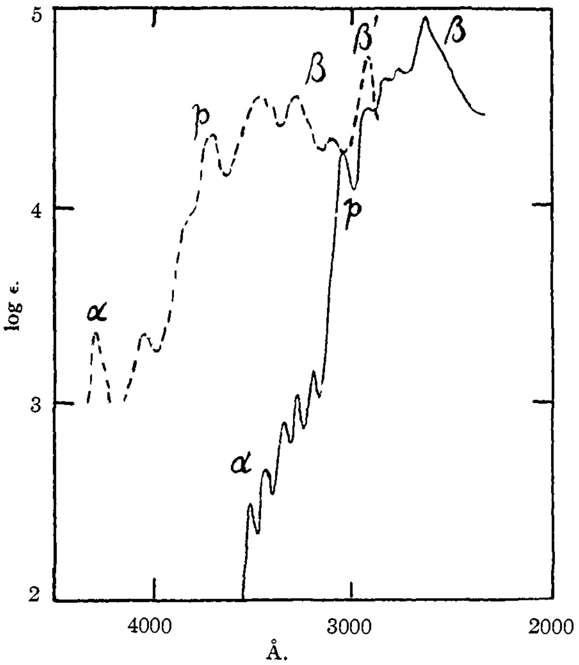


Fig. 2.— - - - -, absorption spectrum of 2,3;8,9-dibenzopicene (V) in 1-methylnaphthalene, from 3400 Å. in benzene, maxima in Å. with log ε in parentheses: α, 4280 (3.35), 4040 (3.35); *p*, 3710 (4.36), 3450 (4.56); β, 3260 (4.56), 3140 (4.32); β', 2930 (4.74). ———, tetrasodium salt of IV in water, maxima in Å. with log ε in parentheses: α, 3520 (2.48), 3430 (2.65), 3340 (2.90), 3275 (3.03), 3195 (3.17); *p*, 3040 (4.24), 2930 (4.48), 2860 (4.64), 2790 (4.67); β, 2640 (4.94).

Anal. Calcd. for $C_{30}H_{18}O_6$: C, 75.94; H, 3.82. Found: C, 75.92; H, 4.18.

Heptaphene-5,18,10,15-diquinone (II).—The acid (A) (20 g.) was dissolved in concentrated sulfuric acid (200 ml.) and heated to 155° for 2 minutes, during which the color changed from red to orange-red. When the solution was diluted with ice at 140°, yellow needles crystallized, which were filtered off and washed with hot ammonia solution and water. Sublimation at 370–380° (5×10^{-4} mm.) followed by crystallization from 1-methylnaphthalene gave bright yellow feathery needles (9.5 g.) of heptaphene-5,18,-10,15-diquinone (II) which decomposed without melting at 545–550° to give a black residue. The diquinone gave a red-orange solution in concentrated sulfuric acid; with alkaline sodium dithionite it formed a violet-red vat which became brown on boiling.

Anal. Calcd. for $C_{30}H_{14}O_4$: C, 82.18; H, 3.22. Found: C, 82.17; H, 3.31.

Heptaphene (III).—The diquinone (6.4 g.), zinc dust (40 g.), and pyridine (200 ml.) were boiled under reflux, and acetic acid (80%, 150 ml.) was added dropwise over a period of 5.5 hours. The color of the solution changed from brown, through a reddish-orange, to a pale orange. A fine orange solid crystallized out during the reaction. The suspension was decanted from the zinc dust,

---

[2] E. Clar, *Ber.*, **73**, 599 (1940).

[3] All melting points are uncorrected and were taken in evacuated capillaries.

and the solid (2 g.) filtered off and washed successively with pyridine, benzene and ether. Crystallization from 1-methylnaphthalene gave light orange plates of heptaphene, m.p. 473–474°. In organic solvents it had a green fluorescence and dissolved to give a violet-red solution in concentrated sulfuric acid. When the pyridine mother liquor from the above filtration was added to water, a precipitate formed which after being washed and sublimed *in vacuo* gave additional heptaphene (1.5 g.).

Anal. Calcd. for $C_{30}H_{18}$: C, 95.20; H, 4.80. Found: C, 95.04; H, 4.98.

Maleic Anhydride Adduct (IV).—Heptaphene (0.1 g.) and excess maleic anhyride were heated under reflux in xylene (20 ml.) until the solution became colorless. Concentration of the xylene gave colorless crystals, m.p. 292–296° dec., of the dianhydride (IV).

Anal. Calcd. for $C_{38}H_{22}O_6$: C, 79.44; H, 3.86. Found: C, 78.71; H, 3.77.

Ring Closure and Reduction of the Isomeric Acids (B).—Treatment of the mixed acids (B) with sulfuric acid, as above, gave a dark greenish-yellow product which was reduced with zinc dust, pyridine and acetic acid. When the pyridine solution was poured into water, a precipitate formed which was sublimed to give a reddish-orange mixture of hydrocarbons. No separation of the mixture could be achieved by crystallization and the very low solubility of the hydrocarbons made complete chromatographic separation difficult. Elution with benzene from alumina, gave an initially colorless band, fluorescing blue in ultraviolet light, which yielded a small quantity of yellow plates, m.p. 485–487°; these showed no depression of the melting point when mixed with a sample of 2,3,8,9-dibenzopicene (V) obtained as below. All other fractions taken from the column were mixtures of the three hydrocarbons. The anthracenotetracene tended to oxidize during the long period required to develop the chromatogram.

Dibenzoylphenanthrene.—Powdered aluminum chloride (22 g.) was added to a paste of benzoyl chloride (23 g.) and phenanthrene (10 g.) at room temperature. The mixture was heated on a steam-bath for 30 minutes. After decomposition, the product was washed with hot dilute acetic acid, hot ammonia solution and water. A small quantity of ether caused the plastic solid material to crystallize. Crystallization from alcohol gave colorless silky needles, m.p. 183–184°, of a dibenzoylphenanthrene.

Anal. Calcd. for $C_{28}H_{18}O_2$: C, 87.02; H, 4.70. Found: C, 86.91; H, 5.07.

2,3,8,9-Dibenzopicene.—A mixture of di-*o*-toluoylphenanthrenes was prepared in a similar manner to dibenzoylphenanthrene. The solid product from the decomposition of the reaction mixture was dissolved in xylene. The xylene solution was extracted with hot dilute hydrochloric acid, hot ammonia solution and water. The xylene was distilled off and the residue of crude diketones pyrolyzed at 400–420° until the evolution of water ceased. Sublimation *in vacuo* of the reaction product yielded a mixture of hydrocarbons which were identified as heptaphene, dibenzopicene and anthracenotetracene by visual spectroscopic examination. The mixture was dissolved in 1-methylnaphthalene, and small portions of maleic anhydride were added to the hot solution until the bands of heptaphene and anthracenotetracene disappeared. Crystallization from the solution yielded pale yellow plates, m.p. 489–490°, of 2,3,8,9-dibenzopicene (V). The crystals dissolved, on being heated, in concentrated sulfuric acid to give a yellowish-green color which changed to olive green. In organic solvents the hydrocarbon showed a strong blue fluorescence.

Anal. Calcd. for $C_{30}H_{18}$: C, 95.20; H, 4.80. Found: C, 95.02; H, 4.99.

2,3,8,9-Dibenzopicene-1,4,7,10-diquinone.—Finely powdered dibenzopicene was boiled with excess chromium trioxide in acetic acid. Addition of water yielded a precipitate which was sublimed *in vacuo* and crystallized from nitrobenzene to give yellow prisms, m.p. 416–417°, of the diquinone. It gave a brown solution in concentrated sulfuric acid and formed a red vat with alkaline sodium dithionite solution. It did not form a phenazine derivative with *o*-phenylenediamine.

Anal. Calcd. for $C_{30}H_{14}O_4$: C, 82.18; H, 3.22. Found: C, 82.47; H, 3.44.

Acknowledgment.—Microanalyses were performed by Mr. J. M. L. Cameron and Miss M. W. Christie of this Department.

GLASGOW, SCOTLAND

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF GLASGOW]

Aromatic Hydrocarbons. LXVIII. Triangulene Derivatives. Part II[1]

BY E. CLAR AND D. G. STEWART

RECEIVED OCTOBER 29, 1953

The syntheses of triangulenequinone and dodecahydrotriangulene from di-*p*-xylylphthalide and di-*m*-xylylphthalide are described.

Weiss, Spitzer and Melzer[2] have shown that dixylylphthalides can be prepared by adding powdered aluminum chloride to *sym*-phthaloyl chloride and a xylene in carbon disulfide. As this method gives a considerable amount of *o*-diaroylbenzene as by-product the yield of phthalide is low, 50 and 25% from *p*- and *m*-xylene, respectively. Fuson, Speck and Hatchard[3] who demonstrated that *o*-diaroylbenzenes are readily formed under such conditions obtained an 81% yield of this compound from mesitylene. We have found that the dixylylphthalides can be prepared free from these by-products by treating a xylene with a preformed complex of *as*-phthaloyl chloride and aluminum chloride.

Two stage oxidation of the phthalides (I, R = H, R = CH_3 and R′ = CH_3 R′ = H), first with boiling dilute nitric acid and then with either alkaline potassium permanganate solution or dilute nitric acid, resulted in a rearrangement which is analogous to that which occurs when di-*o*-tolylphthalide (I, R = R′ = H) is oxidized.[4] The resulting dispirans (II, R = R′ = H; R = H, R′ = CO_2H and R = CO_2H, R′ = H) on heating with copper powder at 350° gave a compound which was identical with the lactone III prepared by Scholl and Donat.[5]

To avoid the above rearrangement the phthalides I were reduced with zinc dust and ethanolic potassium hydroxide solution to the acids IV which on heating in a sodium chloride–zinc chloride melt condensed to the arylanthrones V. Two-stage

---

[1] Part I, THIS JOURNAL, **75**, 2667 (1953).

[2] R. Weiss, A. Spitzer and J. L. Melzer, *Monatsh.*, **47**, 306 (1926).

[3] R. C. Fuson, S. B. Speck and W. R. Hatchard, *J. Org. Chem.*, **10**, 55 (1945).

[4] E. Clar and D. G. Stewart, *J. Chem. Soc.*, 3215 (1951).

[5] R. Scholl and J. Donat, *Ann.*, **512**, 1 (1934).