

513. Aromatic Hydrocarbons. Part LIII. 7 : 8-Benzheptaphene.

By E. CLAR.

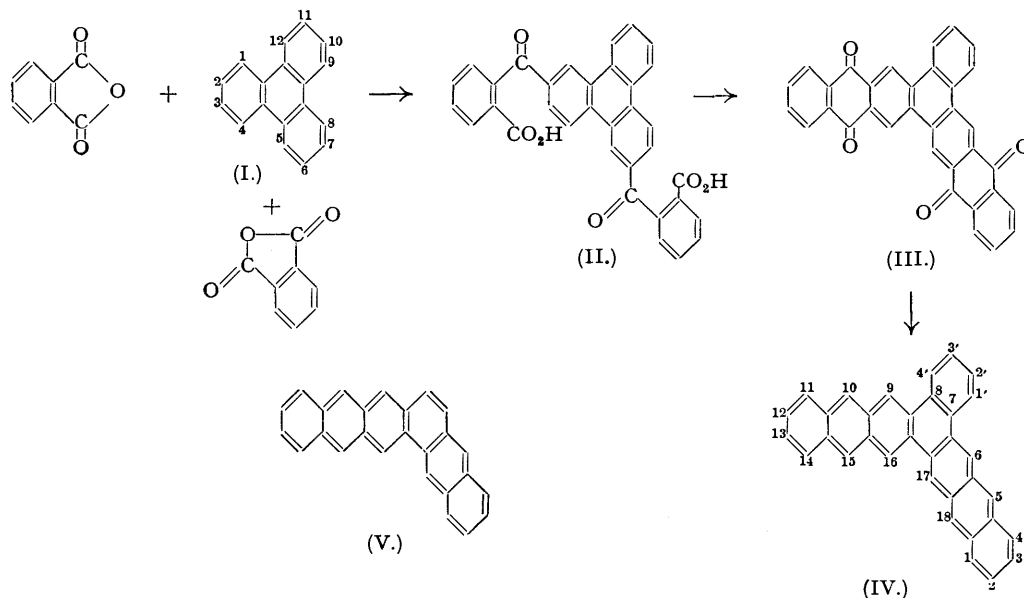
Triphenylene was condensed with two molecules of phthalic anhydride. The resultant dicarboxylic acid was submitted to a double ring-closure, and the diquinone so obtained was reduced to a hydrocarbon, which from its properties and by analogy with the condensation of triphenylene with one molecule of phthalic anhydride is regarded as 7 : 8-benzheptaphene (IV).

TRIPHENYLENE (I) reacts at position 2 with phthalic anhydride and aluminium chloride. Ring closure gives 1 : 2 : 3 : 4-dibenznaphthacene-6 : 11-quinone. No isomeric quinone could be observed (Clar, *Chem. Ber.*, 1948, **81**, 68). Triphenylene reacts thus much more simply than phenanthrene which yields several isomers. The reason obviously is that reaction at the position 1, 4, 5, 8, 9, or 12 would correspond to a direct substitution at position 4 of phenanthrene, which has never been observed.

From this point of view, the result of the condensation of triphenylene with two molecules of phthalic anhydride should be disubstitution at positions 2 : 6, or 2 : 7, or 3 : 5. When this reaction was carried out in tetrachloroethane at 60—80°, a dicarboxylic acid was obtained which from its indefinite melting point evidently consisted of a mixture of isomers. This mixture yielded on ring closure with benzoyl chloride a homogeneous diquinone (III).

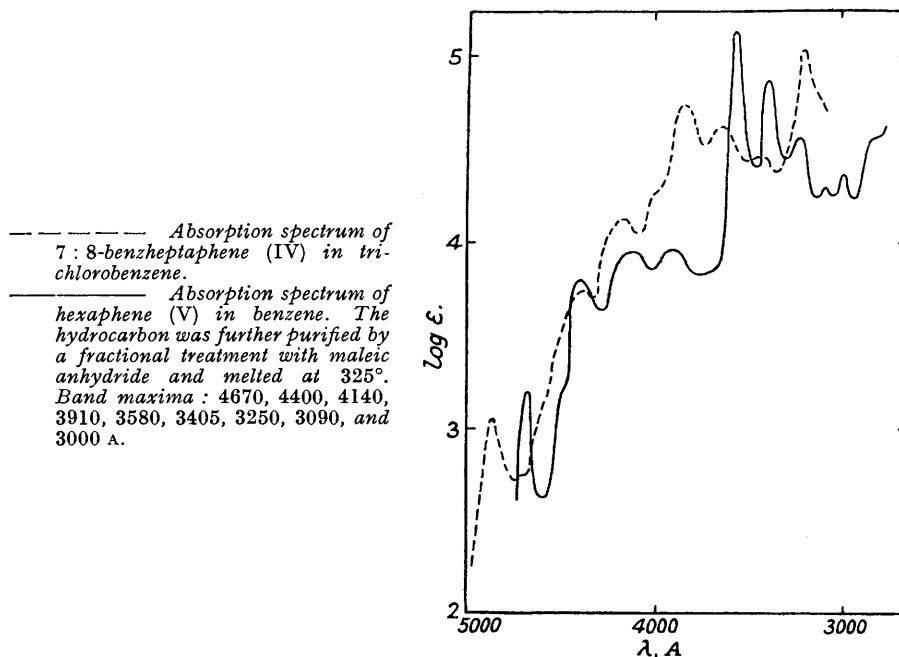
7 : 8-Benzheptaphene (IV) was obtained by the reduction of the diquinone (III) with zinc dust, pyridine, and acetic acid. 7 : 8-Benzheptaphene which contains a double naphthacene structure with four linearly condensed rings, formed dark yellow needles, and resembled in its appearance 1 : 2 : 3 : 4-dibenznaphthacene (Clar, *Chem. Ber.*, 1948, **81**, 68). The absorption spectrum is of the hexaphene type : the middle region (maxima at 4380 and 4180 Å.) was related to the excitation of one electron in a *para*-bond, predominantly dependent on the number of linearly condensed rings, and is almost in the same position as in hexaphene (V)

(Clar, *Ber.*, 1940, **73**, 82); the first (maximum at 4850 Å.) and the last region (maxima at 3850, 3650, 3450, and 3220 Å.) are considerably shifted to the red, owing to the more extended "phene structure."



EXPERIMENTAL.

Di-2:6-o-carboxybenzoyltriphenylene (II) and 2:7- and 3:6-Isomers.—Phthalic anhydride (16 g.) and powdered aluminium chloride (30 g.) in tetrachloroethane (70 c.c.) were heated at 60°, and triphenylene



(5.5 g.) was gradually added. After being heated for $\frac{1}{4}$ hour at 80°, the mixture was decomposed with dilute hydrochloric acid. The tetrachloroethane layer was separated, washed, and extracted with dilute aqueous ammonia. The alkaline extracts were boiled, filtered, and acidified with hydrochloric acid. The

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dicarboxylic acid was recrystallised from acetic acid and formed pale yellow crystals, m. p. 230—250° (uncorr.), which dissolved in concentrated sulphuric acid to give a brown solution, which afterwards became violet (Found: C, 78.2, 77.4; H, 3.8, 3.8. $C_{24}H_{20}O_6$ requires C, 77.8; H, 3.8%).

7 : 8-*Benzheptaphene-5 : 18 : 10 : 15-diquinone* (III).—The above dicarboxylic acid (7 g.), nitrobenzene (150 c.c.), benzoyl chloride (20 c.c.), and concentrated sulphuric acid (1 c.c.) were heated to the boiling point for 20 minutes. The solution became first violet and then reddish-brown. The diquinone (3 g.) which crystallised on cooling was filtered off and washed with nitrobenzene and ether. On repeated recrystallisation from nitrobenzene the *diquinone* yielded greenish-yellow crystals, m. p. 435° (uncorr.; evacuated capillary), which dissolved in concentrated sulphuric acid to give a red solution. A violet vat was formed with sodium dithionite, which soon became brown (Found: C, 83.5; H, 3.4. $C_{34}H_{16}O_4$ requires C, 83.6; H, 3.3%).

7 : 8-*Benzheptaphene* (IV).—The diquinone (3 g.), zinc dust (20 g.), and pyridine (150 c.c.) were boiled and acetic acid (80%; 50 c.c.) was added dropwise. The solution was first red and gradually became yellow. After 5 hours the solution was decanted from the zinc dust and poured into water. Sublimation of the washed precipitate in a vacuum yielded the hydrocarbon. Recrystallised from 1-methylnaphthalene, 7 : 8-*benzheptaphene* formed dark yellow needles, m. p. 410° (uncorr.; evacuated capillary) (Found: C, 95.2; H, 4.9. $C_{32}H_{20}$ requires C, 95.1; H, 4.7%), which dissolved in concentrated sulphuric acid to give a violet red solution, which soon became brown. The fluorescence in organic solvents is blue-green.

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