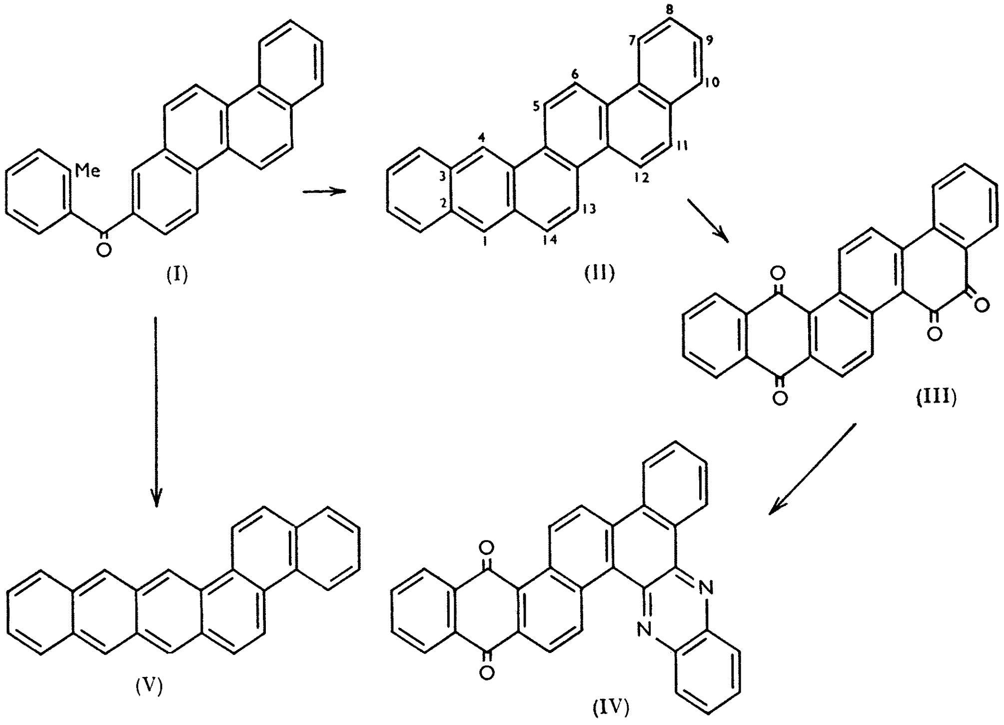
836. 2 : 3-*Benzopicene and Naphtho*(2′ : 3′-1 : 2)*chrysene.*

By E. Clar and W. Kelly.

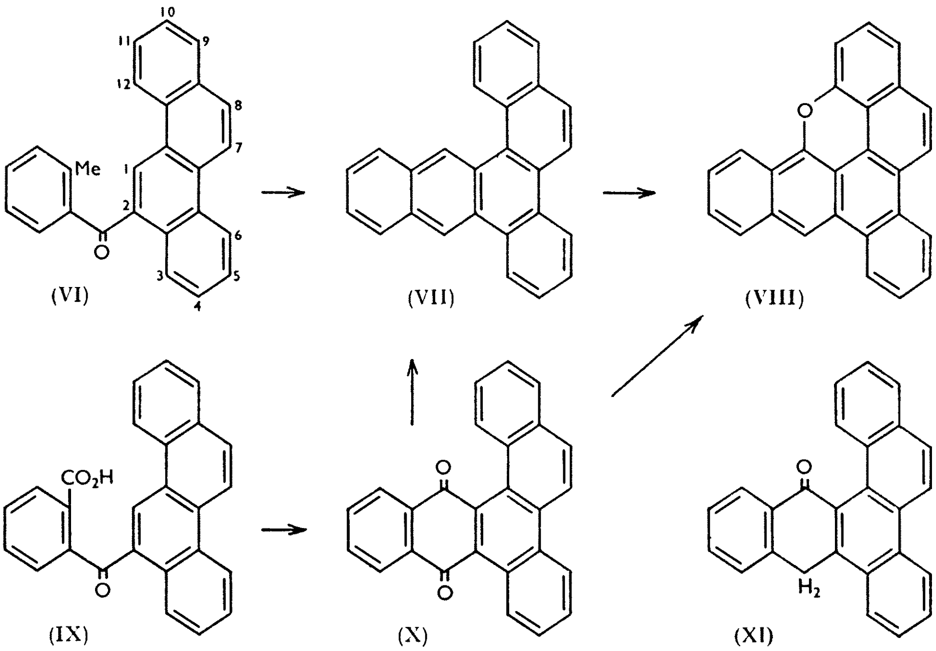
2 : 3-Benzopicene was obtained from a mixture of *o*-toluoylchrysenes, which were prepared by a reaction of *o*-toluoyl chloride, chrysene, and aluminium chloride under drastic conditions. Naphtho(2′ : 3′-1 : 2)chrysene can be easily obtained from the quinone (X) by reduction with zinc dust in pyridine and acetic acid. The oxygen-containing product from the zinc dust melt of the quinone (X) is not the anthrone derivative (XI) as claimed by Beyer and Richter but the cyclic epoxy-compound (VIII).

Chrysene reacts in the Friedel–Crafts reaction under mild conditions in position 2. However, if the reaction with *o*-toluoyl chloride in tetrachloroethane is carried out at 95° a mixture of ketones is formed, which after pyrolysis at 400° yields a mixture of hydrocarbons. This consists of a yellow hydrocarbon (absorption bands in benzene at 4720 and 4420 Å) and a pale yellow hydrocarbon (first band at 4040 Å). Complete chromatographic separation was not achieved and the yellow hydrocarbon could not be obtained pure. It was therefore removed from the mixture by a cautious treatment with maleic anhydride until its absorption bands disappeared. From its higher reactivity and the position of its absorption bands near to the red it might be concluded that it has the structure (V) of a naphthotetracene. This is the only system with four linearly condensed rings which could be formed in this synthesis.



The less reactive pale yellow hydrocarbon gave a diquinone when oxidised with chromic anhydride in acetic acid. This has two *o*-carbonyl groups since it formed a phenazine derivative (IV) with *o*-phenylenediamine. The two carbonyl groups of the *o*-quinone complex cannot be in positions 5 and 6 because treatment with hydrazine hydrate does not produce an azine involving positions 4 and 5. Thus the most likely structure of the diquinone is that given in formula (III), chrysene having reacted at position 4 or 3.

During pyrolysis of the ketone mixture an oxygen-containing product was obtained besides the two hydrocarbons mentioned above. This compound obviously originated from the ketone (VI) which is pyrolysed to (VII) and then oxidised to (VIII). The structure (VIII) was confirmed by synthesis from chrysene, phthalic anhydride, and aluminium chloride which gave the keto-acid (IX) and, by ring closure with benzoyl chloride, the quinone[1] (X). If this quinone was submitted to the zinc dust melt, the compound (VIII) was obtained in good yield. Compound (VIII) contains two hydrogen atoms less than indicated by formula (XI) which was attributed to the product of the zinc dust melt by Beyer and Richter.[2] The structure (VIII) explains why this compound does not enolise with alkali, does not give an acetyl derivative, and cannot be reduced further.



However, the quinone (X) can be readily reduced to the parent hydrocarbon (VII) by reduction with zinc dust in pyridine and acetic acid, a method which avoids the high temperature and condensing action of the zinc dust melt. The absorption spectra of the hydrocarbons (II) and (VII) are recorded in the Figure together with the spectrum of the oxygen-ring compound (VIII). The last shows the strong red shift in comparison with the hydrocarbon (VII) which has also been observed in similar cases.[3]

EXPERIMENTAL

M. p.s were taken in evacuated capillaries. Microanalyses are by Mr. J. M. L. Cameron and Miss M. W. Christie.

Condensation of Chrysene with o-*Toluoyl Chloride.*—Powdered aluminium chloride (60 g.) was added during 4 min. to a mixture of chrysene (46 g.) and *o*-toluoyl chloride (33 g.) in tetrachloroethane (60 ml.) at 95° and stirred for a further 5 min. The orange-red mixture was cooled, decomposed, and diluted with more tetrachloroethane. The organic layer was washed

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[1] I.G. Farbenind. A.-G., G.P. 652,912; Ges. Chem. Ind. in Basel, Swiss P. 179,440; *Chem. Zentr.*, 1936, I, 2637; 1938, I, 2064.

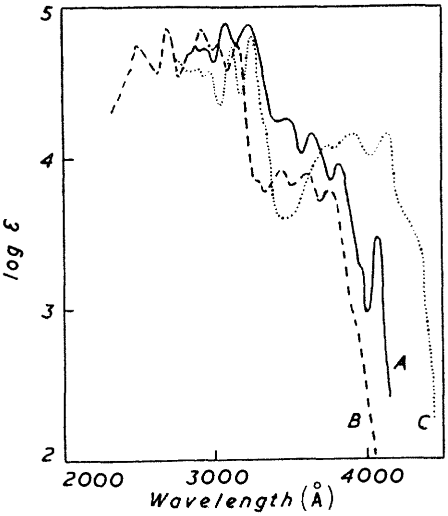
[2] Beyer and Richter, *Ber.*, 1940, **73**, 1319.

[3] Clar, *Ber.*, 1940, **73**, 351; Clar, Kelly, Stewart, and Wright, *J.*, 1956, 2652.

successively with hot dilute hydrochloric acid, hot dilute aqueous ammonia, and hot water. The tetrachloroethane was distilled off and the residue pyrolysed at about 400° for 15 min., to give a black solid (56 g.). 28 g. of this were sublimed in a vacuum. Fractions were collected between 170° and 340° during 45 hr. The initial fractions (collected at 170—220°) were mainly unchanged chrysene. The later fractions (13 g.) were collected together and extracted with 150 ml. of warm benzene.

2 : 3-*Benzopicene* (II).—The residue (4·2 g.) from the above benzene extraction was recrystallised from xylene, giving yellow plates (1·8 g.). Spectroscopy (bands at 4720, 4420, and 4040 Å) showed the plates to be a mixture of two compounds. Attempts to separate them by chromatography were unsuccessful. Several recrystallisations from 1 : 2 : 4-trichlorobenzene containing small quantities of maleic anhydride gave pale yellow plates, m. p. 394—395°, of the *benzopicene* (Found: C, 95·3; H, 5·1. $C_{26}H_{16}$ requires C, 95·1; H, 4·9%). The compound did not dissolve in concentrated sulphuric acid and had a blue fluorescence in xylene solution.

15-*Oxatribenzo*[a,e,jk]*pyrene* (VIII).—The above benzene extract was chromatographed on alumina with benzene as eluant. A first small colourless band gave a small quantity of chrysene. A second yellow band yielded yellow needles, m. p. 288—289° (Beyer and Richter,[2] 285—286°), of the 15-*oxatribenzopyrene* (Found: C, 91·0; H, 4·2. $C_{26}H_{14}O$ requires C, 91·2; H, 4·1%). The compound was identical with that obtained as below by the reduction of naphtho(2′ : 3′-1 : 2)chrysene-1′ : 4′-quinone, and dissolved in concentrated sulphuric acid to a deep red solution.



Absorption spectrum of (*A*) 2 : 3-*benzopicene* (II) *in* C_6H_6 [max. (Å; log ε in parentheses): 4055 (3·46); 3820 (3·96), 3630 (4·15), 3470 (4·26); 3245 (4·88), 3110 (4·89), 2980 (4·74)], (*B*) *naphtho*(2′ : 3′-1 : 2)-*chrysene* (VII) *in* EtOH [max. 3760 (3·77), 3610 (3·89), 3460 (3·91), 3280 (3·85); 3150 (4·74), 3020 (4·75); 2920 (4·84), 2700 (4·84), 2490 (4·75)], *and* (*C*) *of* 15-*oxatribenzo*[a,e,jk]*pyrene* (VIII) *in* C_6H_6 [max. 4140 (4·15), 3910 (4·15), 3720 (4·07); 3260 (4·81), 3115 (4·73), 2980 (4·56), 2890 (4·58)].

2 : 3-*Benzopicene*-1 : 4-11 : 12-*diquinone* (III).—Chromium trioxide (0·26 g.) in water (1 ml.) was added to a suspension of benzopicene (0·1 g.) in acetic acid (6 ml.) After 3 hr. under reflux the suspension was filtered and the orange powder crystallised from nitrobenzene as orange feathery needles of the *diquinone*, m. p. 387—388° (Found: C, 80·6; H, 3·5. $C_{26}H_{12}O_4$ requires C, 80·4; H, 3·1%). The compound gave an orange vat with alkaline sodium dithionite and dissolved in concentrated sulphuric acid to a reddish-brown solution.

An excess of hydrazine hydrate was added to a suspension of the diquinone (III) in hot pyridine. The reddish-orange suspension changed to deep red and the diquinone dissolved completely. The solution was heated under reflux for 20 min. and the pyridine was concentrated to small bulk but no crystallisation took place. The light brown precipitate, formed on addition of water and boiling, crystallised from nitrobenzene as orange needles identical with the benzopicenediquinone (III).

An excess of *o*-phenylenediamine (10 mg.) and the diquinone (III) (14 mg.) in nitrobenzene (3 ml.) were heated under reflux for 30 min. The dark yellow crystals (13 mg.) obtained were recrystallised from nitrobenzene, to give fine yellow needles, m. p. 363—364°, of the *phenazine* (IV) (Found: N, 5·9. $C_{32}H_{16}O_2N_2$ requires N, 6·1%). The compound gave an orange-red vat in alkaline sodium dithionite and dissolved in concentrated sulphuric acid to a violet-red solution.

2-o-*Carboxybenzoylchrysene* (IX).—Powdered aluminium chloride (117 g.) was added, during 5 min., to phthalic anhydride (64 g.) and chrysene (80 g.) in tetrachloroethane (200 ml.) at 90°. The mixture became reddish-orange and the temperature rose to 98°. The reaction quickly subsided and, after decomposition, the tetrachloroethane layer was separated and washed with hot dilute hydrochloric acid and hot water. The tetrachloroethane solution was extracted with rather concentrated ammonia solution which precipitated an ammonium salt. Acidification of this salt gave an acid (80 g.) which on being recrystallised several times from acetic acid gave colourless needles, m. p. 206—211° (Beyer and Richter,[2] m. p. 213—214°), of 2-*o*-carboxybenzoylchrysene. The mother-liquor from the ammonium salt, on acidification, yielded another portion of acid product (24 g.) (Found: C, 82·8; H, 4·6. Calc. for $C_{26}H_{16}O_3$: C, 83·0; H, 4·3%).

Naphtho(2′ : 3′-1 : 2)*chrysene*-1′ : 4′-*quinone* (X).—A solution of 2-*o*-carboxybenzoylchrysene (60 g.) in benzoyl chloride (180 ml.) was heated under reflux. Concentrated sulphuric acid was added dropwise at intervals until a transient blue colour no longer appeared. The solution was boiled for a further 10 min. Orange needles (23 g.) crystallised from the solution on cooling. Recrystallisation from xylene gave orange needles, m. p. 273—274°, of the quinone.

Naphtho(2′ : 3′-1 : 2)*chrysene* (VII).—The quinone (X) (5 g.), zinc dust (5 g.), and pyridine (70 ml.) were heated under reflux and 80% acetic acid (80 ml.) was added during 5 hr. The initial deep orange-red solution changed through pale orange to a yellowish-green. The pyridine solution was filtered into water, and the precipitate was heated above its m. p. in a vacuum, powdered, and chromatographed in benzene on alumina with benzene as eluant. A first colourless band yielded colourless plates, m. p. 187—188° (Beyer and Richter,[2] 185—186°), of naphtho-(2′ : 3′-1 : 2)chrysene. A second yellow band yielded yellow needles, m. p. 288—289°, of the compound (VIII).

When the acid (24 g.) from the mother-liquor of the crystallised ammonium salt of the 2-*o*-carboxybenzoylchrysene was cyclised and the mixture of the quinones reduced as above a mixture of benzopicene (II) and naphthotetracene (V) (identified by its spectrum) was obtained. This indicates that under the latter condition described some phthalic anhydride reacts with a side ring of the chrysene.

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[*Received, April* 15*th*, 1957.]