[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF GLASGOW]

Aromatic Hydrocarbons. LXV. Triangulene Derivatives[1]

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The synthesis of triangulene (I) was attempted to ascertain whether the hydrocarbon was rendered more stable, than is implied by the diradical formula (I), by a molecular orbital structure with trigonal symmetry. The formula (I) expresses in classical terms that triangulene has no Kekulé structure. Triangulenequinone (XI) was synthesized by two methods and its reduction was studied in detail. The results show that triangulene compounds derived from the skeleton (I) are unstable, immediately polymerizing or rearranging, and that dihydrotriangulene derivatives tend strongly to rearrange to trimethylene compounds.

Reduction of di-*o*-tolylphthalide (II) with zinc and ethanolic potassium hydroxide gave the acid (III) which was condensed to the anthrone (IV) in a sodium chloride–zinc chloride melt at 220°. Mild oxidation of IV with dilute nitric or selenious acid gave the oxanthranol (V) which was further oxidized with nitric acid at 200° under pressure to the dicarboxylic acid (VI). This compound was reduced with zinc dust and sodium hydroxide solution to the dihydroanthracene derivative (VII), the structure of which was established by its absorption spectrum, which is that of a benzene derivative.

Oxidation of the phthalide II as described by Clar and Stewart[2] gave the dicarboxylic acid lactone (VIII) in addition to dihydroisobenzofuran-1,3-bisspiro-(3-phthalide), formed by rearrangement. When VI or VIII was dissolved in concentrated sulfuric acid and heated with copper powder to 120°, the blue hydroxytriangulenequinone (X) is formed. This compound, the properties of which agreed with those of a sample prepared by Weisz and Korczyn[3] by a different method, was found to be so acidic that it dissolved in sodium acetate solution.

Triangulene-4,8-quinone (XI), which was formed when VII was treated with concentrated sulfuric acid at room temperature, was also obtained from X by brief reduction in sodium hydroxide solution with zinc dust, followed by reoxidation with oxygen. The absorption spectrum of triangulenequinone is shown in Fig. 1, compared with that of coeranthrone[4] to which it is related.

When hydroxytriangulenequinone (X) was submitted to the zinc dust fusion procedure of Clar[5] a colorless hexahydrotriangulene (IX) was obtained. Its constitution is readily deduced from its absorption spectrum (Fig. 2) which is of the pure pyrene type and which is closely related to that of 2,3-trimethylenepyrene (XXIV). This compound was prepared from naphtho-(2′,7′; 1,8)-anthrone (XXIII)[6] by means of the zinc dust melt and purified by chromatography. The properties of the hydrocarbon indicate that it had not previously been obtained in a pure state.[7]

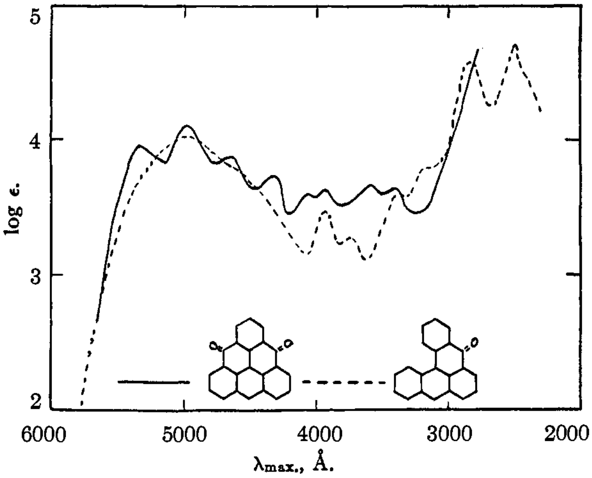

Fig. 1.——, absorption spectrum of 4,8-triangulenequinone (XI) in benzene. Maxima in Å. with log ε in parentheses: 5340 (3.96), 4980 (4.10), 4650 (3.88), 4340 (3.72), 4080 (3.60); 3950 (3.64), 3600 (3.66), 3430 (3.62). - - - - - -, absorption spectrum of coeranthrone in alcohol. Maxima in Å. with log ε in parentheses: 4970 (4.01); 3930 (3.48), 3740 (3.28); 3280 (3.60), 3140 (3.80); 2840 (4.58); 2500 (4.70).

When hexahydrotriangulene (IX) was dehydrogenated by subliming it over a palladium–charcoal catalyst at 310° in a vacuum, it was adsorbed completely into the catalyst and no sublimate was obtained. The activity of the catalyst was carefully tested before and after the application of IX by the dehydrogenation of 9,10-dihydroanthracene (m.p. 105°) and in all cases pure anthracene was obtained. Even when the catalyst was heated to 500° in a vacuum no sublimate was obtained and, as a dimeride of triangulene would have sublimed under such conditions, it must therefore be assumed that polymerization was complete. A similar result was obtained when IX was dehydrogenated in trichlorobenzene with a palladium–charcoal catalyst at 200°. Here the absorption spectrum of 4,8-dihydrotriangulene (XXI) was observed as an intermediate stage of dehydrogenation, but owing to immediate polymerization no absorption of triangulene (I) became visible.

Another attempt to obtain triangulene by dehydrogenation was made using dodecahydrotriangulene (XII), which was prepared from triangulenequinone (XI) by reduction with hydriodic acid and red phosphorus under pressure at 200°. The structure of XII is shown by its absorption spectrum (Fig. 3) which reveals its aromatic naph-

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[1] Presented at the XIIth International Congress of Pure and Applied Chemistry in New York, 1951, *Chem. Eng. News*, **29**, 3967 (1951).

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

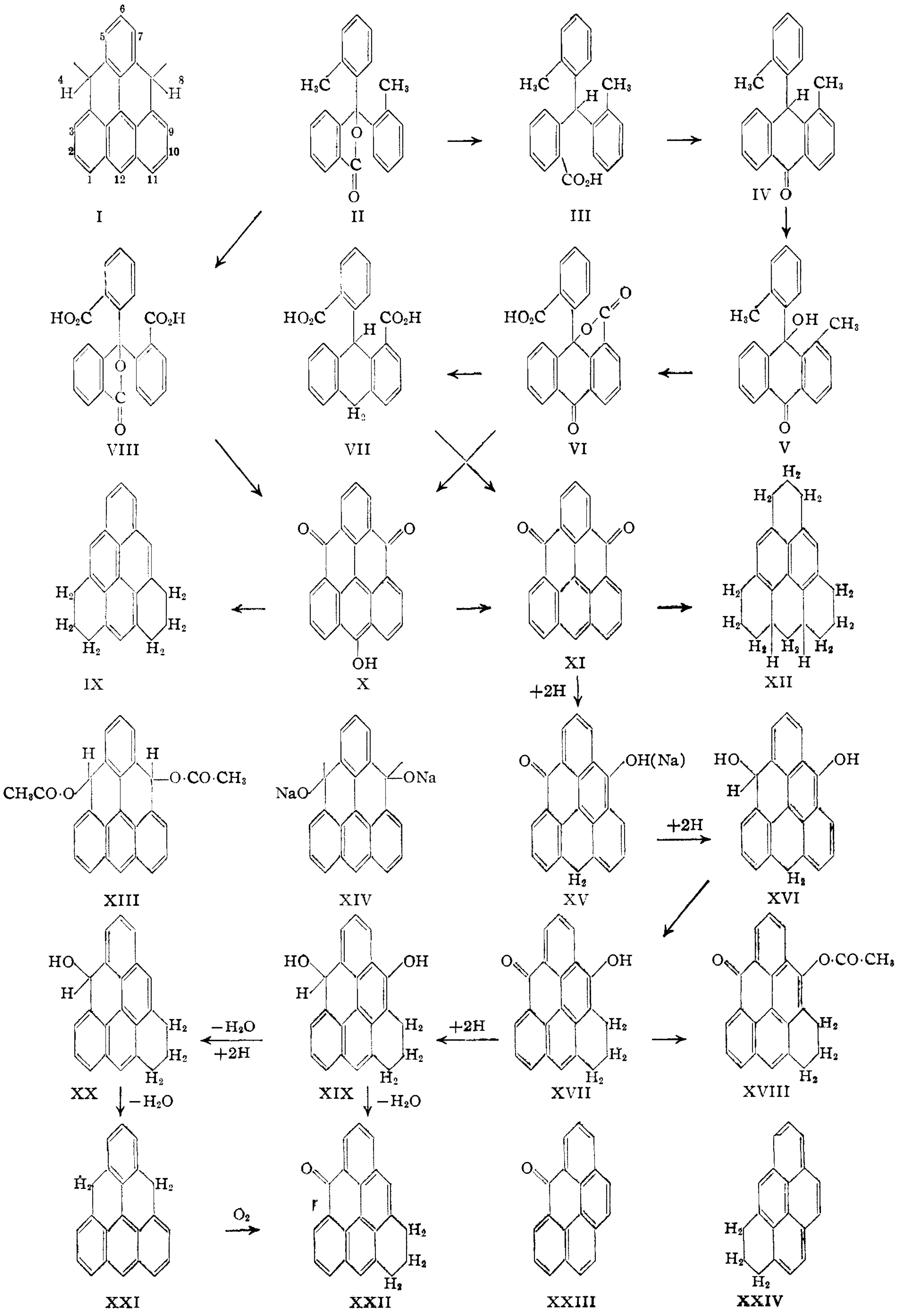
[3] R. Weisz and J. Korczyn, *Monatsh.*, **45**, 207 (1924).

[4] E. Clar and D. G. Stewart, THIS JOURNAL, **74**, 6235 (1952).

[5] E. Clar, *Ber.*, **72**, 1645 (1939).

[6] H. Vollmann, H. Becker, M. Corell and H. Streeck, *Ann.*, **531**, 155 (1937).

[7] R. Scholl and K. Meyer, *Ber.*, **69**, 156 (1936).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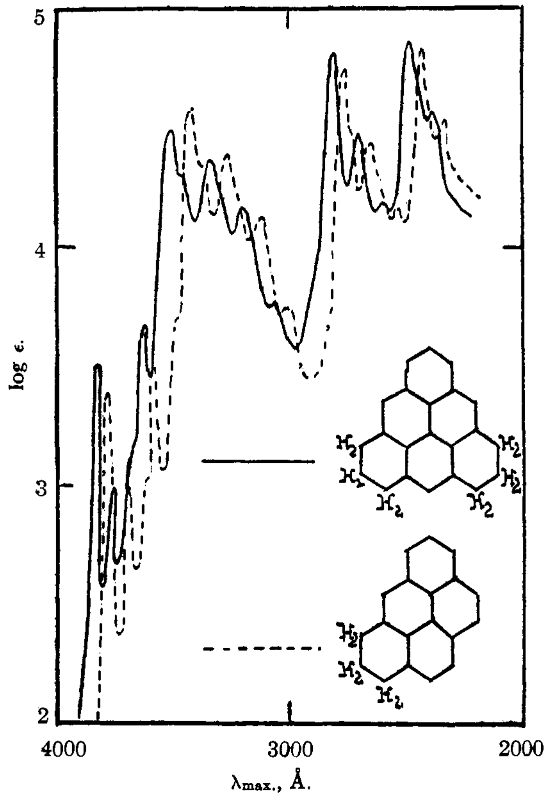

Fig. 2.——, absorption spectrum of 1,2,3,5,6,7-hexahydrotriangulene (IX) in alcohol. Maxima in Å. with log ε in parentheses: 3830 (3.50), 3765 (3.00), 3625 (3.66); 3515 (4.48), 3350 (4.32), 3200 (4.16), 3070 (3.77); 2815 (4.80), 2700 (4.48), 2590 (4.18); 2480 (4.86), 2380 (4.57). - - - - - -, absorption spectrum of 2,3-trimethylenepyrene (XXIV) in alcohol. Maxima in Å. with log ε in parentheses: 3780 (3.40), 3700 (2.87), 3575 (3.44); 3430 (4.57), 3270 (4.40), 3130 (4.12), 3010 (3.75); 2770 (4.74), 2660 (4.45), 2550 (4.18); 2445 (4.84), 2345 (4.55).

thalene complex. When XII was melted with palladium–charcoal under pure carbon dioxide[8] at 200° brisk evolution of hydrogen was observed which when collected corresponded roughly to the formation of hexahydrotriangulene (IX). On heating to 250° a new evolution of hydrogen was observed, but at a greatly reduced rate. After 5 hours, high vacuum sublimation of the residue yielded only some hexahydrotriangulene and no other triangulene derivative could be detected.

The complete polymerization of triangulene under conditions in which even the most reactive aromatic hydrocarbons, like hexacene[9] or 1,2-benzhexacene[10] can be prepared, indicates that triangulene is an unstable diradical I. The interpretation of this result is that Kekulé structures are of paramount importance when considering the stability of aromatic hydrocarbons. No other system of trigonal symmetry with a uniform distribution of paired electrons in molecular orbitals over the whole ring system seems to exist. This excludes the existence of *m*-quinonoid and similar systems which cannot be expressed in terms of Kekulé structures. This result was predicted by Clar[11] from the standpoint of classical structural chemistry and later by Longuet-Higgins[12] from the quantum mechanical standpoint.

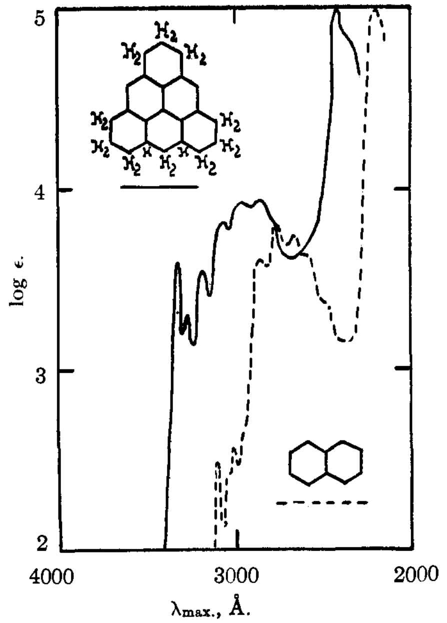

Fig. 3.——, absorption spectrum of dodecahydrotriangulene (XII) in alcohol. Maxima in Å. with log ε in parentheses: 3350 (3.60), 3285 (3.29), 3180 (3.54); 3060 (3.82), 2950 (3.95), 2860 (3.93); 2420 (5.00). - - - - - -, absorption spectrum of naphthalene in alcohol. Maxima in Å. with log ε in parentheses: 3110 (2.48), 3010 (2.56); 2850 (3.62), 2750 (3.80), 2660 (3.75), 2570 (3.64); 2210 (5.00).

This view is further supported by the results obtained from the reduction of triangulenequinone (XI). A superficial observation suggests that trianguleneequinone forms a green vat with alkaline sodium dithionite which dyes cotton green and after oxidation, changes to red. This vat would be derived from the diradical formula XIV. The analysis of the blue sodium salt, however, shows that it contains only one atom of sodium and must therefore have the formula XV. The "vat" therefore results from the reduction of one carbonyl group only and does not prove that trianguleneequinone has quinonoid properties. Moreover the free violet-blue hydroxyphenol XV has properties similar to coeranthronol[13] as would be expected from the formula XV. Further reduction of trianguleneequinone with zinc dust and sodium hydroxide solution gave, after the acidification of the greenish-yellow solution, a brown product, the acetate of which has an absorption spectrum (Fig. 4) closely related to those of naphtho-(2′,7′; 1,8)-anthrone (XXIII) and 1,2,3,8-tetrahydro-8-ketotriangulene (XXII). The compound must, therefore, have the structure XVII. Its formation can be explained by the reduction of the second carbonyl group to give XVI, followed by the

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(8) S. H. Tucker, *Analyst*, **64**, 410 (1939); **67**, 320 (1942); **75**, 170 (1950); *Chemistry and Industry*, 270 (1945).

(9) E. Clar, *Ber.*, **72**, 1817 (1939); Ch. Marschalk, *Bull. soc. chim.*, [5] **6**, 1112 (1939).

(10) E. Clar and Ch. Marschalk, *ibid.*, **17**, 444 (1950).

(11) E. Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, 1941, p. 311; 2nd Edition, 1952, pp. 93, 461.

(12) H. C. Longuet-Higgins, *J. Chem. Phys.*, **18**, 265 (1950).

(13) R. Scholl and J. Donat, *Ann.*, **512**, 1 (1934).

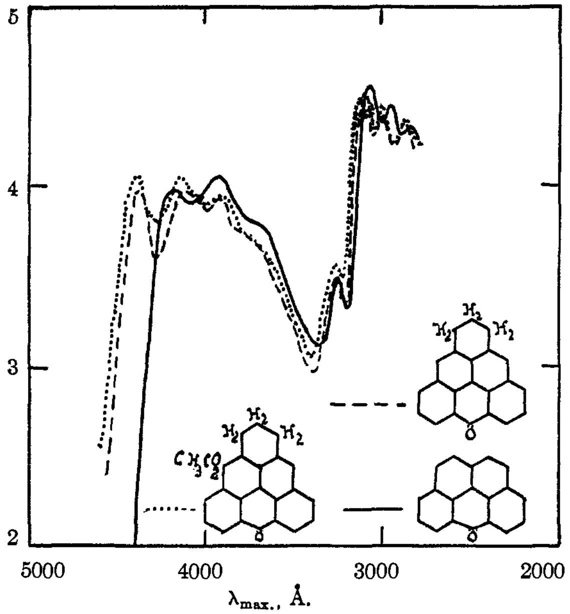

Fig. 4.——, absorption spectrum of naphtho-(2′,7′; 1,8)-anthrone (XXIII) in benzene. Maxima in Å. with log ε in parentheses: 4160 (3.98), 3950 (4.05), 3250 (3.50); 3070 (4.55), 2970 (4.46). - - - - -, absorption spectrum of 1,2,3,8-tetrahydro-8-keto-triangulene (XXII) in benzene. Maxima in Å. with log ε in parentheses: 4400 (3.96), 4140 (3.98), 3930 (3.92); 3275 (3.49); 3110 (4.50), 3000 (4.38), 2880 (4.34). ...., absorption spectrum of 1,2,3,8-tetrahydro-12-acetoxy-8-ketotriangulene (XVIII) in benzene. Maxima in Å. with log ε in parentheses: 4395 (4.04), 4140 (4.04), 3940 (3.98); 3270 (3.57); 3150 (4.47), 3090 (4.44), 3010 (4.45), 2880 (4.36).

migration of three H atoms to give XVII, a rearrangement which seems to be typical for triangulene derivatives of this kind.

Prolonged treatment with zinc dust and sodium hydroxide solution reduced triangulenequinone (XI) to XIX and XX, which on vacuum sublimation lost water and formed 4,8-dihydrotriangulene, XXI and XXII, respectively. The constitution of the latter was established by the absorption spectrum (Fig. 4). In accordance with this formulation, the compound does not show any phenolic properties, being insoluble in strong alkali, and is reduced to an autoxidizable product with zinc dust in acetic acid, as in the case of benzanthrone.

4,8-Dihydrotriangulene (XXI) is so oxidizable in air that it could not be obtained in a pure state. The oxidation product which was formed quantitatively during chromatography is XXII. Dihydrotriangulene was also obtained as by-product from the zinc dust melt of X and during the dehydrogenation of IX. In all cases complete oxidation to XXII took place during the purification. The formation of XXII from XXI is a remarkable example of the above-mentioned rearrangement. XVII, XXI and XXII were also obtained by the reduction of triangulenequinone with zinc dust in acetic acid.

When triangulenequinone XI was reduced with zinc dust in acetic anhydride the diacetate XIII was formed. Since it contains only two hydroaromatic H atoms no rearrangement to a trimethylene compound is possible. As would be expected for a derivative of 4,8-dihydrotriangulene (XXI) it readily oxidizes in air and decomposes on heating.

Experimental

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

Di-*o*-tolylphthalide (II).—This compound was prepared from tri-*o*-tolylcarbinol as described by Clar and Stewart.[2]

2-(Di-*o*-tolylmethyl)-benzoic Acid (III).—Zinc dust (100 g.), activated with copper, was added in portions over 48 hours to a boiling solution of the phthalide (II) (40 g.) in 20% ethanolic potassium hydroxide (300 ml.). After dilution with 500 ml. of water, the hot solution was filtered from the excess zinc dust which was washed with hot water. The filtrate was boiled to remove the alcohol and acidified with concentrated hydrochloric acid, when a white crystalline precipitate (36.5 g., 91%) was obtained. Crystallization from acetic acid or benzene gave clusters of small colorless needles, m.p. 239–240°, lit.[3] m.p. 241–243°. The acid III gave a pale yellow solution in concentrated sulfuric acid.

Anal. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37. Found: C, 83.61; H, 6.14.

1-Methyl-9-(*o*-tolyl)-10-anthrone (IV).—The acid III (20 g.) zinc chloride (10 g.) and sodium chloride (2 g.) were heated with constant stirring to 220° and maintained at that temperature for 15 to 20 minutes. The cold melt was extracted with boiling hydrochloric acid solution and the solid obtained washed with hot ammonia. The anthrone (IV) (18 g., 96%) crystallized from acetic acid in colorless prisms, m.p. 181–182°. The solution in concentrated sulfuric acid was yellow, changing to green on warming.

Anal. Calcd. for $C_{22}H_{18}O$: C, 88.56; H, 6.08. Found: C, 88.44; H, 6.16.

1-Methyl-9-(*o*-tolyl)-oxanthranol (V). (a) With Nitric Acid Solution.—The anthrone IV (3 g.) mixed with 3 ml. of nitrobenzene was refluxed with 150 ml. of nitric acid solution (d. 1.1) for 36 hours. After removal of the nitrobenzene by steam distillation, the solid was filtered off, extracted with dilute sodium hydroxide solution and washed. The oxanthranol (V) (3 g., 95%) crystallized from acetic acid or ethanol in colorless prisms which gave a red melt at 207–209°. The compound gave a magenta solution in concentrated sulfuric acid which changed to blue and then to green on standing.

Anal. Calcd. for $C_{22}H_{18}O_2$: C, 84.03; H, 5.77. Found: C, 84.47; H, 5.74.

(b) **With Selenious Acid Solution.**—The anthrone IV (3 g.), selenium dioxide (5.5 g.) and water (15 ml.) were heated for 10 hours at 220° in a sealed tube. The solid obtained was filtered off, washed and extracted with sodium hydroxide solution. The residue (2.5 g.) crystallized from acetic acid in colorless prisms which were identical with the previous sample of V.

Di-(*o*-carboxyphenyl)-phthalide (VIII).—This compound was obtained as a sirup in 35% yield, together with dihydroisobenzofuran-1,3-bisspiro-(3-phthalide) in the oxidation of di-*o*-tolylphthalide (II) (Clar and Stewart[2]). It could not be crystallized and the crude product was used for condensation.

9-(*o*-Carboxyphenyl)-oxanthranol-1-carboxylic Acid Lactone (VI).—The oxanthranol V (3 g.) was heated under pressure in 40 ml. of nitric acid solution (d. 1.12) at 200° for 10 hours. Crystallization of the product from acetic acid gave first an unidentified by-product (0.7 g.) as yellow plates m.p. 312–314°, which gave a deep red solution with alkaline sodium dithionite. It dissolved yellow in concentrated sulfuric acid and on the addition of copper powder the solution changed to green.

Anal. Found: C, 72.80, 72.66; H, 3.58, 3.32.

Concentration of the mother liquors and further crystallization from acetic acid gave the lactone (VI) as colorless plates (2 g.) which decomposed giving a red melt at 270–275°. It gave a pale yellow solution in concentrated sulfuric acid which did not change on heating to 110°.

Anal. Calcd. for $C_{22}H_{12}O_5$: C, 74.15; H, 3.39. Found: C, 74.10; H, 3.38.

9-(*o*-Carboxyphenyl)-9,10-dihydroanthracene-1-carboxylic Acid (VII).—Zinc dust was added in portions to a refluxing solution of the lactone VI (1.75 g.) in 20% ethanolic potassium hydroxide (75 ml.) and after 16 hours the diluted solution was filtered from excess zinc, which was washed with boiling water. After distilling off the ethanol, the hot filtrate was acidified with hydrochloric acid and the oily precipitate on boiling for 10 minutes, crystallized. When cold, the product was filtered off, washed with cold water and crystallized from acetic acid, colorless prisms (1.5 g.), m.p. 269–270° of the acid (VII) being obtained.

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.93; H, 4.67.

12-Hydroxytriangulene-4,8-quinone (X). (a) From 9-(*o*-Carboxyphenyl)-oxanthranol-1-carboxylic Acid Lactone (VI).—The lactone VI (1 g.) and copper powder (0.3 g.) were heated with 10 ml. of concentrated sulfuric acid at 120° for 1 hour, a deep blue solution being obtained. After filtering hot through sintered glass, the cold solution was poured into 40 ml. of water and the dark blue precipitate filtered off, washed and extracted several times with boiling acetic acid. Crystallization from trichlorobenzene and *o*-toluidine gave microscopic blue needles of (X) which did not melt below 450° but sublimed with slight decomposition in a high vacuum (10^{-6} mm.). The yield was almost the theoretical.

Anal. Calcd. for $C_{22}H_{10}O_3$: C, 81.97; H, 3.13. Found: C, 81.87; H, 3.20.

(b) From Di-(*o*-carboxyphenyl)-phthalide (VIII).—The crude dicarboxylic acid (VIII) (5 g.) was treated as above. The compound obtained (3.8 g.) proved to be identical with that above and its properties agreed with those described for a sample prepared by a different method by Weisz and Korczyn.[3] It dissolved giving blue solutions in concentrated sulfuric acid, in alkali, in basic solvents and in sodium acetate solution. The blue solution in pyridine, when treated with acetic anhydride, changed to red, the blue being regenerated by the addition of ammonia solution.

Triangulene-4,8-quinone (XI). (a) From 9-(*o*-Carboxyphenyl)-9,10-dihydroanthracene-1-carboxylic Acid (VII).—The acid VII (1 g.) and the sodium salt of *m*-nitrobenzenesulfonic acid (0.5 g.) were added to 15 ml. of concentrated sulfuric acid and the solution kept at room temperature for 2 hours. The initial light yellow color of the solution rapidly changed to violet-red, a transitory green stage being observed. After pouring the solution into 150 ml. of water and boiling, the red precipitate was filtered off, washed and crystallized from nitrobenzene, red needles (0.8 g.) being obtained which decomposed without melting at 310–320° to give a black residue. Triangulene-4,8-quinone (XI) sublimed in a vacuum in dark red needles and gave a violet-red solution in concentrated sulfuric acid.

Anal. Calcd. for $C_{22}H_{10}O_2$: C, 86.26; H, 3.29. Found: C, 86.57; H, 3.30.

(b) From 12-Hydroxytriangulene-4,8-quinone (X).—The blue compound X (1 g.) in dilute sodium hydroxide solution was reduced with zinc dust till on exposure to air the blue color did not reappear (after *ca.* 10 min.). After filtering, oxygen was bubbled through the solution and the red precipitate obtained, filtered off, washed and crystallized from nitrobenzene, giving red needles of triangulene-4,8-quinone (XI).

1,2,3,5,6,7-Hexahydrotriangulene (IX).—The blue compound X (1 g.), zinc dust (1.2 g.) and sodium chloride (1.2 g.) were ground together and moist zinc chloride (7 g.) added. The mixture was melted and the temperature raised with constant stirring to 300° over 15 minutes. At 250° a deep red color was observed, but this disappeared on further heating. The cold melt was decomposed with hot dilute acetic acid and the residue extracted with benzene, the solution obtained being chromatographed (alumina). Using petroleum ether (b.p. 40–60°) as eluant, a colorless eluate with a violet fluorescence was obtained, which on concentration gave colorless needles (0.4 g., m.p. 175–176°) of hexahydrotriangulene (IX). It dissolved in concentrated sulfuric acid to give a yellow solution with a dark green fluorescence which changed to green on standing.

Anal. Calcd. for $C_{22}H_{18}$: C, 93.57; H, 6.43. Found: C, 93.80; H, 6.15.

Dodecahydrotriangulene (XII).—Triangulene-4,8-quinone (XI) (0.5 g.), red phosphorus (1 g.), potassium iodide (0.5 g.) and 55% hydriodic acid solution (10 ml.) were heated together under pressure at 210° for 10 hours. Having diluted the mixture with water, the solid was filtered off, washed and extracted with benzene to give a solution which was dried and chromatographed (alumina). Elution with petroleum ether (b.p. 40–60°) gave a colorless, non-fluorescent solution, which on concentration and crystallization from methanol yielded clusters of colorless, silky needles (m.p. 162–163°) (0.25 g.) of dodecahydrotriangulene. The hydrocarbon which sublimed in a vacuum in needles, did not dissolve readily in sulfuric acid, but on warming gave a crimson solution, which on standing became yellow with a green fluorescence.

Anal. Calcd. for $C_{22}H_{24}$: C, 91.61; H, 8.39. Found: C, 91.43; H, 8.35.

A second colorless, violet-fluorescent eluate was obtained with a petroleum ether (b.p. 40–60°)-benzene mixture, which on concentration gave hexahydrotriangulene (IX), m.p. 174–175°, 20 mg.

Dehydrogenation of Dodecahydrotriangulene (XII).—The hydrocarbon XII (0.5 g.) and 20% palladium–charcoal (0.5 g.) were heated together in an air-free carbon dioxide[8] atmosphere, and the hydrogen evolved measured in a nitrometer. At 210°, a brisk evolution was observed and hydrogen (110 ml.) was collected which roughly corresponds to the formation of hexahydrotriangulene (IX). On heating to 250° hydrogen was again given off, but at a greatly reduced speed. After 5 hours, the residue was heated in a vacuum and hexahydrotriangulene (IX) sublimed in small needles, 40 mg., m.p. 173–175°. No other sublimate was obtained even when the temperature was raised to 500°.

Dehydrogenation of Hexahydrotriangulene (IX). (a) By Sublimation over Palladium–Charcoal.—Palladium–charcoal (20%) (6 g.), prepared from granulated, metal-free charcoal, was mounted in a combustion tube. A slow current of air-free carbon dioxide[8] was allowed to enter at one end, while a vacuum (1 mm.) was applied at the other. Prior to dehydrogenation, the catalyst was heated to 350° and the apparatus swept out till free from air. To test the efficiency of the catalyst 9,10-dihydroanthracene (m.p. 106°) (0.1 g.) was sublimed over it at 310° and the theoretical yield of anthracene (m.p. 212–214°) was obtained. The process was then repeated using hexahydrotriangulene (IX) (50 mg.) (m.p. 174°), but no sublimate was obtained, even when the catalyst was heated to 500°. The activity of the catalyst was retested as before and anthracene (m.p. 214°) was obtained. Similar results were obtained on repetition of the above series of reactions.

(b) By Heating in Trichlorobenzene with Palladium–Charcoal.—After palladium–charcoal (20%) (10 mg.) had been boiled with trichlorobenzene (15 ml.) till no oxygen was detectable in the carbon dioxide[8] passing over the surface of the mixture, hexahydrotriangulene (IX) (30 mg.) was introduced. The dehydrogenation was carried out before a spectroscope and in the hot reaction mixture a sharp absorption band at 4600 Å. was seen to develop. On allowing the solution to cool to room temperature, however, a strong band at 4440 Å. and a faint band at 4630 Å. were observed, which disappeared on reheating the solution, the original band only being detectable. No other bands were observed during the course of the reaction. After boiling for 7 hours the solution was diluted with petroleum ether (b.p. 40–60°) and chromatographed (alumina). Elution with petroleum ether (b.p. 40–60°) and concentration yielded some unchanged hexahydrotriangulene (4 mg.), m.p. 172–174°.

4,8-Dihydro-12-hydroxy-8-ketotriangulene (XV).—Finely divided triangulene-4,8-quinone (XI) (0.1 g.) was added to 5% sodium hydroxide solution (15 ml.) containing ethanol (10 ml.). Sodium dithionite (0.1 g.) was introduced and the mixture refluxed till the solid was completely dissolved. The ethanol was then distilled from the green-blue solution, from which on cooling a dark blue solid crystallized. This was filtered off, washed carefully with distilled water containing ammonia, and dried. Analysis showed it to be the sodium salt of (XV), containing water of crystallization.

Anal. Calcd. for $C_{22}H_{11}O_2Na$: C, 79.99; H, 3.36; Na, 6.96. Calcd. for $C_{22}H_{13}O_3Na$: C, 75.86; H, 3.76; Na, 6.63. Found: C, 76.98; H, 3.83; Na, 6.45.

To obtain the free hydroxy compound, the blue solution, prepared as above, was acidified with acetic acid, to give a blue precipitate, which crystallized from acetic acid containing a little sodium dithionite in blue needles (85 mg.) of 4,8-dihydro-12-hydroxy-8-ketotriangulene (XV) which gave a violet-red solution in concentrated sulfuric acid. It dissolved readily in ethanol giving a blue solution which decolorized very rapidly on exposure to light. The addition of a little stannous chloride, however, rendered the solution stable.

Anal. Calcd. for $C_{22}H_{12}O_2$: C, 85.72; H, 3.93. Found: C, 85.52; H, 3.87.

1,2,3,8-Tetrahydro-12-hydroxy-8-ketotriangulene (XVII).—Zinc dust activated with copper, was added in portions to a boiling 15% sodium hydroxide solution (60 ml.) containing finely divided triangulene-4,8-quinone (XI) (1.5 g.). The green color of the solution, which developed rapidly, gradually changed to a pale greenish-yellow which however was not stable but became violet-blue on exposure to the air. After refluxing for 6 hours, the solution was filtered into hydrochloric acid giving a greenish-brown precipitate, which was filtered off, dried and sublimed in a vacuum. The reddish-brown sublimate was crystallized from xylene yielding light brown needles (0.7 g.) of 1,2,3,8-tetrahydro-12-hydroxy-8-ketotriangulene (XVII), which decomposed giving a red melt at 220–225°. In aqueous alkali it gave a blue solution, which on the addition of sodium dithionite and boiling changed to green and then to yellow.

Anal. Calcd. for $C_{22}H_{14}O_2$: C, 85.10; H, 4.55. Found: C, 84.88; H, 4.65.

The compound was acetylated by refluxing with acetic anhydride for 15 minutes and on cooling yellow needles of the acetate (XVIII) were obtained which gave a red-brown melt at 269–272°. In concentrated sulfuric acid, it gave a violet solution which on standing changed to magenta. Hydrolysis with ethanolic sodium hydroxide gave a blue solution.

Anal. Calcd. for $C_{24}H_{16}O_3$: C, 81.80; H, 4.58. Found: C, 81.55; H, 4.77.

1,2,3,8-Tetrahydro-8-ketotriangulene (XXII). (a) **From Zinc Dust Melt of (X).**—In the chromatographic purification of IX, a second orange-red band was observed, a sample of which gave a sharp absorption band at 4405 Å. in benzene and at 4440 Å. in trichlorobenzene. On eluting with a benzene–ether mixture, the color of the band changed to pale yellow and a yellow-green eluate was obtained which on concentration yielded yellow needles, m.p. 258–259°, of 1,2,3,8-tetrahydro-8-ketotriangulene (XXII). The compound, which was insoluble in alkali, gave a brown solution in concentrated sulfuric acid, which on standing rapidly changed to dark red. Sublimation in a vacuum or recrystallization from acetic anhydride did not alter its constitution.

Anal. Calcd. for $C_{22}H_{14}O$: C, 89.78; H, 4.80. Found: C, 89.25; H, 4.75.

(b) **From the Dehydrogenation of (IX) in Trichlorobenzene.**—In the chromatogram of the reaction mixture an orange-red band was observed as above. Elution again gave a yellow-green solution but the quantity present was too minute to be isolated. Spectrographic tests, however, showed the presence of (XXII).

(c) **From the Zinc/Sodium Hydroxide Reduction of (XI).**—The xylene mother liquors from the crystallization of XVII were concentrated and chromatographed (alumina). Elution with a benzene–ether mixture gave a yellow-green solution which yielded yellow needles (0.2 g.), m.p. 258–259° identical with the previous sample of (XXII).

(d) **From the Zinc/Acetic Acid Reduction of (XI).**—When zinc dust was added to boiling acetic acid (50 ml.) containing triangulene-4,8-quinone (XI) (0.5 g.), a short-lived violet-blue solution was obtained which very rapidly decolorized. After refluxing for 5 hours, the clear yellow solution was concentrated and diluted with water containing sodium dithionite giving a precipitate which was filtered off, washed and sublimed in a vacuum from the excess zinc dust. Extraction of the sublimate with alkaline sodium dithionite gave a green solution from which was obtained a brown precipitate on acidification with acetic acid. This crystallized from xylene in light brown needles (0.1 g.) which were identical with the previous sample of 1,2,3,8-tetrahydro-12-hydroxy-8-ketotriangulene (XVII). The residue from the extraction was resublimed and crystallized from xylene (charcoal) to give yellow needles (0.3 g.), m.p. 256–258°, of 1,2,3,8-tetrahydro-8-ketotriangulene (XXII).

4,8-Diacetoxy-4,8-dihydrotriangulene (XIII).—Triangulene-4,8-quinone (XI) (0.1 g.) was dissolved in acetic anhydride (20 ml.) containing a little sodium dithionite, and zinc dust was added. A light yellow solution with a green fluorescence was obtained which after boiling for one hour, was filtered from the zinc into a sodium dithionite solution. The acetic anhydride slowly hydrolyzed to give a pale yellow precipitate of 4,8-diacetoxy-4,8-dihydrotriangulene (XIII) which polymerized when crystallization was attempted. The compound, which melted with decomposition at 160–170°, rapidly darkened to an orange-brown color when exposed to air. In concentrated sulfuric acid, it gave a yellow-green solution which quickly changed to brown.

Anal. Calcd. for $C_{26}H_{18}O_4$: C, 79.17; H, 4.60. Found: C, 79.86; H, 4.35.

Naphtho-(2′,7′-1,8)-anthr-10-one (XXIII).—Crystallized naphthanthrone (XXIII) (1 g.), prepared from pyrene as described by Vollmann, Becker, Corell and Streeck,[6] was dissolved in benzene and chromatographed (alumina). Elution with benzene completely removed a colorless violet-fluorescent band, and the second pale yellow band was washed through with a benzene–ether mixture. The pale yellow eluate yielded on concentration yellow elongated plates, m.p. 252–253°, lit.[6] m.p. 242–243° (0.8 g.) of naphthanthrone (XXIII) which dissolved red in concentrated sulfuric acid.

Anal. Calcd. for $C_{18}H_{10}O$: C, 89.74; H, 3.96. Found: C, 89.58; H, 4.26.

2,3-Trimethylenepyrene (XXIV).—Sodium chloride (2 g.) and moist zinc chloride (10 g.) were added to an intimate mixture of naphthanthrone (XXIII) (1 g.) and zinc dust (2 g.). The mixture was melted and the temperature raised over 15 minutes to 300° with constant stirring. After decomposition of the cold melt with dilute acetic acid, the residue was filtered off, washed and dried. Chromatographic purification (alumina), with petroleum ether (b.p. 40–60°) as eluant, yielded colorless crystals (0.8 g.), m.p. 112–113°, lit.[7] m.p. 107–108°, of 2,3-trimethylenepyrene (XXIV) which in concentrated sulfuric acid gave a yellow, green-fluorescent solution changing to dark green on standing.

Anal. Calcd. for $C_{19}H_{14}$: C, 94.20; H, 5.80. Found: C, 94.42; H, 5.52.

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