2,2-Bis-(dineopentylacetyl)-propane (XI).—Alkylation of 10 g. (0.03 mole) of 1,1-bis-(dineopentylacetyl)-ethane (VI) with sodium and methyl iodide[11] gave 8 g. or 76% of 2,2-bis-(dineopentylacetyl)-propane, m. p. 65–66°. *Anal.* Calcd. for $C_{27}H_{52}O_2$: C, 79.5; H, 12.7. Found: C, 79.8; H, 12.8. This compound gave a negative enol test with ferric chloride; it was unaffected by refluxing for twenty-four hours with 60% sodium hydroxide; it did not discharge the red color of a carbon tetrachloride solution of bromine. A sample run in the Grignard machine liberated 0.63 equivalent of methane and added 1.36 equivalents of methylmagnesium bromide. Both of these reactions occurred at the boiling point of dibutyl ether. No reaction took place at room temperature.

Summary

1. The bromomagnesium enolates of methyl and ethyl dineopentylcarbinyl ketones react as true Grignard reagents.

2. These enolates have been used to prepare several new compounds including beta-diketones, beta-keto acids and beta-ketols.

3. The diketones, bis-(dineopentylacetyl)-methane, 1,1-bis-(dineopentylacetyl)-ethane and 2,2-bis-(dineopentylacetyl)-propane, were not cleaved by refluxing with 60% alkali.

4. The reactions of 2,2-bis-(dineopentylacetyl)-propane emphasize the fact that the tertiary hydrogen of the dineopentylcarbinyl group is tightly bound and that this group exerts a pronounced steric effect on an adjacent carbonyl. This diketone is the only compound yet studied in which the tertiary hydrogen of the dineopentylcarbinyl group can be forced to react as an enol hydrogen.

STATE COLLEGE, PENNSYLVANIA

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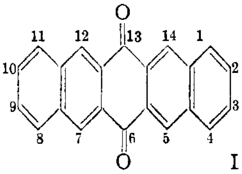
[COMMUNICATION NO. 842 FROM THE KODAK RESEARCH LABORATORIES]

Action of Grignard Reagents on Certain Pentacenequinones, 6,13-Diphenylpentacene

BY C. F. H. ALLEN AND ALAN BELL

In continuation of the investigation of the behavior of polynuclear ketones with the Grignard reagent, 6,13-pentacenequinone, I, and 5,7,12,14-pentacenediquinone, XXI, have been examined.[1] The former is of particular interest because in one of the possible bond structures, all the double bonds radiate from the central ring. This arrangement would be expected to be the most stable of the possibilities, since, in accordance with the Fries rule, it has two normal naphthalene nuclei.[2] No such substance has yet been described. Since it contains a crossed conjugated system,[3]



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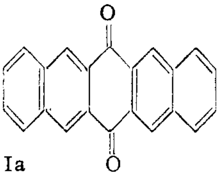

Ia

it would be expected to resemble dibenzalacetone in its behavior with phenylmagnesium bromide; the reaction should proceed stepwise, requiring two treatments with the Grignard reagent.[4]

Phenylmagnesium bromide reacts with the pentacenequinone to give mainly (70%) a diol IV as a result of 1,2-addition to the carbonyl groups, but, at the same time, a small amount (15%) of a diketone II is formed by 1,4-addition. The latter substance furnishes 5,14-diphenyl-6,13-pentacenequinone, III, on air oxidation of the alkaline solution. The formation of the diketone may be taken as evidence in favor of the location of the double bonds in one ring. The structure of the quinone III was determined by alkaline fusion, when 1,4-diphenylnaphthalene, 1,4-diphenylnaphthalene-2-carboxylic acid, and β-naphthoic acid were formed.

The bond structure of quinone III is written to correspond with I. When this quinone is treated with an excess of phenylmagnesium bromide, a mixture results from which a tetraphenylquinone V and the corresponding stereoisomeric diketones Va can be isolated. The structure of the quinone V was shown by cleavage with sodium amide, which gave only 1,4-diphenylnaphthalene. There was no trace of the diol VI, formed by 1,2-addition. This result would be expected in view of the known facts about hindrance to 1,2- and 1,4-addi-

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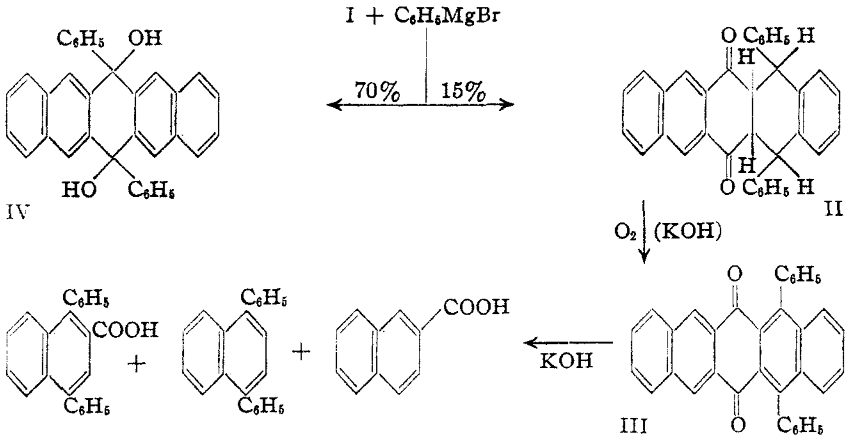
(1) Allen and Overbaugh, THIS JOURNAL, **57**, 740, 1322 (1935); Allen and Gilman, *ibid.*, **58**, 937 (1936); Allen and Bell, *ibid.*, **62**, 2408 (1940); Allen and McGibbon, *Can. J. Res.*, **B16**, 35 (1938).

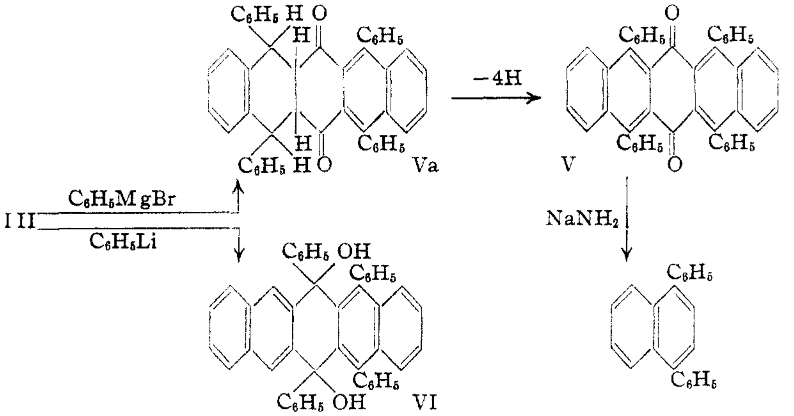
(2) (a) Fries, Walter and Schilling, *Ann.*, **516**, 248 (1935). Also footnote 1, page 252. (b) Fieser in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, Chap. 2, pp. 92, 107–110.

(3) Of course, the molecule actually contains two similar crossed conjugated systems, permitting a greater number of possible products. according to whether one or both react in each treatment.

(4) Allen and Blatt in Gilman, "Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1938, Chap. 6, p. 598.



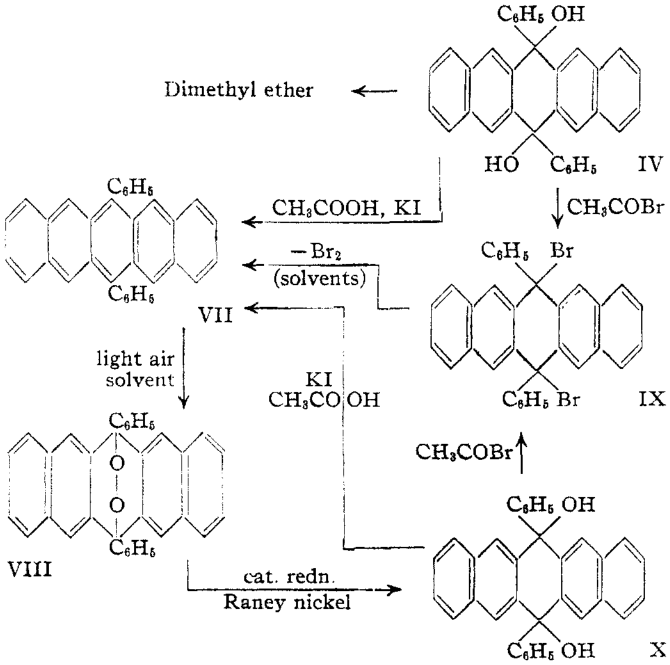
tion.[5] The action of phenyllithium, however, gives one of the two possible stereoisomeric diols.



As in the preceding Grignard treatment, the production of the ketone Va is possible only by virtue of a 1,4-addition, and shows that the double bonds are placed as shown in III. It is highly probable that they are so arranged in I, since there is no reason to assume that the introduction of phenyl groups in the first reaction with the Grignard reagent will bring about a change. This chemical evidence, thus, points to the radiating bond structure I for 6,13-pentacenequinone.

Having completed the examination of the 1,4-addition products, the reactions of the diol IV were next determined and some rather interesting results were secured. Upon reduction with potassium iodide in acetic acid, a bluish-red hydrocarbon, 6,13-diphenylpentacene, VII, remains.

This hydrocarbon is not attacked by atmospheric oxygen in solution, if kept in the dark (it is attacked rapidly in sunlight) but in the diffuse laboratory light the solution slowly becomes colorless, and a peroxide VIII results. Catalytic reduction of the peroxide furnishes a diol; this is a stereoisomer of the diol formed by the action of phenylmagnesium bromide on the pentacenequinone, I, for both diols give the same dibromide, IX, when treated with acetyl bromide. The diol from the peroxide is assigned the *cis* configuration, X, since it results from a ring scission—the Grignard product is, thus, *trans*. The *trans* diol readily furnishes a dimethyl ether, which does not give a hydrocarbon by Bachmann's method.[6] In the dibromide the bromine atoms are very loosely held, for they are lost by simply boiling with a solvent. For example, when acetone is used, the products are 6,13-diphenylpentacene and bromoacetone. These reactions are summarized by the following chart.



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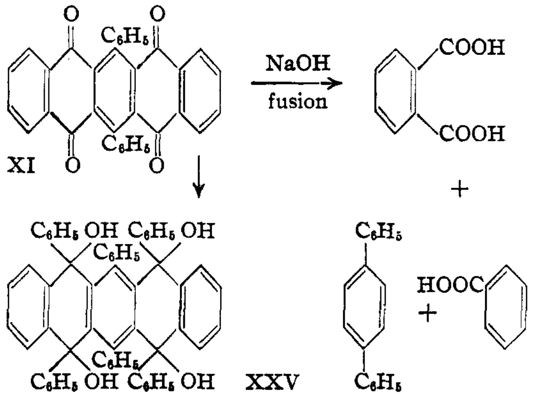
(5) Ref. 4, page 583.

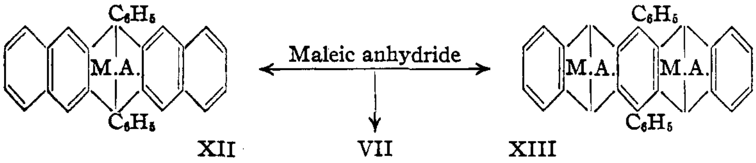
(6) Bachmann and Chemerda, THIS JOURNAL, **60**, 1023 (1938).

Upon vigorous oxidation, 6,13-diphenylpentacene gives 6,13-diphenyl-5,7,12,14-diquinone, XI; its structure is shown by the nature of the cleavage products from alkaline fusion, —*p*-terphenyl, and phthalic and benzoic acids.



With phenylmagnesium bromide, the diquinone gave a tetraol, XXV, which could not be reduced to a hydrocarbon by potassium iodide in acetic acid.

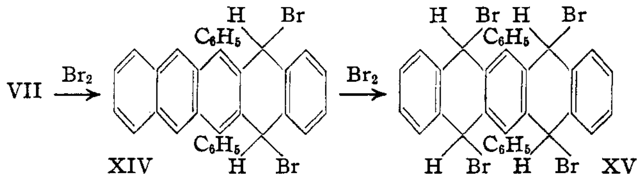
6,13-Diphenylpentacene adds both one and two molecules of hydrogen, bromine, and maleic anhydride. The mono- and di-addition products from maleic anhydride are obtained at the same time. The mono-addition product is unchanged by further treatment with an excess of the reagent, so it is not an intermediate; the most probable formulas resulting from the reaction with maleic anhydride are indicated below (XII, XIII).



The formation of a di- or tetrabromide can be largely controlled by the amount of bromine used, one mole giving principally a dibromide. This is isomeric with the product from the action of acetyl bromide on the diols. While both dibromides give colored solutions in boiling acetone, the differences in this solvent are very marked; the one from the diol goes into solution at once, and the crystalline hydrocarbon separates in a few minutes; whereas the new isomer remains undissolved, the reddish color of the solution gradually deepening with prolonged boiling. Since the new dibromide is not identical with the one secured from the diol, but intermediate in the formation of the tetrabromide, it is probably the 5,14-addition product XIV.

The tetrabromide XV loses all its bromine when treated with zinc dust or boiled in alkaline solutions, and the hydrocarbon is regenerated. If heated by itself, hydrogen bromide is evolved, and an amorphous bromine-containing polymer of extremely high melting point and sparing solubility (except in benzene) results; the green benzene solution is highly fluorescent. An excess of bromine upon either the dibromide IX secured via the diol or upon the tetrabromide results in substitution, as hydrogen bromide is evolved.

6,13-Diphenylpentacene does not appear to be reduced by sodium amalgam, nor does it add metallic sodium, but treatment with hydrogen in the presence of a Raney nickel catalyst gives a variety of substances hydrogenated to a varying degree. After one-half hour, the principal product is a dihydro derivative; after twenty-four hours this is converted into a mixture of tetrahydro and hexahydro derivatives, neither of which is further altered. In a single instance, a second dihydro derivative was secured in small yield from a six-hour reduction.

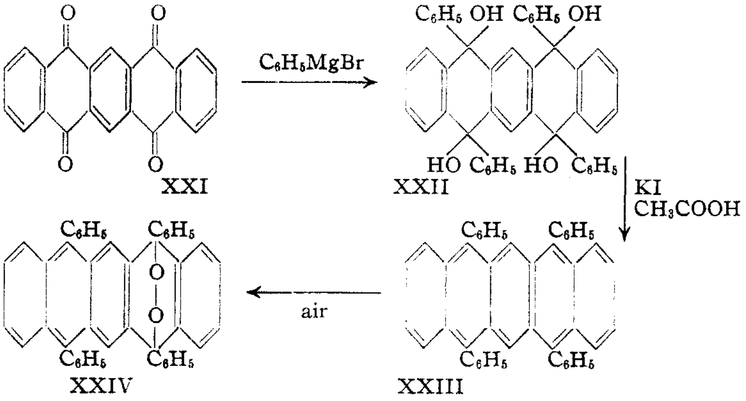


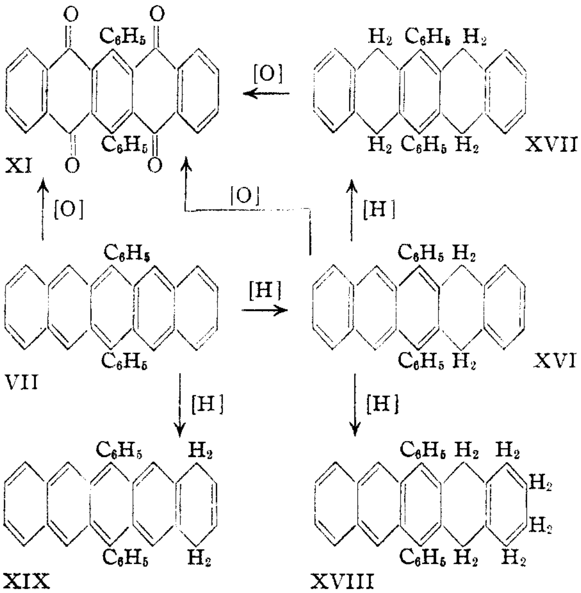
Like the parent hydrocarbon, the first dihydro derivative combines with atmospheric oxygen, which it slowly loses (during a period of ten days at 100° *in vacuo*), regenerating the starting material. It adds one equivalent of maleic anhydride. It is oxidized to 6,13-diphenylpentacene-5,7,12,14-diquinone, XI. The structure that seems best in accord with all these properties and the above-mentioned further reduction products is 6,13-diphenyl-5,14-dihydropentacene, XVI.

The tetrahydro derivative does not add maleic anhydride, but is oxidizable to the same diquinone, XI. Since it is incapable of further reduction, it is probably completely benzenoid, and is assigned the structure 6,13-diphenyl-5,7,12,14-tetrahydropentacene, XVII.

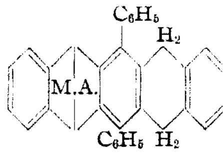
The hexahydro derivative gives strongly fluorescent solutions in solvents such as benzene; the fluorescence disappears as soon as more than one equivalent of maleic anhydride is added. It was not found possible to isolate an addition product—the hydrocarbon was recovered each time. This implies that the equilibrium is far on the side of the components, even more than that of 9,10-diphenylanthracene.[7] Structure XVIII is tentatively assigned to this hydrocarbon.

The second dihydro compound was not obtained in sufficient amount for a complete study; it did not give the diquinone XI upon oxidation. However, since only the two above polyhydro derivatives were secured under all the experimental conditions, any dihydro derivative must be convertible into one or the other of these by further reduction; but one structure XVI can give both. Therefore, the structure 6,13-diphenyl-1,4-dihydropentacene, XIX, seems highly probable for the second dihydro compound.





The maleic anhydride addition product of the 5,14-dihydro derivative probably has the structure XX for the unsaturation of that hydrocarbon terminates at the 7,12-positions, as evidenced by the formation of the tetrahydro compound; thus, XX is formed from XVI.



XX

A choice among the three possible bond structures of 6,13-diphenylpentacene is not satisfactory, owing to the different plausible interpretations of the available evidence. All the facts can be reconciled with any of the structures. The bond arrangement shown in VII has been suggested for pentacene itself.[3]

5,7,12,14-Pentacenediquinone, XXI, gave a tetraol, XXII, when treated with an excess of phenylmagnesium bromide. Upon treatment with potassium iodide in acetic acid, a purple hydrocarbon, 5,7,12,14-tetraphenylpentacene, XXIII, results; its solutions are somewhat bluer than the diphenyl homolog. This gives only a monoperoxide, XXIV, with atmospheric oxygen.

The maxima in the absorption curves of the colored hydrocarbons VII and XXIII are given in Table I; the values enclosed in parentheses are those of less density.

Table I

Maxima in mμ

VII	220	(246)	305	(331)	(348)	(477)	509	547	592
XXIII	260	(299)	312	(347)	(362)	(492)	524	563	609

Experimental

A. The 6,13-pentacenequinone was secured by chromic acid oxidation of crude dihydropentacene[8] essentially as described by Mills[9] for tetrahydropentacene. The yield of crude quinone was 76%, which dropped to 61% after two recrystallizations from nitrobenzene. The yellow needles, m. p. 385–387°, give a brilliant blue color with an intense red fluorescence in concentrated sulfuric acid.

The 5,7,12,14-pentacenediquinone was obtained by Mills' procedure.[10]

B. The Grignard Reactions. a. The Diphenylpentacenequinone and the *trans* Diol IV.—To a solution of phenylmagnesium bromide (588 g. of bromobenzene, 91.2

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[7] Bachmann and Kloetzel, This Journal, **60**, 481 (1938).

[8] Marschalk, *Bull. soc. chim.*, [5] **4**, 1535 (1937); **5**, 156 (1938).

[9] Mills and Mills, *J. Chem. Soc.*, **101**, 2194 (1912).

[10] We are indebted to Dr. S. H. J. Greenwood for a supply of this material.

g. of magnesium, 1400 cc. of ethyl ether) filtered to remove traces of metal and diluted by 1400 cc. of butyl ether was added 100 g. (0.33 mole) of pentacenequinone; the solid dissolved to give a green solution, which was heated for two hours on the steam-bath, the ethyl ether being allowed to distill. After cooling, the residue was decomposed by chipped ice, and acidified by addition of 1 liter of 50% acetic acid. The insoluble material (110 g.) was filtered; the filtrate was steam-distilled, the dried residue triturated with 400 cc. of ether, and the 9.3 g. of additional solid combined with the first. The mixture of the *trans*-diol IV and diketone II was easily separated by extraction with two 500-cc. portions of boiling dioxane in which the diol is insoluble. The crude diol was extracted three times, using 500 cc. of hot alcohol each time, and dried; the yield was 91 g. (70%). For analysis, it was recrystallized twice from toluene and once from dioxane; it formed prisms; m. p. 315°.

Anal. Calcd. for $C_{34}H_{24}O_2$: C, 87.9; H, 5.2. Found: C, 88.0; H, 5.4.

The tetrahydro-5,14-diphenylpentacene-6,13-quinone (II) was obtained by removing the dioxane *in vacuo*, and washing the yellow residue with hot alcohol; the yield was 19 g. (15%). It was dissolved in alcoholic potash (green solution) and aerated; yellow needles of 5,14-diphenyl-6,13-pentacenequinone (III) separated in a yield of 13.8 g. The quinone separates from chlorobenzene in fine yellow rods, m. p. 309°, and gives a blue color with concentrated sulfuric acid. It is not reduced by sodium hydrosulfite.

Anal. Calcd. for $C_{34}H_{20}O_2$: C, 88.7; H, 4.4. Found: C, 88.6; H, 4.4.

The relative amounts of 1,2 and 1,4-addition were unaffected by the presence of cuprous chloride, nor was there any reduction of diol to hydrocarbon when metallic magnesium was present.

The alkaline fusion was carried out by heating a finely-ground mixture of 1 g. of the quinone and 6 g. of potassium hydroxide at 310° for ten minutes and at 290° for an additional ten minutes. The crude cooled melt was dissolved in water, and the 1,4-diphenylnaphthalene extracted with chloroform. It was twice recrystallized from alcohol and compared with an authentic specimen; the mixed melting point was not depressed. Acidification of the aqueous solution precipitated a mixture of β-naphthoic and 1,4-diphenylnaphthoic acids, which were separated by differential solubility in cold acetic acid, and identified by melting points, alone and admixed with known specimens.

b. **5,7,12,14-Tetraphenyl-6,13-pentacenequinone** (V).—This was obtained from 5 g. of 5,14-diphenyl-6,13-pentacenequinone (III) and filtered phenylmagnesium bromide (from 30 g. of bromobenzene, 5 g. of magnesium, and 125 cc. of ethyl ether) at room temperature for forty hours. After appropriate manipulations, 3.9 g. (60%) of a mixture of the stereoisomeric tetrahydro derivatives (Va) was secured; it was separated by fractional crystallization from acetic acid. The yellow stereoisomeric diketones separate as rods; m. p. (A) 272° and (B) 266°.

Anal. Calcd. for $C_{46}H_{32}O_2$: C, 89.6; H, 5.2. Found: (A) C, 89.5; H, 4.7; (B) C, 89.2; H, 4.9.

In the Grignard machine the diketones do not give off gas immediately, showing that they are not enolized. During a half-hour of heating at 100°, a little gas is liberated; this is of doubtful significance, because 2.1 additions are found.

On being heated at 300°, the diketones melted, then gradually solidified and eventually the quinone V resulted; this crystallized well from pyridine or cymene, in yellow rods; m. p. 397°. It gives a blue color, which slowly turns purple, with concentrated sulfuric acid, and is not reduced by sodium hydrosulfite.

Anal. Calcd. for $C_{46}H_{28}O_2$: C, 90.2; H, 4.6. Found: C, 89.6; H, 4.6.

The structure was shown by cleavage with sodium amide in cymene, refluxing overnight and working up by appropriate manipulation; 1 g. of quinone gave 0.58 g. (75%) of 1,4-diphenylnaphthalene.

The 5,6,13,14-tetraphenyl-6,13-diol (VI) was prepared in the usual way from phenyllithium and the quinone III in ethyl ether. It crystallized from benzene in prisms; m. p. 392°.

Anal. Calcd. for $C_{46}H_{32}O_2$: C, 89.6; H, 5.2. Found: C, 89.8; H, 5.2.

It is unaffected by potassium iodide in acetic acid. A green solution with bright yellow-green fluorescence is produced by iron and acetic acid.

c. **5,7,12,14-Tetraphenyl-5,7,12,14-tetrahydroxy-5,7,12,14-tetrahydropentacene** (**XXII**).—The reaction was carried out as described above, using the filtered Grignard reagent from 31.4 g. of bromobenzene, 4.9 g. of magnesium, and 75 cc. of ether, replacing the ethyl ether by an equal amount of butyl ether, and adding 3.2 g. of pentacenediquinone. The insoluble portion, after decomposition by iced acetic acid, was worked up by means of acetone and benzene; the tetraol separated from benzene in rods; m. p. 270°. There was but one product, the yield of which was 4.6 g. (76%).

Anal. Calcd. for $C_{46}H_{34}O_4$: C, 84.9; H, 5.3. Found: C, 84.5; H, 5.3.

C. **6,13-Diphenylpentacene** (VII).—A mixture of 30 g. each of the *trans*-diol and potassium iodide in 800 cc. of glacial acetic acid was refluxed for one hour and allowed to cool. The reddish-purple solid was filtered and recrystallized from nitrobenzene, from which it separated in purple needles containing solvent of crystallization; m. p. 305°, (VIIa); the yield was 25 g. While the hydrocarbon is formed in hot acetic acid alone, the addition of the potassium iodide greatly decreases the time required. To remove the nitrobenzene, the purple solid (VII) suspended in acetic acid, alcohol or ether, was refluxed for twenty minutes. 6,13-Diphenylpentacene (VII) forms violet-blue needles; m. p. 318–320°.

Anal. Calcd. for $C_{34}H_{22}.C_6H_5O_2N$ (VIIa): C, 86.8; H, 4.9; N, 2.5; for $C_{34}H_{22}$ (VII): C, 94.8; H, 5.2. Found: (VIIa) C, 88.1; H, 4.7; N, 2.3; (VII, five days, *in vacuo*), C,[10a] 94.5, 94.6; H, 5.1, 5.0.

The hydrocarbon dissolves in benzene to give a magenta-colored solution which exhibits a brilliant orange-red fluorescence under an ultraviolet lamp; the solution retains its color in the dark, but in sunlight becomes colorless. The solution now contains the peroxide.

[10a] Most of the hydrocarbons described in this paper burned with difficulty, and gave slightly low values for carbon.

a. **6,13-Diphenylpentacene-6,13-peroxide** (**VIII**) was most conveniently secured by dissolving 1 g. of the hydrocarbon in 500 cc. of carbon disulfide and exposing it to sunlight until the color had disappeared. After partial evaporation and two recrystallizations from the same solvent, an addition product of the peroxide and solvent resulted. The carbon disulfide of crystallization was removed after standing for eight days at room temperature or twenty hours at 100° *in vacuo*. The peroxide crystallizes in prisms, which, in a capillary tube, begin to turn purple at about 208° and melt to a magenta liquid at 221–222°; no gas is evolved.

Anal. Calcd. for (A) [$(C_{34}H_{22}O_2)_4 \cdot CS_2$]: C, 85.4; H, 4.6; S, 3.3; (B) $C_{34}H_{22}O_2$: C, 88.3; H, 4.8. Found: (A) C, 86.1; H, 4.2; S, 3.3; (B) C, 88.3; H, 4.8.

b. **6,13-Diphenylpentacene-5,7,12,14-diquinone** (**XI**).—To a boiling suspension of 10 g. of the hydrocarbon in 200 cc. of acetic acid was added through a dropping funnel, over one-half hour, a solution of 20 g. of chromium trioxide in 200 cc. of dilute acetic acid. After a further fifteen minutes, 5.5 g. of crude quinone was filtered from the cooled solution. It separates from chlorobenzene in fine orange rods, m. p. 423°, and gives a red color with concentrated sulfuric acid. It is not reduced by sodium hydrosulfite.

Anal. Calcd. for $C_{34}H_{18}O_4$: C, 83.3; H, 3.7. Found: C, 83.2; H, 3.7.

The alkaline fusion was carried out in a distilling flask, using 2.5 g. of the quinone and 15 g. of potassium hydroxide at 290–300°. The *p*-terphenyl, which sublimed, was collected and identified in the usual way; a further amount was secured from a benzene extraction of an aqueous solution of the cooled melt.

The alkaline solution was decolorized by charcoal, filtered, acidified, and extracted with ether. By appropriate manipulations, this afforded *o*-phthalic acid or/and anhydride (73%) and benzoic acid (16%), identified in the customary manner.

5,6,7,12,13,14-Hexaphenyl-5,7,12,14-tetrahydropentacene-5,7,12,14-tetrol (**XXV**) was secured by the action of phenylmagnesium bromide on an ether–benzene solution of the diquinone XI, essentially as described under B. It separates in prisms; m. p. 304°. It is not reduced by potassium iodide in acetic acid, but gives a green solution with iron and acetic acid.

Anal. Calcd. for $C_{58}H_{42}O_4$: C, 86.8; H, 5.3. Found: C, 86.6; H, 5.2.

c. **Bromination; 5,7,12,14-Tetrabromo-6,13-diphenyl-5,7,12,14-tetrahydropentacene** (**XV**).—To 5 g. of 6,13-diphenylpentacene in 50 cc. of carbon tetrachloride was added 4 g. of bromine in the same solvent. The whole mixture was refluxed for fifteen minutes—a vigorous reaction appeared to take place, but there was no evolution of hydrogen bromide. After cooling a yellowish solid was filtered, washed, and refluxed with acetone until it was no longer colored; the yield was 8 g. It separates from benzene in prisms, m. p. 205°, with decomposition. This substance was unaffected when refluxed for a short time with acetone, alcohol, and benzene, in contrast to the 6,13-dibromide.

Anal. Calcd. for $C_{34}H_{22}Br$: Br, 48.2. Found: Br, 49.0.

5,14-Dibromo-6,13-diphenyl-5,14-dihydropentacene (**XIV**).—This substance was secured in the same manner as the above, using but one equivalent of bromine. The insoluble greenish-yellow solid was recrystallized from benzene, from which it separates in fine prisms, m. p. 235° with decomposition.

Anal. Calcd. for $C_{34}H_{22}Br_2$: Br, 27.1. Found: Br, 26.9.

This dibromide adds a second equivalent of bromine to give the tetrabromide above.

Reactions of the Tetrabromide. (a) **Zinc Dust Reduction.**—When zinc dust was added to 1 g. of the tetrabromide in 25 cc. of hot benzene, it became a deep magenta; after five minute's heating, the insoluble material was filtered, and recrystallized from nitrobenzene. The solid was identical with the purple hydrocarbon previously described. (b) **Pyrolysis.**—Hydrogen bromide was evolved copiously when 1 g. of the tetrabromide was heated above its melting point for one hour. The residue was boiled with methanol, leaving a dull greenish-olive, amorphous powder; the latter was very soluble in benzene, giving a brilliant green solution with a green fluorescence. The only method of purification found was reprecipitation of benzene solutions by alcohol. It had not melted up to 500°.

Anal. Found: Br, 14.5; mol. wt., 1300, 1500 (in benzene).

The remaining bromine was not removed by treatment with zinc dust in boiling benzene.

d. **Reductions.** (a) **6,13-Diphenyl-7,12-dihydropentacene** (**XVI**).—A suspension of 5 g. of 6,13-diphenylpentacene in 50 cc. of dioxane at 95–100° was treated with hydrogen in the presence of a Raney nickel catalyst for one hour; the initial purple color changed to yellow with a brilliant green fluorescence. The filtered solution was evaporated *in vacuo*, leaving a residue of 4.5 g.; this was recrystallized once each from dioxane and benzene, from which the dihydro compound separated in yellow rods; m. p. 247–248°. This was a "dioxide"; the oxygen was lost after ten days at 100° *in vacuo*, leaving a dull orange hydrocarbon. There was no change in melting point. The dihydro compound is white, if precautions are taken to exclude oxygen. In benzene solution, this adds on oxygen from the air, to give the yellow dioxide.

Anal. Calcd. for (a) $C_{34}H_{24}$: C, 94.4; H, 5.6; (b) $C_{34}H_{24}O_2$: C, 87.9; H, 5.1. Found: (a) C, 94.2; H, 5.6; (b) C, 87.6; H, 5.5.

The yellow benzene solution of the dihydro compound appears to have a brilliant green fluorescence in daylight, but fluoresces blue under an ultraviolet lamp. The solid itself shows a bright yellow fluorescence under the same lamp.

6,13-Diphenyl-5,7,12,14-tetrahydropentacene (**XVII**) was secured after a twenty-six hour reduction period of 6,13-diphenylpentacene or the above dihydro compound. As reduction progressed, the intense green fluorescence became bluish-violet. The reaction product was a mixture of the di- and tetrahydro derivatives, which were separated by repeated crystallizations from benzene. From 1 g. of the starting material were isolated 0.3 g. of the dihydro and 0.5 g. of the tetrahydro hydrocarbons. The tetrahydro derivative forms white prisms; m. p. 329–331°. It is unaffected by a further seventy-two hour treatment with hydrogen and Raney nickel catalyst.

Anal. Calcd. for $C_{34}H_{26}$: C, 94.0; H, 6.0. Found: C, 92.8, 93.0; H, 5.9, 6.0.

Both these reduction products were easily oxidized by chromium trioxide in acetic acid to 6,13-diphenylpentacene-5,7,12,14-diquinone (XI), m. p. 422; the quinone crystallized out from the reaction mixture as rapidly as formed, owing to its insolubility.

Hexahydrodiphenylpentacene (XVIII).—When the above reduction procedure was continued for one hundred twenty hours, 4 g. yielded 1 g. of the above tetrahydro derivative and 2.5 g. of a hexahydro compound which formed yellow prisms (from benzene); m. p. 252°. When 1 g. of the 7,12-dihydro-6,13-diphenylpentacene was reduced for twenty-four hours, it gave 0.5 g. of the tetrahydro and 0.2 g. of the hexahydro derivatives.

Anal. Calcd. for $C_{34}H_{28}$: C, 93.6; H, 6.4. Found: C, 93.0; H, 6.4.

6,13-Diphenyl-1,4-dihydropentacene (XIX).—In one instance, after fractional crystallization of a reduction mixture that had run for six hours, 2 g. of starting hydrocarbon gave 1 g. of the above dihydro compound, and 0.7 g. of an isomer (prisms), m. p. 295.

Anal. Calcd. for $C_{34}H_{24}$: C, 94.4; H, 5.6. Found: C, 93.5; H, 5.6.

Neither of the last two reduction products gave the diquinone XI on chromic acid oxidation. An amorphous yellow solid resulted which was recrystallized from heptane; m. p. 167°.

Anal. Calcd. for $C_{34}H_{25}O_7$: C, 74.9; H, 4.6; mol. wt., 545. Found: C, 75.2; H, 4.6; mol. wt., 588 (in benzene).

e. Maleic Anhydride Addition Products.—A solution of 5 g. of the 6,13-diphenylpentacene, 3.8 g. of maleic anhydride and 50 cc. of xylene was refluxed for one hour. On cooling, the crystalline (rods) 1:1 addition product (XII) that had separated was filtered; the yield was 3.6 g.; m. p. 335–337°. The filtrate was evaporated to dryness and the residue boiled with water; the insoluble material, 3.8 g., is the dianhydride (XIII). After several recrystallizations from benzene and acetic acid it formed plates; m. p. 255° with decomposition.

Anal. Calcd. for (XII), $C_{38}H_{24}O_3$: C, 86.4; H, 4.5; for (XIII), $C_{42}H_{26}O_6$: C, 80.5; H, 4.2; mol. wt., 622. Found: (XII), C, 86.4; H, 4.8; (XIII), C, 80.2; H, 4.4; mol. wt., 633, 630; (by titration) 632.

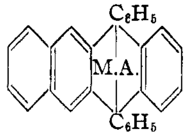
The two anhydrides are readily distinguished by the solubilities and fluorescence of the potassium salts. The salt from the monoanhydride is very sparingly soluble in hot water, but easily dissolves in warm alcohol—these solutions have a strong blue fluorescence. The salt of the dianhydride is very soluble in cold water and the solution is not fluorescent.

In a similar manner, the addition product from 6,13-diphenyl-7,12-dihydropentacene (XVI) was secured from equal weights of the components. It separates from benzene in prisms that melt with decomposition at 190°.

Anal. Calcd. for $C_{38}H_{26}O_3$: C, 86.0; H, 4.9. Found: C, 86.3; H, 5.1.

Under similar conditions there was no addition to the 6,13-diphenyl-5,7,12,14-tetrahydropentacene (XVII).

Naphthacene–Maleic Anhydride Addition Products.—For purposes of comparison, maleic anhydride was added to naphthacene and 5,12-diphenylnaphthacene. The addition product (XXVI) from the latter separates from benzene in tiny rods; m. p. 331°. With alcoholic potash, it formed a potassium salt insoluble in cold water, but readily soluble in 80% alcohol. It separates from hot water in shining plates. For the addition product with naphthacene, the melting point of a pure specimen was found to be 293–294° (Clar gives 273–282°).[11]



XXVI

Anal. Calcd. for $C_{22}H_{14}O_3$ (Clar's anhydride): C, 81.0; H, 4.3; for $C_{34}H_{22}O_3$ (XXVI): C, 85.4; H, 4.6. Found: (Clar's) C, 80.7; H, 4.2; (XXVI) C, 85.1; H, 4.6.

D. The *cis*-Diol X; Reduction of the Peroxide VIII.—In a small apparatus for catalytic reduction, 1 g. of the peroxide in 50 cc. of dioxane was reduced by hydrogen for six hours at 100°, in the presence of Raney nickel catalyst.[12] After appropriate manipulation, 0.9 g. of the diol, m. p. 269–270°, which separates in prisms from dioxane, was obtained.

Anal. Calcd. for $C_{34}H_{24}O_2$: C, 87.9; H, 5.2. Found: C, 87.6; H, 5.0.

Upon reduction with potassium iodide and acetic acid, as described under the *trans*-isomer, this diol also gave the purple hydrocarbon. With acetyl bromide it formed the dibromide IX, as described in detail under the *trans*-diol.

E. Reactions of the *trans*-Diol IV.—Reduction to the hydrocarbon already has been described.

(a) The ether, *trans*-6,13-diphenyl-6,13-dimethoxy-6,13-dihydropentacene, was secured by allowing a mixture of 10 g. of the diol, 20 cc. of methanol and 0.2 cc. of concentrated sulfuric acid to stand in the ice-chest overnight. The solid was filtered, the product taken up in benzene, washed with dilute ammonium hydroxide, and recrystallized twice from benzene–methanol; it separates in prisms, m. p. 258°, in a yield of 5 g.

Anal. Calcd. for $C_{36}H_{28}O_2$: C, 87.8; H, 5.7. Found: C, 87.6; H, 5.8.

It was unaffected when treated with metallic sodium by Bachmann's procedure.

(b) 6,13-Diphenyl-6,13-dibromo-6,13-dihydropentacene (IX) was secured from either diol by the following procedure. On refluxing 5 g. of the substance in 40 cc. of acetyl bromide for one-half hour, hydrogen bromide was evolved copiously. A solid was filtered from the hot solution and washed first with alcohol and then with ether; the yield was 4.5 g. If a sample in a capillary tube is placed in a bath above 200°, the substance melts with decomposition at 250–252°, but if heated in the ordinary

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[11] Clar, *Ber.*, **65**, 518 (1932).

[12] "Organic Syntheses," **21**, 15 (1941).

manner, it darkens and shrinks at 220° without melting up to 320°. It was unaffected by water, alcohol and dilute sodium hydroxide. The crude material was analyzed, for no method of purification was discovered.

Anal. Calcd. for $C_{34}H_{22}Br_2$: C, 69.2; H, 3.9; Br, 27.1. Found: C, 68.4; H, 3.8; Br, 25.8.

Hydrogen bromide in acetic acid appears to give the same dibromide.

When solutions of the dibromide in acetone, benzene or acetic acid are refluxed, they become magenta-colored and bluish-red crystals of 6,13-diphenylpentacene separate. The solutions contain bromide ions and, from the acetone treatment, lachrymatory bromoacetone remains. When the dibromide is treated with bromine, hydrogen bromide is given off at once, indicating substitution.

F. 5,7;12,14-Tetraphenylpentacene (XXIII).—After a mixture of 0.6 g. each of the tetraol (XXII) and potassium iodide in 15 cc. of acetic acid had been refluxed for fifteen minutes, purple prisms separated. They separated easily from nitrobenzene; m. p. 306–308°; the yield was 0.4 g.

Anal. Calcd. for $C_{46}H_{30}$: C, 94.8; H, 5.2. Found: C, 94.9; H, 5.2.

A benzene solution appears red by reflected light but blue-violet by transmitted light, and exhibits an orange-red fluorescence (less intense than that of the diphenyl homolog) under an ultraviolet lamp. With acetic acid and iron this tetraol also gives a solution having the same color of red, but the fluorescence is yellowish-green. In the light, its benzene solutions were rapidly decolorized, and a monoperoxide (XXIV), crystallizing in prisms, m. p. 250°, resulted. The solid gives a brownish melt without gas evolution.

Anal. Calcd. for: $C_{46}H_{30}O_2$: C, 89.9; H, 4.9. Found: C, 90.1; H, 4.9.

Summary

6,13-Pentacenequinone appears to have a radiating bond structure. This conclusion is based upon its behavior with phenylmagnesium bromide, which resembles that of α,β-unsaturated ketones having a crossed conjugated system.

6,13-Diphenylpentacene, a bluish-red hydrocarbon, has been secured and certain of its reactions determined. In solution it takes up atmospheric oxygen (very rapidly in sunlight) and gives a peroxide.

6,13-Diphenylpentacene adds one or two equivalents of hydrogen, bromine, and maleic anhydride. The interrelation of the various products is described.

The properties and reactions of two stereoisomeric diphenylpentacene diols are described.

Certain other related highly phenylated pentacenes are described.

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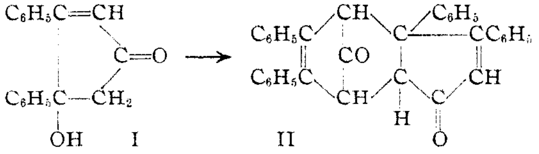
Carbonyl Bridge Compounds

BY C. F. H. ALLEN AND J. VAN ALLAN

A few years ago it was shown that the bimolecular product, formed when anhydroacetonebenzil (I) was treated with acidic dehydration agents, was a polynuclear compound containing a carbonyl bridge, (II).[1] In a series of reactions this was degraded to *o*-diphenylbenzene, showing the presence of this ring system. Since that time, a portion of the degradation products have been synthesized,[2] confirming the results of some of the steps of the degradation.



In order to learn more about this type of compounds, and hoping to explain some of the unusual properties, attention was turned to the methylated homolog (III). This substance was selected in order to avoid any uncertainty that might be connected with the presence of mobile hydrogen atoms. α,β-Dimethylanhydroacetonebenzil (III) is now readily accessible, owing to the availability of diethyl ketone. It had been dehydrated by Gray[3] long ago to give a bimolecular product, which was not further studied.

The methylated bimolecular product (IV) seemed to be homogenous, but in most reactions it behaved as though it were dissociated into its diene component, 2,5-dimethyl-3,4-diphenylcyclopentadienone (VI); this could not be isolated. Thus, on treatment with 2,4-dinitrophenylhydrazine, a monomolecular dinitrophenylhydrazone (V) resulted; this same derivative was also secured directly from the dimethylanhydroace-

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(1) Allen and Spanagel, THIS JOURNAL, **55**, 3773 (1933).

(2) Allen, Bell, Bell and Van Allan, *ibid.*, **62**, 656 (1940).

(3) Gray, *J. Chem. Soc.*, **95**, 2134 (1909).