Potentiometric titrations of rhodizonate and tetrahydroxyquinone were used for identification and quantitative estimation of these substances or their mixtures. The usual potentiometric oxidation–reduction potential apparatus and procedure for conducting titrations in the absence of oxygen was employed, details of which have been described previously.[3] The titrations were carried out in buffer of *p*H 9.26 where the components of the two systems, rhodizonic acid-tetrahydroxyquinone, and tetrahydroxyquinone-hexahydroxybenzene were stable and yet sufficiently separated to make interpretation of the results easy.[4]

The sample of potassium rhodizonate (3 to 4 mg. weighed to 0.1 mg.) was added as solid to 55 ml. of buffer, deoxygenated by passage of purified nitrogen, and titrated with deoxygenated sodium hydrosulfite ($Na_2S_2O_4$) in the same buffer, resulting in a curve as illustrated in the figure. A sample was reduced with hydrogen gas in the presence of colloidal palladium and, after hydrogen gas removal by purified nitrogen, was reoxidized by titration with standard potassium ferricyanide contained in the same buffer. A curve similar in form to that obtained in the hydrosulfite reduction was obtained. Slightly less than four equivalents of ferricyanide were used in the reoxidation.

Samples of tetrahydroxyquinone oxidized to rhodizonic acid with ferricyanide at *p*H 9.26 used essentially the two required equivalents; however, when first reduced to hexahydroxybenzene (hydrogen gas with palladium as catalyst) and reoxidized to rhodizonic acid with ferricyanide, somewhat less than four equivalents were required. The above observations indicate that during the reduction with hydrogen a portion of the hexahydroxybenzene was converted into an electromotively inactive substance, possibly to inositol.[5]

For the quantitative determination of a mixture, the ratio of tetrahydroxyquinone to rhodizonic acid was determined from the oxidation–reduction potential of the buffered solution containing the sample. Titration of a weighed sample with standard ferricyanide determined the amount of tetrahydroxyquinone present. From these data the amount of each could be calculated.

Potentiometric observations of solutions of the original oxidized product give an indication of its structure. The colorless, water-soluble material obtained by oxidation of inositol with nitric acid, when added (about 6 mg. to 55 ml.) to deoxygenated buffer of *p*H 9.87 yielded a yellow solution. The oxidation–reduction potential of this solution, as determined by the usual procedure,[4] at first was such as to indicate the presence of rhodizonic acid salts with a little tetrahydroxyquinone salt. The yellow color then slowly faded to a very pale purple, and the potential after about twenty-five minutes indicated the presence of virtually only tetrahydroxyquinone salt. During the next twenty-five minutes the potential became progressively more negative, and finally indicated a ratio of about 25% tetrahydroxyquinone salt to 75% hexahydroxybenzene salt. This phenomenon together with the slowness of formation of potassium rhodizonate during its preparation even in the presence of excess oxygen as described above, indicates that the original oxidized inositol product was principally a substance, probably triketo-trihydroxycyclohexane, which slowly liberated hexahydroxybenzene at low acidities or alkalinities.

Summary

Methods for the preparation of pure salts of rhodizonic acid and tetrahydroxyquinone are described.

The color changes obtained when using these substances as an indicator for sulfate titrations with barium salts are probably due to salts of rhodizonic acid.

ST. LOUIS, MISSOURI RECEIVED JULY 15, 1941

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[3] P. W. Preisler and L. H. Hempelmann, THIS JOURNAL, **58**, 2305 (1936).

[4] P. W. Preisler, E. S. Hill, E. Ronzoni and L. Young, *J. Biol. Chem.*, **123**, XCV (1938); complete report in publication.

[5] H. Wieland and R. S. Wishart, *Ber.*, **47**, 2082 (1914).

[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

9-Vinylphenanthrenes. III. α-(9-Phenanthryl)-stilbene

BY FELIX BERGMANN

In a recent paper[1] we described the synthesis of α-(9-phenanthryl)-stilbene (II) by dehydration of the carbinol I. From the mother liquors of II there was obtained an isomeric hydrocarbon (IIa) the structure and reactions of which are discussed in this paper.

By addition of lithium the isomers II and IIa could both be converted into α-(9-phenanthryl)-dibenzyl (III). They therefore represent a pair of geometric isomers although the simultaneous formation of *cis–trans* isomeric ethylenes on dehydration of an alcohol has rarely[2] been observed. The relationship between the two "stilbenylphenanthrenes" is further proved by conversion of IIa into II by heating with iodine in nitrobenzene solution. The behavior of II and IIa toward alkali metal might be expected to resemble the analogous behavior of stilbene and isostilbene, each of which gives[3,4] the same mix-

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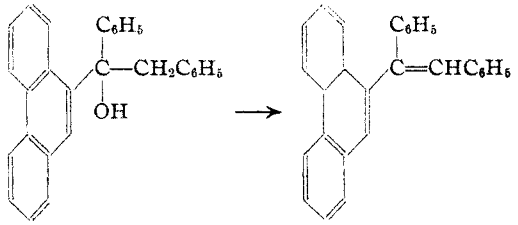
[1] F. Bergmann and E. Bergmann, THIS JOURNAL, **62**, 1699 (1940).

[2] See E. Bergmann and Weiss, *Ber.*, **64**, 1485 (1931); E. Bergmann, *et al.*, *Ann.*, **500**, 122 (1933).

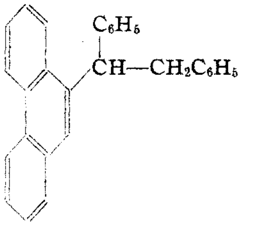
[3] Schlenk and E. Bergmann, *ibid.*, **463**, 106 (1928).

[4] Wright, THIS JOURNAL, **61**, 2106 (1939).

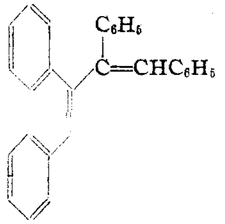
ture of stereoisomeric addition products. In striking contrast thereto we have shown that the lithium addition products of II and IIa must also be stereoisomers, since they give different dicarboxylic acids upon reaction with carbon dioxide. Apparently there is no great difference in stability between the two stilbenylphenanthrenes because in each of them a pair of aromatic nuclei is situated on the same side of the double bond. The reaction products of the lithium addition compounds allow one to ascribe, with more or less certainty, definite steric configurations to II and IIa. The latter substance yielded a dicarboxylic acid and an orange-red by-product, $C_{28}H_{18}$, which must be a cyclization product since it contains two hydrogen atoms *less* than the original hydrocarbon.[5]



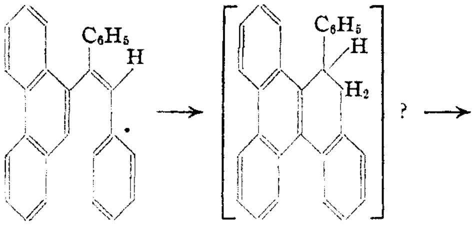
I II



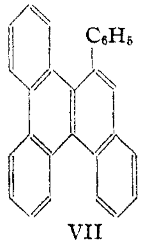
III



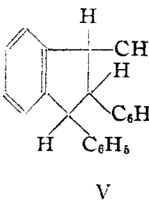
IV



IIa VI



VII



V

It already has been mentioned[1] that 1,2,3,4-tetraphenylbutadiene-1,3 (IV) may be considered as the open chain analog of II or IIa. This hydrocarbon yields, by addition of sodium, besides dibenzylstilbene a hydrindene derivative, V,[2] which contains two hydrogen atoms *more* than the original butadiene.[6] The different behavior of IIa can best be explained by the series of reactions IIa → VI → VII. The hydrocarbon IIa is first cyclized to the dihydro compound VI which, as a derivative of α- and β-phenylnaphthalene,[7] undergoes spontaneous dehydrogenation to 10-phenyl-1,2,3,4-dibenzphenanthrene (VII). Such a reaction would form a special type of cycloisomerization by an alkali metal and we would therefore prefer to postpone a further discussion of its mechanism until the hypothetical structure of VII can be proved by an independent synthesis. Based upon the assumed structure of VII, IIa must be represented as bearing its phenyl groups in *trans* position to each other. To the dicarboxylic acid derived from IIa can now be ascribed the formula VIII in which anhydride formation is obviously sterically hindered. With acetic anhydride, it is converted into black needles of the formula $C_{29}H_{18}O$. It is to be assumed that carbon dioxide is split off with greater ease from the quaternary carbon atom; then the remaining carboxyl group condenses with the neighboring benzene ring to yield the indone derivative IX with simultaneous dehydrogenation.

The isomer II on the other hand holds its phenyl groups in *cis* position with respect to the double bond. The dicarboxylic acid derived from II is more stable and is isolated directly in the form of its crystalline anhydride (X). In this respect II resembles 1,1,2-triphenylethylene[3] which also yields directly the corresponding triphenylsuccinic anhydride. The difference in behavior between the dicarboxylic acids derived from II and IIa with regard to anhydride formation recalls the different stability of meso- and *d,l*-diphenylsuccinic anhydride.[8] The meso acid is converted to the anhydride with difficulty and is always partly isomerized into the *d,l*-form.

The reaction of the lithium addition compound of II with alcohol yielded, besides III, a small amount of an isomeric hydrocarbon $C_{28}H_{22}$. It is probable that this represents the "normal" cycli-

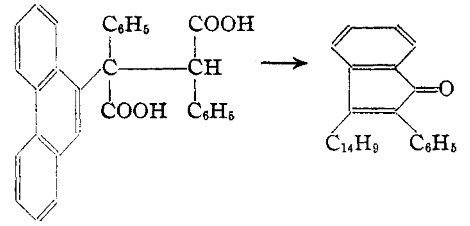
[5] The same hydrocarbon, $C_{28}H_{18}$, accompanies III when this is prepared from IIa and lithium.

[6] Lithium effects the same cyclo-isomerization of IV as sodium.

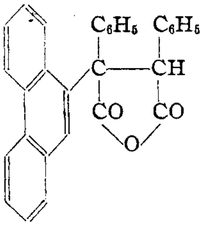
[7] Compare the similar behavior of dihydro-β-phenylnaphthalene; Spaeth, *Monatsh.*, **33**, 1029 (1912).

[8] Verkade and Hartman, *Rec. trav. chim.*, **52**, 945 (1933).

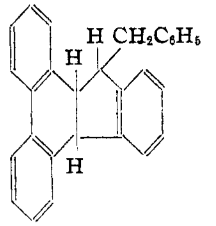
zation product, corresponding to V, and therefore can be formulated as 1,2,3,4-dibenz-9-benzyl-10,11-dihydrofluorene (XI). Other cyclization possibilities cannot, however, be excluded.



VIII IX



X



XI

Experimental

α-(9-Phenanthryl)-stilbene (II and IIa).—The crude sirup obtained from dehydration of I[1] could be induced to crystallize only with difficulty. After trituration with a mixture of glacial acetic acid and acetone slow crystallization set in, yielding first the isomer II; m. p. 167°. The isomeric IIa was isolated from the mother liquor and showed a m. p. of 140° after six recrystallizations from high-boiling petroleum ether.

Anal. Calcd. for $C_{28}H_{20}$: C, 94.4; H, 5.6. Found: C, 94.2; H, 5.9.

From 30 g. of I there were obtained about 15 g. of II and 3 g. of IIa. No picrates and no addition products with bromine or with maleic anhydride could be obtained from either of the isomers. They are not attacked by boiling hydriodic acid in glacial acetic acid.

Isomerization of IIa into II.—A sample (150 mg.) of the low-melting isomer was dissolved in nitrobenzene (5 cc.), a crystal of iodine was added and the solution was refluxed for two hours. After removal of the solvent by steam distillation the insoluble residue was taken up in acetone and recrystallized from high-boiling petroleum ether; m. p. and mixed m. p. with II, 166–167°.

Reaction of II with Lithium.—When II (5 g.) was shaken with lithium (1 g.) in ether a red-violet solution was soon obtained. Decomposition of the addition compound with ethanol yielded a mixture of two substances. A small amount of stout prisms was separated from the bulk of lancets by fractional crystallization from butyl acetate. The lancets, when absolutely pure, are colorless and melt at 197° (III). No picrate could be obtained.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.85; H, 6.15. Found: C, 93.6; H, 6.0.

The second hydrocarbon (XI) was recrystallized many times from butyl acetate, whereupon a few mg. of pure sample, m. p. 236°, was obtained as yellow prisms.

Anal. Calcd. for $C_{28}H_{22}$: C, 93.85; H, 6.15. Found: C, 93.9; H, 6.5.

The addition product of II (7 g.) and lithium (1.4 g.) was decolorized with carbon dioxide at 0° and, after extraction with water and acidification a yellowish precipitate was obtained. One crystallization from glacial acetic acid followed by several from xylene gave X in colorless prisms; m. p. 256–258° dec.

Anal. Calcd. for $C_{30}H_{20}O_3$: C, 84.1; H, 4.7. Found: C, 84.2; H, 4.9.

When the crude acid was dissolved in boiling acetic anhydride there appeared colorless needles which melted at 276° after being recrystallized from ethyl benzoate. The amount available of this product was too small to enable a differentiation between the possible structures of a diketone or monocarboxylic acid. On being heated with concentrated sulfuric acid the compound gives first a deep-violet color which changes to red.

Anal. Calcd. for $C_{29}H_{18}O_2$: C, 87.4; H, 4.5. For $C_{30}H_{18}O_2$: C, 87.8; H, 4.4. Found: C, 87.3; H, 4.5.

When water was added to the acetic anhydride mother liquor a second compound was obtained which was recrystallized from a mixture of xylene and high-boiling petroleum ether; m. p. 248–249°. This substance is formed by the loss of one molecule of carbon dioxide from the dicarboxylic acid corresponding to X.

Anal. Calcd. for $C_{29}H_{20}O_2$: C, 87.0; H, 5.0. Found: C, 86.9; H, 5.5.

The aforementioned compound reacted vigorously with diazomethane and the product crystallized immediately. Beautiful prisms are obtained from high-boiling petroleum ether; m. p. 175–176°.

Anal. Calcd. for $C_{30}H_{22}O_2$: C, 87.0; H, 5.3; mol. wt., 414. Found: C, 86.75; H, 5.3; mol. wt. (Rast), 393.

The ester is saponified by hydriodic acid with great difficulty and our micro-methoxyl determinations are therefore too low, even though the reaction time was extended to two and one-half hours: found 6.0 instead of the 7.5% required.

Reaction of IIa with Lithium.—A sample of IIa (1 g.) was shaken with lithium (0.2 g.) in absolute ether for three days and the resulting dirty-violet solution was decolorized with ethanol. The colorless reaction product was recrystallized several times from butyl acetate in order to remove a second substance which, although present in minute amounts, is held tenaciously. When pure, III melted at 197° and showed no depression of m. p. when mixed with the corresponding substance prepared from II.

When the addition compound from IIa (1.2 g.) was decolorized with carbon dioxide at 0° there was obtained a neutral product as well as an acidic product. The neutral substance (VII) crystallized from xylene–petroleum ether in orange-yellow plates; m. p. 185°.

Anal. Calcd. for $C_{28}H_{18}$: C, 94.9; H, 5.1. Found: C, 94.9; H, 5.3.

The acidic substance was precipitated as a yellowish powder by sulfuric acid and could not be recrystallized from any organic solvent. In an attempt to convert the acid into an anhydride it was dissolved in hot acetic anhydride, whereupon a vigorous reaction set in accompanied by evolution of a gas. The solution became deep-green and deposited (IX) in black needles on cooling. When crystallized from butyl acetate the compound IX melts at 255°. With cold concentrated sulfuric acid the compound gives a red-violet color; on heating a change to blue-violet, rose and finally yellowish-green occurs.

Anal. Calcd. for $C_{29}H_{18}O$: C, 91.1; H, 4.7. Found: C, 91.2; H, 4.9.

Summary

α-(9-Phenanthryl)-α,β-diphenylethanol yields two geometrically isomeric ethylenes upon dehydration. In the addition of alkali metal to these isomers two sterically different metal-organic compounds are formed. A probable steric formula is ascribed to each of the two "stilbenylphenanthrenes" based upon the products of the alkali metal addition reaction.

REHOVOTH, PALESTINE RECEIVED FEBRUARY 10, 1941

[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Structure and Absorption Spectra. III. Normal Conjugated Dienes

BY ROBERT BURNS WOODWARD

It is now clearly recognized[1] that the conjugated diene chromophore may manifest absorption in one of two broad regions, according to whether the two double bonds comprising the absorbing system are or are not present in a single ring. The former class as a whole absorbs sufficiently far to the red (255–290 mμ) to necessitate the postulation of a first order environmental effect, comparable in magnitude with the linear introduction of an additional double bond.[2] The second class, however, may be considered normal, and the variations (215–250 mμ) within the group are certainly the result of second order environmental effects similar to those discussed in connection with α,β-unsaturated ketones in the first paper of this series.[3] This communication is concerned with the substitution-type classification of these normal dienes.[4]

Inspection of the position of the band maxima for a number of dienes reveals immediately that simple substitutive effects cannot be the sole factor in causing variations within the group, since in some cases dienes of the same substitution type, *e. g.*, 1,1′-dicyclohexenyl (Table I, compound 6) and 2-hydroxy-α,β-dicyclohexylidene-ethane (Table I, compound 7) have different values of $\lambda_{\max.}$, while in other cases compounds of different substitution type, *e. g.*, allylidenecyclohexane (Table II, compound 4) and zingiberene (Table II, compound 6) have identical maxima. These facts indicate clearly that one or more positional factors are superimposed upon the expected substitutive effect.

The nature of this positional factor is discernible without difficulty. It has been[5] pointed out that the introduction of strain into a given chromophore will labilize the electronic system with a consequent shift toward the red of the absorption band associated with the system. It is well known that a double bond exocyclic to a six-membered ring is unstable by *ca.* 3.5 k. c. with respect to the corresponding endocyclic compound.[6] Further evidence of the strained character of such bonds may be found in the very high reactivity of cyclohexanone, and in the equilibrium data for systems of the type Δ^1-cyclohexenyl-1-acetic acid ⇄ cyclohexylidene-acetic acid.[7] It is therefore reasonable to assume that a diene chromophore containing such exocyclic linkages would absorb nearer the red than the corresponding system lacking such linkages, but of the same substitution type.

In actual fact, this assumption is amply justified. Table I lists the symmetrical dienes[8] of known structure whose absorption characteristics

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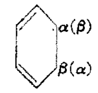
[1] Fieser and Campbell, THIS JOURNAL, **60**, 160 (1938); Bergmann and Hirschmann, *J. Org. Chem.*, **4**, 40 (1939); Callow, *J. Chem. Soc.*, 462 (1936).

[2] Possibly the electrons of the single bond which is α,β to each of the double bonds of the diene chromophore are sufficiently labilized to permit oscillations approximating those of a conventional six-electron system such as that of the trienes.



[3] Woodward, THIS JOURNAL, **63**, 1123 (1941).

[4] Booker, Evans and Gillam, *J. Chem. Soc.*, 1453 (1940), in an excellent paper containing valuable new data have classified dienes into several groups, *e. g.*, acyclic, acyclic with a cyclic substituent, semicyclic, bicyclic, etc. It will be evident from the sequel that the presence or absence of a ring in a normal diene has no intrinsic effect on the position of $\lambda_{\max.}$, except in so far as the structure is such that the ring exerts a normal substitutive or positional effect.

[5] Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939).

[6] *Cf.* Hückel, "Theoretische Grundlagen der organischen Chemie," 2nd edition, p. 72.

[7] Linstead, *J. Chem. Soc.*, 1603 (1930).

[8] *I. e.*, symmetrical in so far as the substitutive and positional factors about the double bonds are concerned.