[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

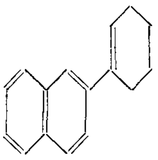
Observations on the Reactivities of Dienes, Especially toward Maleic Anhydride. II

BY FELIX BERGMANN AND ERNST BERGMANN

In a previous paper[1] we investigated the ability of exocyclic double bonds to form a "dienic system" with one nuclear double bond of an aromatic compound. We now wish to submit additional observations on the reactivity of such systems.

Vinylnaphthalenes.—We have found in our previous experiments that only α-vinylnaphthalene is able to undergo a diene reaction, whereas 1-(α-naphthyl)-cyclopentene-1 and 1-(6′-methoxynaphthyl-2′)-cyclopentene-1 were unreactive. In the meantime, Bachmann and Kloetzel[2] described the proper conditions for the condensation of these dienes with maleic anhydride. In the case of 1-(α-naphthyl)-cyclohexene-1 we have not succeeded with the method of these authors, namely, the use of a tenfold excess of the anhydride without any solvent. The cyclohexene derivative was previously reported by Cook and Lawrence[3] to resist also the attack of various agents, which are characteristic for double bonds. 1-(β-Naphthyl)-cyclohexene-1 (I), however, which we prepared from cyclohexanone and β-naphthylmagnesium bromide, gave the chrysene derivative (II).[4] It may be noted, also, that the picrates of the two cyclohexenyl naphthalenes show the characteristic difference in color, which we already observed for reactive and unreactive dienes. The α-derivative forms an orange-yellow picrate, the β-compound a red one.

Vinylanthracenes.—2-Isopropenylanthracene (III), which was prepared from 2-acetylanthracene and methylmagnesium iodide, contains two systems, which may be regarded as dienic, (1) the exocyclic and the neighboring 1,2-nuclear double bond and (2) the 9,10-unsaturated system. The well crystallized condensation product of (III) and maleic anhydride, however, must correspond to (IV) and not to (V). This follows from the ultraviolet absorption spectrum, which shows a broad absorption band without any fine structure, as is usual in compounds of the styrene type.[5] On the other hand, the substance (V) should show the spectrum of a substituted naphthalene.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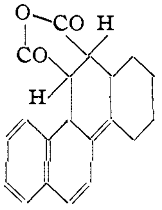

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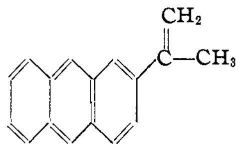

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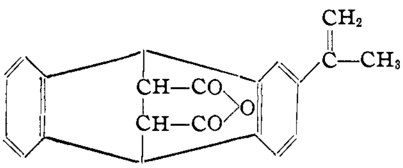

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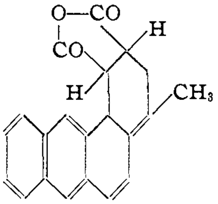

V

9-Vinylphenanthrenes.—In the series of 9-vinylphenanthrene derivatives we reported a different behavior.[1] For example, 9-propenylphenanthrene (VI) and β-(9-phenanthryl)-styrene (VII) reacted with maleic anhydride, whereas α-(9-phenanthryl)-styrene did not. We can now add to this series one more unreactive diene, namely, α-(9-phenanthryl)-stilbene (VIII), which was synthesized from 9-phenanthrylmagnesium bromide and desoxybenzoin. It seems to us that the substitution of three neighboring carbon atoms of butadiene by aromatic groups hinders its condensation with philodienic components, whereas the phenylation of two neighboring atoms does not. In order to examine the generality of this phenomenon, we prepared the corresponding α-vinylstilbene derivatives (1,2-diphenyl-1,3-butadienes), which may be regarded as open-chain analogs of the 9-vinylphenanthrenes.

1,2-Diphenylpentadiene-1,3 (IX),[6] similar to (VI), is very autoxidable and therefore can be obtained only with great difficulty in an analytically pure state. It combines readily with maleic anhydride to give 3,4-diphenyl-6-methyl-1,2,3,6-tetrahydrophthalic anhydride (X). The corre-

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[1] Ernst Bergmann and Felix Bergmann, THIS JOURNAL, **59**, 1443 (1937).

[2] Bachmann and Kloetzel, *ibid.*, **60**, 2204 (1938).

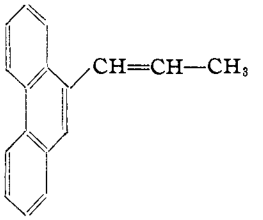
[3] Cook and Lawrence, *J. Chem. Soc.*, 1431 (1936).

[4] With benzoquinone, too, reaction occurred, leading unexpectedly to a hydrocarbon (see Experimental Part).

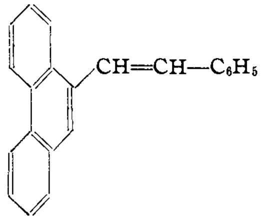
[5] Ley and co-workers, *Z. physik. Chem.*, **74**, 31 (910); *Ber.*, **67**, 1331 (1934); Pestemer and Wiligut, *Monatsh.*, **66**, 119 (1935).

[6] Burton, *J. Chem. Soc.*, 748 (1932).

sponding aromatic compound, 3,4-diphenyl-6-methyl-phthalic anhydride, was also prepared by using nitrobenzene as solvent and could be converted into 2-methyl-4-phenyl-fluorenone-1-carboxylic acid (XI). 1,2,4-Triphenylbutadiene-1,3 (XII) was obtained by us in a new liquid form stereomeric to that described by Bergmann and Ukai[7]; it gave the normal addition product (XIII), behaving in this respect like (VII). Furthermore, it already has been shown[8] that 1,2,3,4-tetraphenylbutadiene-1,3 (XIV) is unreactive toward maleic anhydride, in analogy to (VIII). For comparison with α-(9-phenanthryl)-styrene, it was necessary to prepare 1,2,3-triphenylbutadiene-1,3 (XV). So far we have been unable to realize this synthesis and we will report on it in a forthcoming paper.



VI



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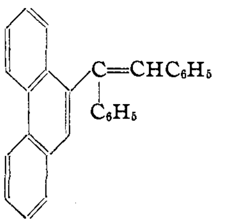
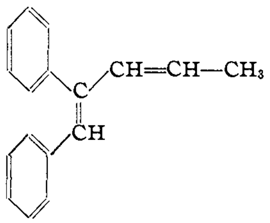
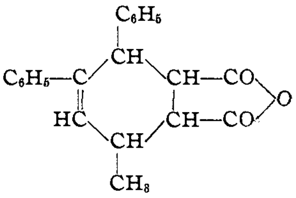


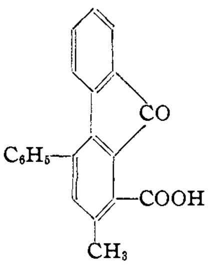
VIII



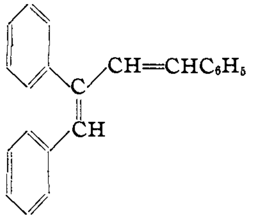
IX



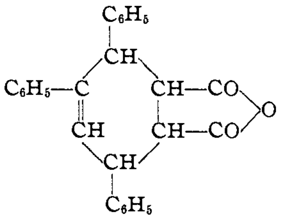
X



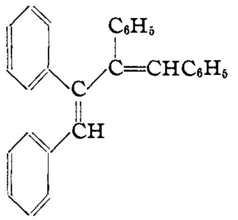
XI



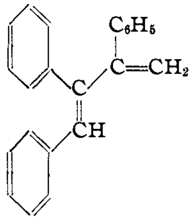
XII



XIII



XIV



XV

Whereas in these experiments the two series of compounds showed a comparable behavior, there are other reactions, in which the 9,10-double bond of phenanthrene behaves as part of an aromatic system. This was obvious particularly in the addition of alkali metals. For example, IX adds easily two atoms of lithium; hydrolysis of the organo-alkali compound gives a dihydro derivative $C_{17}H_{18}$, which according to the well-known regularities of alkali addition to phenylated olefins should be 1,2-diphenylpentene-3 (XVI), although allylic rearrangement into 1,2-diphenylpentene-2 may have occurred.[9] XII, too, adds readily 2 atoms of lithium; the liquid hydrolysis product should be formulated as the 1,4-addition product, 1,2,4-triphenylbutene-2 (XVII) or as the corresponding 1,2,4-triphenylbutene-1. It is isomeric with the 1,2,4-triphenylbutene-3, which has been obtained, also as a liquid, by Bergmann and Ukai.[7]

On the other hand, 9-propenylphenanthrene behaves differently from IX. Under the influence of lithium metal it undergoes a dimerization and yields, after hydrolysis, probably (XVIII). This observation recalls the difference in behavior between hexaphenylethane and dibiphenylene-diphenylethane[10] or the dimerizing reaction between benzalfluorene, cinnamylidene-fluorene or furfurylidene-fluorene and sodium powder as compared with that of, *e. g.*, triphenylethylene.[11] VII, the analog of XII, was already reported[1] to give, by alkali addition, α-phenyl-β-(9-phenanthryl)-ethane.

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(7) Bergmann and Ukai, *Ber.*, **66**, 54 (1933).

(8) Weizmann, E. Bergmann and Haskelberg, *J. Chem. Soc.*, 391 (1939).

(9) We shall try to decide about this minor point by means of the ultraviolet absorption spectrum.

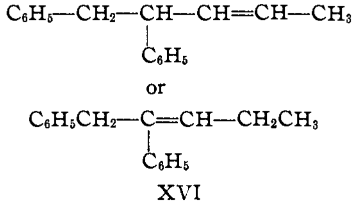
(10) Schlenk, Herzenstein and Weickel, *Ber.*, **43**, 1754 (1910).

(11) Schlenk and Bergmann, *Ann.*, **463**, 63 (1928).

Especially in the addition of bromine, β-(9-phenanthryl)-styrene behaves like *sym*-diphenylethylene. It yielded the crystalline 1,2-addition product (XIX), whose structure is proved by the reaction with methyl alcoholic potassium hydroxide solution; by hydrobenzoinic rearrangement, benzyl 9-phenanthryl ketone (XX) is formed.[12] For comparison with an authentic specimen, we first attempted to synthesize XX from the ketimine XXI, which could be prepared easily from 9-cyanophenanthrene and benzylmagnesium chloride. But XXI was unusually resistant to all hydrolytic agents; we cannot exclude the possibility that it had undergone cyclo-isomerisation. Finally we obtained XX by cautious oxidation of 9-phenanthrylbenzylcarbinol.

The occasional non-reactivity of the 9,10-double bond in β-(9-phenanthryl)-styrene and related compounds is further demonstrated by the fact that it cannot be cyclized to 1,2,3,4-dibenzphenanthrene-dihydride-9,10 (XXII) by means of aluminum chloride, the only defined reaction product being phenanthrene.[13] VI behaves in the same way.

Finally, the twofold character of the 9,10-double bond of phenanthrene is clearly shown by the reactions of 9-allylphenanthrene. It behaves toward lithium as an open-chain derivative of cyclopentadiene, yielding the brown-red substitution product XXIII. This is asserted by the fact that even after prolonged interaction with the metal, 9-allylphenanthrene is regenerated by hydrolysis of XXIII. With benzaldehyde, XXIII gives the alcohol XXIV.

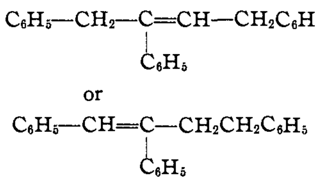


$$C_6H_5{-}CH_2{-}\underset{\substack{|\\ C_6H_5}}{CH}{-}CH{=}CH{-}CH_3$$

or

$$C_6H_5CH_2{-}\underset{\substack{|\\ C_6H_5}}{C}{=}CH{-}CH_2CH_3$$

XVI

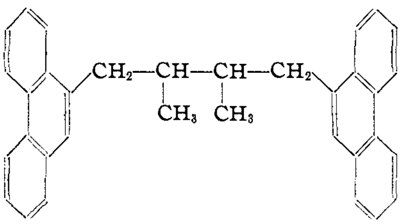


$$C_6H_5{-}CH_2{-}\underset{\substack{|\\ C_6H_5}}{C}{=}CH{-}CH_2C_6H_5$$

or

$$C_6H_5{-}CH{=}\underset{\substack{|\\ C_6H_5}}{C}{-}CH_2CH_2C_6H_5$$

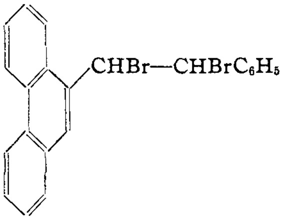
XVII



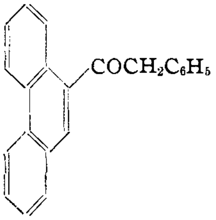
XVIII

At the same time, however, a certain amount of 9-allylphenanthrene was isomerized into 9,10-cyclopentenophenanthrene (XXV),[14] a type of reaction which has been observed before[15] in the case of 1,2,3,4-tetraphenylbutene-1.[16]

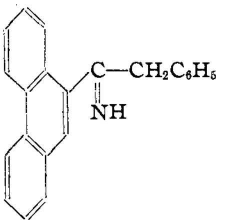
As this cyclization to an indane derivative requires an adjacent aromatic double bond, the formation of XXV from 9-allylphenanthrene besides XXIII corresponds clearly with the variable behavior of 9-vinylphenanthrenes, which sometimes react as butadiene derivatives, but in other cases as aromatically substituted ethylenes.



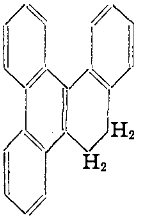
XIX



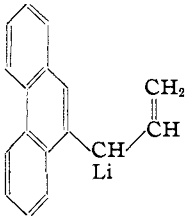
XX



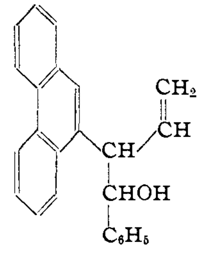
XXI



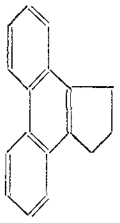
XXII



XXIII



XXIV



XXV

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[12] Instances of such rearrangements in an **alkaline** medium are rare, but not unknown.

[13] For an analogous splitting reaction see Dodds, *et al.*, *Nature*, **141**, 248 (1938).

[14] Described by Bachmann and Kloetzel, THIS JOURNAL, **59**, 2207 (1937); Weizmann, E. Bergmann and T. Berlin, *ibid.*, **60**, 1331 (1938); Bradsher, *ibid.*, **61**, 3139 (1939).

[15] Bergmann, Winter and Schreiber, *Ann.*, **500**, 122 (1933).

[16] The same cyclization by means of aluminum chloride failed. A high melting hydrocarbon was obtained in this experiment, which probably owes its formation to a dimolecular process.

Experimental

1-(α-Naphthyl)-cyclohexene-1 was prepared according to Cook and Lawrence.[3] In supercooled state, it had $n^{28}D$ 1.6314. For the **picrate**, which crystallized from isopropyl alcohol in orange-yellow needles, we observed a slightly higher m. p. (129°) than the British authors. *Anal.* Calcd. for $C_{22}H_{19}O_7N_3$: C, 60.4; H, 4.4. Found: C, 60.2; H, 5.0. When the hydrocarbon (2.7 g.) was heated at 110° with maleic anhydride (13.5 g.) for six hours, no condensation took place.

1-(β-Naphthyl)-cyclohexene-1 (I).—When cyclohexanone (10 g.) was added to the Grignard solution, prepared from 2-bromo-naphthalene (21 g.) and magnesium turnings (2.5 g.), a vigorous reaction took place. After four hours of boiling, the mass was decomposed with ice and dilute sulfuric acid and the crude reaction product heated with the same weight of potassium hydrogen sulfate for one hour at 150–160°, extracted with ether and after treating with sodium carbonate solution and drying, distilled. The fraction, boiling at 144° under 2 mm. pressure, crystallized spontaneously; from methanol, nacreous plates, m. p. 61–62°; yield, 7 g. *Anal.* Calcd. for $C_{16}H_{16}$: C, 92.3; H, 7.7. Found: C, 92.4; H, 7.6. The **picrate**, prepared in alcoholic solution from equal weights of the components, formed long, red rods (from methanol), m. p. 78°. *Anal.* Calcd. for $C_{22}H_{19}O_7N_3$: C, 60.4; H, 4.4. Found: C, 60.1; H, 4.6.

Reaction with Maleic Anhydride.—1-(β-Naphthyl)-cyclohexene-1 (1 g.) and maleic anhydride (5 g.) were thoroughly mixed and heated at 100° for twelve hours. The orange-yellow melt was dissolved in aqueous potash solution and precipitated with acetic acid. As the crystalline powder, so obtained (0.6 g.), could not be recrystallized from the common solvents, it was distilled at 1.5 mm. Between 250 and 300° a viscous oil passed over, which solidified on trituration with benzene. The **addition product** (II) crystallized from light-petroleum (b. p. 130°) and some benzene in yellow needles, exhibiting a distinct greenish luster, m. p. 216°. *Anal.* Calcd. for $C_{20}H_{18}O_3$: C, 78.4; H, 5.9. Found: C, 78.9; H, 5.1.

Reaction with Benzoquinone: 1-(β-Naphthyl)-cyclohexene-1 (0.25 g.) and *p*-benzoquinone (1.25 g.) were heated at 100° for four hours. The brown reaction product was triturated with alcohol and recrystallized from light-petroleum (b. p. 130°). Analysis of the colorless leaflets, m. p. 178°, so obtained, showed that a hydrocarbon $C_{22}H_{16}$ had been formed; we have not tried to elucidate its structure. *Anal.* Calcd. for $C_{22}H_{16}$: C, 94.3; H, 5.7. Found: C, 94.3; H, 5.7.

2-Isopropenylanthracene (III).—2-Acetylanthracene (5 g.)[17] in benzene (100 cc.) was added to a Grignard solution, prepared from methyl iodide (7 g.) and magnesium (1 g.). After four hours of boiling, the reaction product was isolated in the usual way. It crystallized spontaneously and formed slightly yellowish leaflets (from benzene), m. p. 154°; yield, 4 g. *Anal.* Calcd. for $C_{17}H_{14}$: C, 93.6; H, 6.4. Found: C, 93.5; H, 6.4.

Reaction with Maleic Anhydride.—The hydrocarbon (2 g.) was heated in boiling xylene (25 cc.) with maleic anhydride (1.5 g.) for one hour. The addition product (IV) separated spontaneously and was recrystallized from butyl acetate as needles, m. p. 266°; yield, 1 g. Concd. sulfuric acid gives a brown-red color reaction; the butyl acetate solution exhibits a slight violet fluorescence, probably due to slight dissociation of (IV). *Anal.* Calcd. for $C_{21}H_{16}O_3$: C, 79.8; H, 5.1. Found: C, 79.2; H, 4.8.

Reactions with Phenanthrene Derivatives

α-(9-Phenanthryl)-stilbene (VIII).—To the Grignard solution from magnesium (1.2 g.) and 9-bromophenanthrene (13 g.), desoxybenzoin (10 g.) in benzene was added. The reaction product, (9-phenanthrylphenylbenzylcarbinol), after six hours of boiling and decomposition with ice-cold sulfuric acid, crystallized on trituration with light-petroleum (b. p. 80°); from butyl alcohol or xylene parallelepipeda, m. p. 191–192°; yield, 6.5 g. *Anal.* Calcd. for $C_{28}H_{22}O$: C, 89.8; H, 5.9. Found: C, 89.8; H, 6.0. This carbinol was heated at 180–190° with twice its weight of potassium hydrogen sulfate for one hour and the hydrocarbon (VIII) so formed extracted with chloroform. It crystallized, on trituration with glacial acetic acid and acetone, and was purified by recrystallization from light-petroleum (b. p. 130°); m. p. 162° (plates). *Anal.* Calcd. for $C_{28}H_{20}$: C, 94.4; H, 5.6. Found: C, 94.4; H, 5.3. No picrate and no addition product with maleic anhydride could be obtained.

9-(α,β-Dibromo-β-phenylethyl)-phenanthrene (XIX).—When to β-(9-phenanthryl)-styrene (2.8 g.)[1] in carbon tetrachloride (28 cc.), bromine (1.6 g.) in carbon tetrachloride (6.5 cc.) was added, the dibromide (XIX) crystallized spontaneously. It was collected after twenty-four hours of standing at +5° and was purified by addition of low-boiling light-petroleum to its chloroform solution; needles (from xylene), m. p. 184–185° (decompn.). At room temperature, concd. sulfuric acid gives no color reaction; on heating, the substance dissolves, giving a transient blue, then green solution. *Anal.* Calcd. for $C_{22}H_{16}Br_2$: C, 60.0; H, 3.6. Found: C, 60.2; H, 3.8.

9-(β-Phenacetyl)-phenanthrene (XX).—(a) The above dibromide (0.5 g.) was heated with 10% methyl alcoholic potash solution (25 cc.) in a sealed tube at 150° for four hours. The reaction product was treated with water and chloroform and the chloroform residue distilled (bath-temperature 240°; pressure 0.02 mm.) and after trituration with light-petroleum (b. p. 40–60°) recrystallized from a mixture of xylene and light-petroleum; long prismatic crystals, m. p. 136°. With concd. sulfuric acid, the crystals become brown-red and then give a deep yellow solution. *Anal.* Calcd. for $C_{22}H_{16}O$: C, 89.2; H, 5.4. Found: C, 88.9, 89.1; H, 5.5, 5.7.

(b) To 9-phenanthrylbenzylcarbinol (3 g.) in glacial acetic acid (25 cc.) was added a solution of chromic anhydride (0.67 g.) in 60% acetic acid (8 cc.). After twelve hours of standing, the mixture was heated at 100° for four hours, diluted with water and extracted with chloroform. The chloroform residue crystallized on standing and was recrystallized from a mixture of benzene and low-boiling light-petroleum; m. p. and mixed m. p. 136°.

Benzyl-(9-phenanthryl)-ketimine (XXI).—The reaction between 9-cyanophenanthrene (7 g.)[18] and benzylmagnesium chloride (5 g. benzyl chloride, 1 g. magnesium) resulted in a copious brownish precipitate. On decomposi-

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[17] German Patent 492,247; *Friedlaender*, **16**, 1195 (1931).

[18] Mosettig and van de Kamp, THIS JOURNAL, **54**, 3328 (1932).

tion with cold dilute sulfuric acid, part of the reaction product did not dissolve in the amount of ether present and was therefore separated and dissolved in chloroform. The residue of both of these solutions was triturated with a mixture of acetone and light-petroleum (b. p. 40–60°) and recrystallized from light-petroleum (b. p. 130°) as clusters of needles, m. p. 195°. *Anal.* Calcd. for $C_{22}H_{17}N$: C, 89.5; H, 5.8; N, 4.7. Found: C, 89.6; H, 6.1; N, 4.4. The ketimine was recovered unchanged, after treatment with aqueous–acetonic hydrochloric acid[19] and with concentrated hydrochloric acid at 150° for four hours in a sealed tube.[20]

Attempted Cyclizations.—(**a**) To a well-stirred suspension of aluminum chloride (3 g.) in carbon disulfide (25 cc.), β-(9-phenanthryl)-styrene (VI) (5 g.) in the same solvent (30 cc.) was added at −20°. A brown resin separated; after twenty-four hours of standing at room temperature, the product was treated with ice-cold concentrated hydrochloric acid and distilled *in vacuo* (1.5 mm.). At 130–140°, a crystalline sublimate was obtained, which after crystallization from alcohol, had m. p. 99° and was identified as phenanthrene by the method of mixed m. p. A second fraction distilled between 300 and 350°; it formed a viscous, brown resin, which could neither be induced to crystallize nor be converted into a picrate.

(**b**) Aluminum chloride (8 g.) was added at 0° to a solution of **9-propenylphenanthrene** (7 g.)[1] in carbon disulfide (10 cc.). The solution became reddish, and a black solid precipitated. The reaction product, after treatment with cold concentrated hydrochloric acid, was again distilled at 1.5 mm. From the first fraction b. p. 155–160°, on standing, separated crystals, which were identified as phenanthrene; a second fraction, b. p. 360–370°, was an extremely viscous resin, which would not crystallize.

(**c**) 9-Allylphenanthrene (8 g.)[1] in carbon disulfide (25 cc.) was added to a well-stirred suspension of aluminum chloride (7.5 g.) in carbon disulfide (50 cc.) at −20°. The reaction product was separated by distillation under 1 mm. pressure into unchanged allylphenanthrene, identified by its picrate,[1] and a viscous oil, which crystallized on trituration with acetone; from butyl acetate or xylene long needles, m. p. 264°. The structure of this compound has not been elucidated. *Anal.* Calcd. for $(C_{17}H_{14})_n$: C, 93.6; H, 6.4. Found: C, 93.2; H, 6.2.

9-Propenylphenanthrene (VI) and Lithium.—The hydrocarbon, on shaking with an excess of lithium turnings,[21] gave a brown-red viscous ethereal solution; after decomposition with alcohol, distillation gave a small head fraction, consisting of some unchanged starting material, and 1,4-di-(9-phenanthryl)-2,3-dimethylbutane (XVIII), b. p. 300–310° (0.8 mm.) as a viscous oil, which crystallized on standing with acetone. From butyl acetate or xylene colorless prisms, m. p. 222°. *Anal.* Calcd. for $C_{34}H_{30}$: C, 93.2; H, 6.8. Found: C, 93.2; H, 6.8.

9-Allylphenanthrene and Lithium.—9-Allylphenanthrene was shaken with an excess of lithium turnings in ether for thirty hours. The liquid product obtained by addition of alcohol to the brown-red mass was fractionated. It distilled at 150–160° (0.8 mm.) and deposited, on trituration with methyl alcohol, crystals, which were recrystallized from xylene and formed platelets, m. p. 155–156°. They proved identical with 9,10-cyclopentenophenanthrene (XXV).[14] The liquid part, which was highly unsaturated toward bromine, was converted into the picrate of 9-allylphenanthrene.[1] The ratio between the two reaction products varied in various experiments.

Reaction with Benzaldehyde.—To the organo-metal solution, obtained as above from 9-allylphenanthrene (11 g.), benzaldehyde (10.6 g. = 2 mols) was added. The decolorized reaction product was treated with dilute sulfuric acid, washed thoroughly with water and distilled *in vacuo.* After a head fraction, the desired α-phenyl-β-(9-phenanthryl)-Δ^{γ}-butene-α-ol (XXIV) distilled at 0.03 mm. pressure between 250 and 300° and on repeated fractionation at 250–260° (1.5 mm.). *Anal.* Calcd. for $C_{24}H_{20}O$: C, 88.9; H, 6.2. Found: C, 88.5; H, 5.7.

Reactions of 1,2-Diphenylpentadiene-1,3 (IX).—The hydrocarbon, prepared according to Burton,[6] had b. p. 138–140° (1.5 mm.) and n^{25}D 1.6232. Although its solution in benzene–alcohol turned orange-red, on addition of picric acid, no crystalline picrate could be isolated.

Reaction with Maleic Anhydride.—The hydrocarbon (1.2 g.) and maleic anhydride (0.5 g.) were heated in boiling xylene (10 cc.) for three hours. 3,4-Diphenyl-6-methyl-1,2,3,6-tetrahydrophthalic anhydride (X) was precipitated by means of low-boiling light-petroleum and was recrystallized from light-petroleum (b. p. 130°); stout, slightly yellowish crystals, m. p. 168–169°. *Anal.* Calcd. for $C_{21}H_{18}O_3$: C, 79.2; H, 5.7. Found: C, 78.7; H, 5.9. The corresponding aromatic 3,4-diphenyl-6-methylphthalic anhydride[22] was recrystallized from the same solvent and had m. p. 161°. *Anal.* Calcd. for $C_{21}H_{14}O_3$: C, 80.3; H, 4.5. Found: C, 80.4; H, 4.3.

2-Methyl-4-phenyl-fluorenone-1-carboxylic Acid (XI).—The aromatic anhydride (0.450 g.) was dissolved in benzene (20 cc.) and heated for six hours with aluminum chloride (0.450 g.). The brown-red mass was decomposed by means of concentrated hydrochloric acid and the reaction product isolated from the benzene layer. From a mixture of xylene and light-petroleum (130°) stout, yellow crystals, m. p. 196°. *Anal.* Calcd. for $C_{21}H_{14}O_3$: C, 80.3; H, 4.5. Found: C, 80.2; H, 4.6.

1,2-Diphenylpentene-(3) (XVI).—The hydrocarbon (VI) was shaken in ethereal solution with an excess of lithium turnings. After eighteen hours, the dark-red solution was decanted from the excess of the metal and cautiously decomposed with alcohol. The reaction product boiled at 120° (0.04 mm.) and formed a mobile, colorless liquid. *Anal.* Calcd. for $C_{17}H_{18}$: C, 91.9; H, 8.1. Found: C, 91.5; H, 8.1. A small high-boiling fraction (b. p. 190–200° (0.02 mm.)) has not been investigated.

Reactions of 1,2,4-Triphenylbutadiene-(1,3) (XII).—This hydrocarbon was prepared from α-phenylcinnamic aldehyde (6 g.)[6] in benzene solution and a solution of benzylmagnesium chloride (6.3 g. benzyl chloride; 1.2 g. of magnesium turnings). The reaction was violent; the crude reaction product, isolated as usual, was boiled with acetic anhydride (50 cc.) for two hours and then distilled.

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[19] Schlenk and Bergmann, *Ann.*, **464**, 34 (1928).

[20] Fieser, THIS JOURNAL, **61**, 141 (1939).

[21] For the technique of the organo-alkali experiments, see Schlenk in Houben-Weyl, "Methoden der organischen Chemie," Vol. IV, Georg Thieme, Leipzig, 1924, p. 959.

[22] Its preparation will be described in a forthcoming paper.

From the fraction, b. p. 180–190° (2 mm.); $n^{25}D$ 1.6355, a crystalline crop was secured on trituration with light-petroleum (b. p. 80–100°). After recrystallization from isopropyl alcohol, it formed hexagonal plates, m. p. 110°, and was identical with the hydrocarbon, described by Bergmann and Ukai[7] (m. p. 104–105°). With 2 mols of picric acid in isopropyl alcohol, orange-red needles are formed, which on standing turn into a mixture of dark-red crystals and the colorless plates of the initial hydrocarbon; on further standing, the dark-red crystals disappear too. On heating, the hydrocarbon also dissolves, and when the solution cools down to room temperature, the same effect is reproduced.

The liquid isomer, remaining after the separation of the solid hydrocarbon, was used for the following reactions.

Reaction with Maleic Anhydride.—The hydrocarbon (1 g.) and maleic anhydride (0.4 g.) in xylene (10 cc.) were boiled for three hours. On addition of low-boiling light-petroleum, 3,4,6-triphenyl-1,2,3,6-tetrahydrophthalic anhydride (XIII) crystallized. From butyl acetate, needles, m. p. 208–209°; yield 0.3 g. *Anal.* Calcd. for $C_{26}H_{20}O_3$: C, 82.1; H, 5.3. Found: C, 82.6; H, 5.8.

Reaction with Lithium Metal.—The reaction was carried out as above; the dark-brown solution, on hydrolysis, gave 1,2,4-triphenylbutene-(2) (XVII) as a colorless, viscous oil, b. p. 140° (0.03 mm.); $n^{19}D$ 1.5992. *Anal.* Calcd. for $C_{22}H_{20}$: C, 93.0; H, 7.0. Found: C, 92.9; H, 7.0.

Summary

1. The different reactivities of 1- and 2-vinylnaphthalenes and 2-vinylanthracenes toward maleic anhydride are examined. 2-Isopropenylanthracene shows addition exclusively at the 9,10-double bond.

2. The reactivity of 9-vinylphenanthrenes is compared with the conjugated system of the corresponding α-vinylstilbenes, as regarding the diene reaction and the addition of alkali metals, and the ambiguous character of the 9,10-double bond of phenanthrene is demonstrated.

3. 9-Allylphenanthrene, too, shows the peculiarities of the 9,10-double bond of phenanthrene by the two ways it reacts with lithium.

REHOVOTH, PALESTINE RECEIVED OCTOBER 17, 1939

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF THE UNIVERSITY OF NEW HAMPSHIRE AND TRINITY COLLEGE (CONN.)]

A Direct Synthesis of Resolvable Biaryls[1]

BY EDWARD R. ATKINSON AND H. J. LAWLER

It has long been known that diazotized amines decompose in the presence of certain reducing agents to form biaryls along with other products, including the common replacement derivatives, as shown by the generalized equation

$$RN_2X \longrightarrow R{-}R + R{-}N{=}N{-}R + R{-}O{-}R + R{-}\overset{H}{N}{-}R + RX + RH + ROH + RNH_2 + N_2$$

The reaction, which occurs in aqueous solution, invariably leads to symmetrically substituted biaryls[2] and seems to be a genuine reduction; in these respects it differs from the better known Gomberg reaction[3] which is currently being investigated by Waters and others.[4]

The facts concerning the reaction in question may be correlated with respect to (a) the nature of the diazotized amine, (b) the reducing agent used and (c) the experimental conditions which include a number of variables. In an effort to determine the relative importance of these factors and to extend the general applicability of this reaction to matters of synthesis, an extensive study of the reaction has been undertaken.

At the present time it is not possible to state the potential use of the reaction in the synthesis of biaryls and because of this it has not had wide application. However, Vorländer and Meyer,[5] Hunn,[6] and Huntress and his students[7] have used this method for the preparation of diphenic acid and a number of symmetrical substitution products; the preparation of certain binaphthyl dicarboxylic acids from diazotized naphthylamine carboxylic acids has been described in the patent literature.[8]

We have prepared *d,l*-4,6,4′,6′-tetrachlorodiphenic acid (II) and the analogous bromo compound (III) in two steps, starting with the readily available anthranilic acid.

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(1) A preliminary notice of this work was presented at the Rochester meeting of the A. C. S., September, 1937.

(2) The possibility of preparing unsymmetrical biaryls by the use of mixtures of diazotized amines is being investigated.

(3) Gomberg and Bachmann, THIS JOURNAL, **46**, 2339 (1924); Gomberg and Pernert, *ibid.*, **48**, 1372 (1926).

(4) Hey and Waters, *Chem. Rev.*, **21**, 175–183 (1937), and later papers in the *Journal of the Chemical Society* by Waters, Grieve, Hay, Heilbron.

(5) Vorländer and Meyer, *Ann.*, **320**, 122–144 (1902).

(6) Hunn, THIS JOURNAL, **45**, 1024–1030 (1923).

(7) (a) Huntress, "Organic Syntheses," John Wiley and Sons, New York, 1932, Collective Volume I, page 216; (b) THIS JOURNAL, **55**, 2561 (1933); (c) **55**, 4268 and 4270 (1933).

(8) German Patent 445,390, *Friedländer*, **15**, 300 (1928).