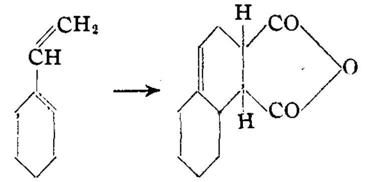
[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

Diene Reactions, Involving Aromatic Nuclei. A Contribution to the Knowledge of the Phenanthrene System

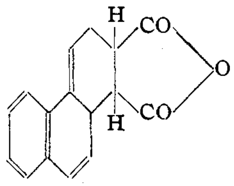
BY ERNST BERGMANN AND FELIX BERGMANN

The joining by the Diels–Alder method of a second ring to a cyclic system according to the scheme

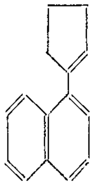


can hardly be expected to take place when the nuclear double bond belongs to an aromatic ring. As a matter of fact, there is only one substance in the benzene series which gives a positive response to the maleic anhydride test, *asym.*-diphenylethylene,[1] although the physical properties of all styrene derivatives point to the existence of a real conjugated system in them.

In the naphthalene series, it has been reported recently by Cohen[2] after previous failures of various authors[3] that α-vinylnaphthalene adds maleic anhydride to form (I). That the substance is not an aromatic naphthalene derivative formed by migration of the semi-cyclic double bond in (I) may be concluded from the fact that it does not form a picrate (see below). But the condensation reaction proved to be of no general value, α-vinylnaphthalene being unable to react with citraconic-anhydride, cinnamic aldehyde or fumaroyl dichloride;[4] only ethyl acetylene-dicarboxylate gave an ill-defined oily condensation product. 1-Cyclopentenylnaphthalene (II), which we prepared from cyclopentanone and 1-naphthylmagnesium bromide, and 6-methoxy-2-cyclopentenylnaphthalene (III), obtained with 6-methoxy-2-naphthylmagnesium bromide,[5] did not react even with maleic anhydride, the reaction with (III) being expected to lead to the building of the sterol skeleton.[5a]



I



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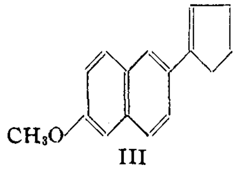

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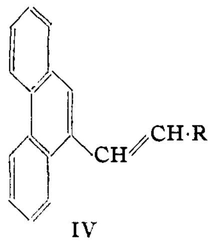

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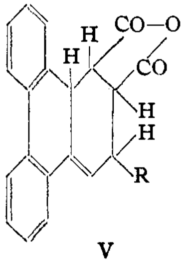

V

We expected an easier reaction with the cyclic double bond if the above system involved the middle ring of a phenanthrene system, which exhibits a certain olefinic character.[6] This hope was fully materialized by our experiments. The interesting properties and reactions which we observed with the new substances will be described in this paper.

From methyl-(9-phenanthryl)-carbinol, prepared according to Bachmann,[7] from 9-phenanthrylmagnesium bromide and acetaldehyde, 9-vinylphenanthrene (IV, R = H) could be obtained only in a polymeric state,[8] by means of potassium hydrogen sulfate. By Tschugaeff's method (thermolytic decomposition of the methyl xanthogenate of the carbinol), under certain experimental conditions, (IV, R = H) was secured as a yellow oil, which underwent spontaneous oxidation but could be converted, by reaction with maleic anhydride,

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(1) Th. Wagner-Jauregg, *Ber.*, **63**, 3218 (1930); *Ann.*, **491**, 1 (1931).

(2) Cohen, *Nature*, **136**, 869 (1935).

(3) Robinson and Walker, *J. Chem. Soc.*, 1530 (1935); Arbusow and co-workers, *Chem. Zentr.*, **107**, I, 2744 (1936).

(4) Kuhn and Wagner-Jauregg, *Ber.*, **63**, 2662 (1930).

(5) Fries and Schimmelschmidt, *ibid.*, **58**, 2840 (1925); Weizmann and co-workers, *J. Chem. Soc.*, 1367 (1935).

(5a) For the chemical behavior of other substituted α-vinylnapthalenes, see Salkind and Soniss, *Chem. Zentr.* **108**, I, 1934 (1937).

(6) For spectrochemical evidence with regard to the character of the middle ring see Anschuetz and Krollpfeiffer, *Ann.*, **430**, 230 (1923); Anschuetz and Kraul, *ibid.*, **443**, 184 (1925); Schlenk and Bergmann, *ibid.*, **463**, 84 (1928).

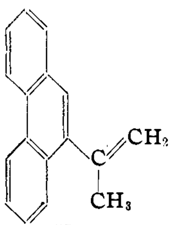
(7) Bachmann, THIS JOURNAL, **56**, 1363 (1934).

(8) Cf. Pschorr, *Ber.*, **39**, 3128 (1906).

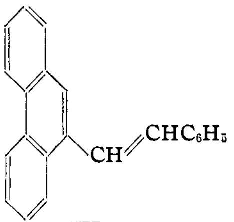
into a tetrahydrotriphenylenedicarboxylic acid (V, R = H). But under apparently equal conditions, sometimes 9-ethylphenanthrene was formed instead of (IV, R = H). This seems extremely surprising in view of the use of Tschugaeff's method in terpene chemistry for the preparation of pure unsaturated substances, but a similar failure has been observed in a second case to be discussed below.

The corresponding 9-propenylphenanthrene (IV, R = CH_3) was prepared from 9-allylphenanthrene by isomerization with alcoholic potash solution; it is markedly more stable than IV. It adds maleic anhydride (V, R = CH_3). The question of the position of the double bond in V seems to us settled by the observation that V (R = CH_3) decolorizes bromine solution, which is not to be expected when the double bond extends between C_9 and C_{10}.

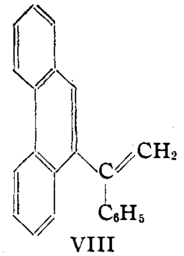
9-Isopropenylphenanthrene (VI), obtained by the Grignard reaction with acetone, behaved toward maleic anhydride like (IV), so that the addition of a methyl group to the 9-vinylphenanthrene system apparently is without influence on the diene reactions.[9] Therefore, it is theoretically interesting that 9-styrylphenanthrene (VII) behaves differently from 1′-(9-phenanthryl)-1′-phenylethylene (VIII), only the former giving a maleic anhydride addition product (IX).



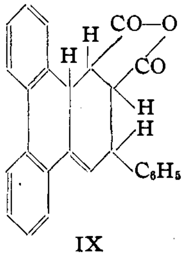
VI



VII



VIII



IX

(VIII) resembles the *asym.*-diphenylethylene (see above) but for the blocked ortho-position which may lower the reactivity of the *asym.*-diphenylethylene system;[10] (VII) on the other hand behaves like a true derivative of 1,4-diphenylbutadiene.[11] Apparently, to the lack of symmetry in (VIII) as compared with (VII) we have to ascribe the difference in reactivity toward maleic anhydride, a fact which may be described in terms of the theory of residual affinities,[12] or of the recent suggestions of Arndt and Eistert.[13] (VIII), which could be prepared easily from 9-phenanthrylmagnesium bromide and acetophenone, is also nearly the only hydrocarbon of the whole series we had, not giving a crystalline picrate, and since the m. p. of the substance is rather high (142° as compared with 118° of XVII), we had to bring constitutional proof. This has been done with sodium powder, which adds to *asym.*-diarylethylenes by a dimerizing reaction,[14] therefore converting the hydrocarbon (VIII) into (X). This was eventually hydrolyzed to give 1′,4′-diphenyl-1′,4′-di-(9-phenanthryl)-butane. It may be noted that here again is observed the well-known marked contrast in the proneness of double bonds toward sodium metal and other "molecular" reagents.

9-Styrylphenanthrene (VII) was prepared by interaction between 9-phenanthrylmagnesium bromide and phenylacetaldehyde. The (9-phenanthryl)-benzylcarbinol first obtained could be dehydrated by esterification with acetic anhydride and thermolysis of the acetyl derivative, while Tschugaeff's method gave 9-(β-phenylethyl)-phenanthrene (XI) in quantitative yield. The constitutional relation between the obtained two hydrocarbons (VII and XI) was ensured by reduction of (VII) through the disodium derivative, which on hydrolysis gave XI. The disodium derivative most probably has the formula (XII), but on hydrolysis, during which alkalinization of the medium cannot be avoided, it is isomerized so as to yield (XI). A similar shift has been observed in the case of benzhydrylideneindene by Schlenk and Bergmann.[15]

The dicarboxylic acid obtained by interaction

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(9) This is not always so. Compare Diels and Alder, *Ber.*, **62**, 554 (1929); Chuang and Han, *Ber.*, **68**, 876 (1935).

(10) For similar cases *cf.* Bergmann and Bondi, *Ber.*, **64**, 1455 (1931).

(11) This easily adds maleic anhydride or α-naphthoquinone. Diels and Alder, *ibid.*, **62**, 2081 (1928); Kuhn and Wagner-Jauregg, *ibid.*, **63**, 2662 (1930); and unpublished results of Dr. Haskelberg in our Laboratory.

(12) Schlenk and Bergmann, *Ann.*, **479**, 42 (1930); Bergmann and co-workers, *Ber.*, **63**, 2559 (1930); **64**, 1457 (1931).

(13) Arndt and Eistert, *ibid.*, **68**, 193 (1935); Eistert, **69**, 2393 (1936).

(14) Schlenk and Marcus, *Ber.*, **47**, 473 (1914); Schlenk and Bergmann, *Ann.*, **463**, 1 (1928).

(15) Schlenk and Bergmann, *ibid.*, **463**, 61 (1928).

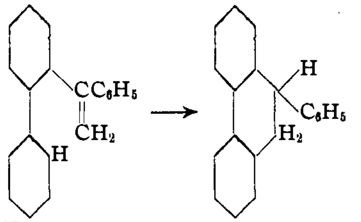
of (XII) with dry carbon dioxide gas, in any case, could not be induced to form an anhydride. This behavior is to be expected in case of a structure of the dicarboxylic acid similar to (XII). The difference between (VII) and (VIII) finds another expression in the fact that 9-styrylphenanthrene (VII) is able to form a dipicrate, thereby also resembling 1,4-diphenylbutadiene,[16] while from *asym.*-phenanthrylphenylethylene (VIII) no picrate was isolated, although in xylene solution a red color was developed on mixing the two compounds.[17] With regard to picrates, another regularity may be mentioned here: While those of the "active" dienes of this series are orange-red to red, 9-cyclohexenylphenanthrene, *e. g.*, which does not display dienic activities, gives a yellow picrate. It may be pointed out that 9-allylphenanthrene, which although unsaturated has no conjugated system, gives a yellow picrate as well as phenanthrene itself or 9-ethylphenanthrene.[18]

9-Cyclopentenylphenanthrene (XIII) was obtained from cyclopentanone through (9-phenanthryl)-cyclopentanol. It is differentiated from most of the other substances of this series by being liquid. Maleic anhydride gives (XIV), a derivative of cyclopentenotriphenylene recently described by Bergmann and Blum-Bergmann.[19] Its formation is a very clear-cut example of the reversibility of the diene reaction. (XIV) is insoluble in cold xylene and crystallizes completely on cooling the boiling reaction mixture. After a period of heating, a certain amount of (XIV) is obtained; if one heats anew the mother liquor, a new crop is obtained similarly, etc., while on heating the original mixture for even very long times one does not increase the yield obtained after the first period.

In contrast with (XIII), its higher homolog, 9-cyclohexenylphenanthrene (XV), similarly prepared, is a rather high melting substance (m. p. 132°); it has already been pointed out that the yellow tinge of its picrate points to a more saturated character of the hydrocarbon. As a matter of fact, although easily decolorizing bromine solution and although giving a violet color reaction with hot concd. sulfuric acid, it does not react with maleic anhydride, even under drastic conditions, to form a derivative of the hitherto unknown system of 1,2,3,4-dibenzphenanthrene (XVI).[20] The possibility that the double bond of the cyclohexenyl nucleus is not conjugated, is ruled out by the failure to shift it toward the phenanthrene system as in the case of 9-allylphenanthrene. Since, furthermore, we were unable to isomerize (XV) into 5,6-benzofluoranthene[21] (XVII), aluminum chloride leaving our hydrocarbon unattacked, we feared that the isomerization might have taken place spontaneously. This was refuted by the oxidation of our hydrocarbon, which gave phenanthrenequinone, while (XVII) is expected to yield phenanthrenequinone-1-carboxylic acid.

We suggest that the double bond in (XV) is fixed in a position so as to make the diene reaction sterically impossible (see formula). We hope to approach this problem by physical methods; meanwhile it may be stated that an analogous behavior has been reported recently by Cook and Lawrence[22] for 1-cyclohexenylnaphthalene, which proved extremely resistant toward various agents. A final proof of the validity of formula XV is to be seen in the dehydrogenation to form 9-phenylphenanthrene (XVIII).[23] Cook and Lawrence have ascribed the behavior of 9-cyclohexenylnaphthalene to a weakening of the olefinic character of the double bond by the residual affinities of the naphthalene nucleus. This suggestion is not sufficient in our case since it does not explain the differing behavior of the cyclopentenyl compound (XIII).

9-Phenylphenanthrene (XVIII) readily added metallic lithium;[24] the violet addition product on hydrolysis gave a substance supposed to be 9,10-dihydro-9-phenylphenanthrene. It was identical with a hydrocarbon of the same composition obtained by Bergmann and Bondi[25] in the (isomerizing) action of phosphorus pentachloride on *o*-phenyldiphenylethylene. This reaction, therefore has to be formulated as



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[16] Thiele and Henle, *Ann.*, **347**, 305 (1906).

[17] *asym.*-Diphenylethylene gives no picrate at all.

[18] For similar observations see Kuhn and Winterstein, *Helv. Chim. Acta*, **11**, 144 (1928).

[19] Bergmann and Blum-Bergmann, THIS JOURNAL, **58**, 1678 (1936).

[20] Barry, Cook, *et al.*, *Proc. Roy. Soc.* (London), **B117**, 318 (1935).

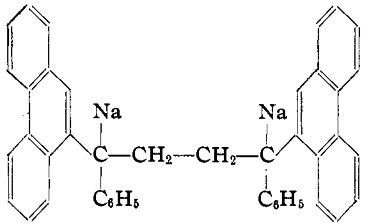
[21] For nomenclature see J. v. Braun and Anton, *Ber.*, **67**, 1051 (1934).

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

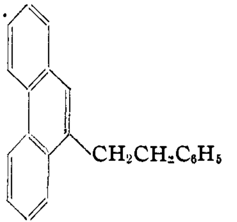
[23] Koelsch, THIS JOURNAL, **56**, 480 (1934).

[24] For similar behavior of 9,10-diphenylphenanthrene see Schlenk and Bergmann, *Ann.*, **463**, 89 (1928).

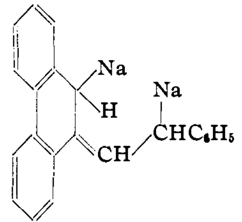
[25] Bergmann and Bondi, *Ber.*, **64**, 1460, 1476 (1931).



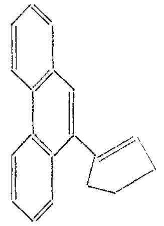
X



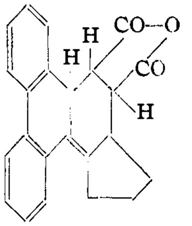
XI



XII



XIII

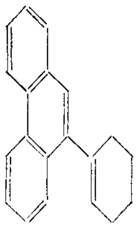


XIV

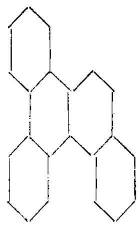
In 9,9'-diphenanthryl[7] (XIX), too, a conjugated system exists, but here again no reaction with maleic anhydride could be forced, evidently for reasons similar to the case of 9-cyclohexenylphenanthrene (XV). This is especially remarkable in view of the ability of benzanthracene and perylene to add maleic anhydride, but in these compounds the conjugated system is structurally fixed in the *cis*-position.[26] On the other hand, sodium metal added in the 1,4-position, the violet alkali-organic product evidently being a double compound between (XX) and the starting material.[27] On hydrolysis, from (XX) the corresponding 10,10'-dihydro-9,9'-diphenanthrylidene was obtained as a yellow, fluorescent substance. The ability to form a black crystalline perbromide may be quoted in support of the suggested structure.[28] The sodium reaction of diphenanthryl (XIX) is analogous to that of 9-styrylphenanthrene.

The reaction of 9-phenanthrylmagnesium bromide with α-hydrindone and α-tetralone, respectively, was also studied. α-(9-Phenanthryl)-indene and α-(9-phenanthryl)-α-dialin (XXI, XXII) were obtained as crystalline substances, both unsaturated toward bromine but resistant to maleic anhydride. The former hydrocarbon gave a yellow picrate in accordance with its low dienic activity, the latter gave no picrate at all, which may be due to the slight solubility of (XXII) in common solvents.[29]

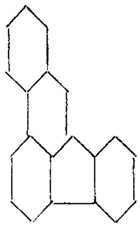
In the experimental part a few experiments have been described which were expected to yield the really dienic systems of 1-vinylcyclohexene-1 or α-vinyl-3,4-dialin. We were unable to prepare pure 1-vinylcyclohexanol-1 from 1-ethynylcyclohexanol-1, as catalytic hydrogenation proceeded with great rapidity until the final stage of 1-ethylcyclohexanol-(1). Tetralone was converted by sodium acetylide mainly into its enolate. A very interesting result has been obtained in the interaction between sodium acetylide and ethyl β-benzoylpropionate, although a substance of the composition of the expected γ-phenyl-γ-ethynyl-γ-hydroxybutyric acid (XXIII) was isolated only



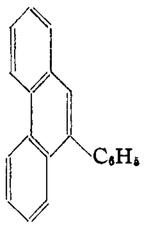
XV



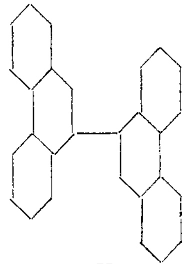
XVI



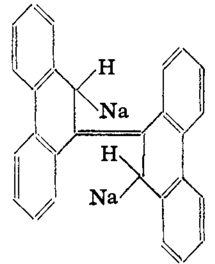
XVII



XVIII



XIX



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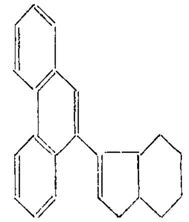
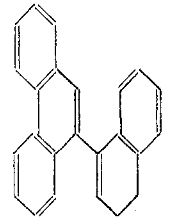
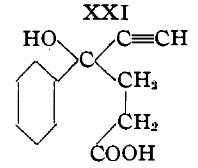


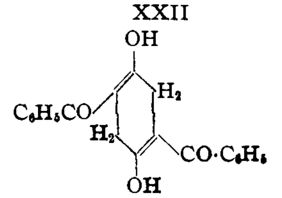
XXI



XXII



XXIII



XXIV

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(26) Clar, *Ber.*, **65**, 846, 1425 (1932); **69**, 1686 (1936).

(27) *Cf.* Bamberger and Lodter, *Ann.*, **288**, 75 (1895); Schlenk and Bergmann, *ibid.*, **463**, 92 (1928); Scott, Walker and Hansley, THIS JOURNAL, **58**, 2442 (1936).

(28) *Cf.* Bergmann and Corte, *Ber.*, **66**, 39 (1933); see also for references Brass and Clar, *ibid.*, **65**, 1660 (1932); **69**, 690, 1977 (1936); Zinke and Pongratz, *ibid.*, **69**, 1591 (1936); **70**, 214 (1937).

(29) Dimroth and Bamberger, *Ann.*, **438**, 67 (1924).

TABLE I

Grignard reaction First component	G.	Sec. component	Mg, g.	Product Name of compound	Yield, g.	B. p., °C.	B. p., Mm.	M. p., °C.	Formula	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
α-Bromonaphthalene	27.6 cc.	Cyclopentanone	48.6 (4.9)	1-Cyclopentenylnaphthalene (II)[a]	13.1	115	0.04		$C_{15}H_{14}$	92.8	92.6	7.2	8.0
6-Methoxy-2-bromonaphthalene	23.7	Cyclopentanone	8.4 (4.8)	6-Methoxy-2-cyclopentenylnaphthalene[b]	15.0			148	$C_{16}H_{16}O$	85.7	85.9	7.1	7.1
9-Bromophenanthrene	25.7	Allyl bromide	12.1 (2.4)	9-Allylphenanthrene[c]	13.0	161–163	1.25	51	$C_{17}H_{14}$	93.6	93.2	6.4	6.4
9-Bromophenanthrene	25.7	Acetone	6.5 (2.4)	9-Isopropenylphenanthrene[d]	9.2[e]	163	20	38	$C_{17}H_{14}$	93.6	93.6	6.4	6.8
9-Bromophenanthrene	25.7	Acetophenone	12.5 (2.4)	1′-(9-Phenanthryl)-1′-phenylethylene (VIII)[f]	4.5[e]	180–190	1	142[g]	$C_{22}H_{16}$	94.3	94.0	5.7	5.7[h]
9-Bromophenanthrene	25.7	Phenylacetaldehyde	12.5 (2.4)	9-Phenanthrylbenzylcarbinol[i,j]	16.0			120	$C_{22}H_{18}O$	88.6	88.9	6.0	6.4
				9-Styrylphenanthrene (VII)[k]		220–240	0.4[l]	118[m]	$C_{22}H_{16}$	94.3	94.2	5.7	5.9
											94.2		6.1
9-Bromophenanthrene	25.7	Cyclopentanone	8.4 (2.4)	9-Cyclopentenylphenanthrene (XIII)[d,n]	5.0[e]	185	.85		$C_{19}H_{16}$	93.4	93.4	6.6	6.7
											93.1		6.7
9-Bromophenanthrene	25.7	Cyclohexanone	10.0 (2.4)	9-Cyclohexenylphenantbrene (XV)[d,o]	5.0	190–200	1.25	132[p]	$C_{20}H_{18}$	93.0	92.8	7.0	7.2
9-Bromophenanthrene	25.7	α-Hydrindone	13.5 (2.4)	α-(9-Phenanthryl)-indene (XXI)[d,q]	10.0	230	0.7	121.5[r]	$C_{23}H_{16}$	94.5	94.6	5.5	5.5
9-Bromophenanthrene	15.0	α-Tetralone	9.0 (1.5)	α-(9-Phenanthryl)-α-dialin (XXII)[d,s]	1.0[t]	220–300	1.25	184.5[g]	$C_{24}H_{18}$	94.1	93.6	5.9	6.1

[a] The crude product was heated with potassium hydrogen sulfate (40 g.) to 160° for one hour. Pure product: $n^{20}\mathrm{D}$ 1.6285, d^{24} 1.0611, hence MR = 62.8, MR calcd. 63.5. Conjugation has not been taken into account.

[b] Leaflets from butanol. Brown-red sulfuric acid reaction.

[c] $n^{20}\mathrm{D}$ 1.6280, needles from methanol.

[d] The crude product was heated with oxalic acid (twice its weight) to 150° for two hours. Pure product: $n^{22}\mathrm{D}$ 1.6765, recrystallized from methanol.

[e] A relatively large amount of phenanthrene was recovered on fractional distillation, apparently due to the carbonyl compound reacting partly in its enolic form. In the case of acetophenone the amounts of phenanthrene and acetophenone recovered were equivalent.

[f] Prisms from benzene or propyl alcohol.

[g] The distillate crystallized on trituration with acetone.

[h] Calcd. for $C_{22}H_{16}$: mol. wt., 280. Found: mol. wt. (in camphor), 279.

[i] Needles from benzine or butanol.

[j] The carbinol (2 g.) was boiled with acetic anhydride (10 cc.) for ten hours and the product distilled.

[k] Prisms from propyl alcohol; intense blue fluorescence.

[l] This is the boiling point of the acetyl derivative, which on distillation splits off acetic acid.

[m] The distillate crystallized on trituration with acetone.

[n] Without heating the crude product with oxalic acid, (9-phenanthryl)-cyclopentanol could be obtained as a viscous oil, b. p. 212° (3 mm.), $n^{31}\mathrm{D}$ 1.6855, but only in relatively small yields, due to partial spontaneous dehydration. Furthermore, some 9,9′-diphenanthryl has been secured from the fraction, b. p. 220–250° (3 mm.). *Anal.* Calcd. for $C_{19}H_{18}O$: C, 87.0; H, 6.9. Found: C, 87.6; H, 6.5. $n^{18}\mathrm{D}$ 1.6941, $d^{17.2}$ 1.1384, hence MR = 80.8, MR calcd. = 77.4. Brown-red sulfuric acid reaction.

[o] Plates from propanol or butanol. Red-violet color with concd. sulfuric acid.

[p] The distillate crystallized on trituration with methyl alcohol.

[q] White needles from benzine or propyl alcohol.

[r] Purified through the picrate.

[s] From ligroin or butyl acetate as rhombohedra with intense blue fluorescence.

[t] Besides phenanthrene, 4 g. of tetralone could be recovered in this case, b. p. 80° (25 mm.).

in small yield; from this acid we intended to proceed to the corresponding γ-vinyl-γ-phenylvinylacetic acid. The main product was a red crystalline di-*p*-hydroxy diketone, to which we ascribe the formula (XXIV), its formation from 2 mols. of the starting material being self-explanatory.

Experimental

The Grignard reactions leading to the desired substances and the properties of the latter are listed in Table I, the isolated picrates in Table II. The picrates have often been used not only for characterization, but also for final purification of the hydrocarbons.

α-Vinylnaphthalene and Maleic Anhydride.—Our results are not in complete accordance with those of Cohen.[2] α-Vinylnaphthalene (15.4 g.) and maleic anhydride (9.8 g.) were boiled for two hours in xylene solution (50 cc.). The treatment of the precipitate and of the mother liquor residue gave the same results. The product was recrystallized from glacial acetic acid, leaving an insoluble part, whereby tetrahydrophenanthrene-1,2-dicarboxylic acid was obtained, after several recrystallizations lancet-shaped prisms, m. p. 244° (dec.). *Anal.* Calcd. for $C_{16}H_{14}O_4$: C, 71.1; H, 5.2. Found: C, 69.9, 70.0; H, 5.3, 5.3. The insoluble part was recrystallized from a mixture of glacial acetic acid and acetic anhydride, then from toluene; m. p. 169–170°. It consisted of the corresponding anhydride (I). *Anal.* Calcd. for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Found: C, 76.6, 76.3; H, 5.0, 5.0.

Attempted Synthesis of 9-Vinylphenanthrene.—Methyl-(9-phenanthryl)-carbinol was prepared according to Bachmann from 9-phenanthrylmagnesium bromide and acetaldehyde. When heated with three volumes of acetic anhydride, a crystalline *acetyl derivative* was obtained, m. p. 107°. *Anal.* Calcd. for $C_{18}H_{16}O_2$: C, 81.8; H, 6.1. Found: C, 81.7; H, 6.0. Heating the carbinol with potassium hydrogen sulfate gave a polymer (dimer?) which could be distilled at 0.2 mm.; b. p. 280°. From its alcoholic solution a red picrate, m. p. 173°, could be isolated, which gave the expected analytical figures. *Anal.* Calcd. for $(C_{22}H_{15}O_7N_3)_n$. N, 9.7. Found: N, 9.2.

TABLE II

PICRATES OF HYDROCARBONS

Hydrocarbon	Prepared in	Formula	M. p., °C.	Analyses Calculated C	Analyses Calculated H	Analyses Calculated N	Analyses Found C	Analyses Found H	Analyses Found N	Remarks
1-Cyclopentenylnaphthalene (II)	Alcohol	$C_{21}H_{17}O_7N_3$	82	59.6	4.0		59.8	4.8		From alcohol orange-yellow needles
9-Allylphenanthrene	Alcohol	$C_{23}H_{17}O_7N_3$	115	61.7	3.8	9.4	61.8	4.2	9.5	From alcohol yellow
9-Propenylphenanthrene (IV)	Alcohol	$C_{23}H_{17}O_7N_3$	108	61.7	3.8		62.3	4.3		Orange-red prisms from alcohol
9-Isopropenylphenanthrene (VI)	Alcohol	$C_{23}H_{17}O_7N_3$	108	61.7	3.8		62.0	4.1		From alcohol
9-Styrylphenanthrene (VII)	Alcohol	$C_{34}H_{22}O_{14}N_6$	164	55.3	3.0		54.2	3.2		Red needles, which cannot be recrystallized, since they easily lose part of the picric acid, to yield a yellow, undefined product
9-Cyclopentenylphenanthrene (XIII)	Alcohol	$C_{25}H_{19}O_7N_3$	120	63.4	4.0	8.9	63.2	4.35	8.7	Red needles, from alcohol
9-Cyclohexenylphenanthrene (XV)	Butanol	$C_{26}H_{21}O_7N_3$	141–142	64.1	4.3		64.3	4.8		Orange-yellow prisms from butanol
9,9′-Diphenanthryl (XIX)	Benzene	$C_{40}H_{24}O_{14}N_6$	163	59.1	3.0		60.1	3.3		Orange-red; from xylene–benzine
α-(9-Phenanthryl)-indene (XXI)	Propanol	$C_{29}H_{19}O_7N_3$	132	66.8	3.7	8.1	67.2	4.0	8.3	Yellow needles, from propanol
9-(β-Phenylethyl)-phenanthrene (XI)	Alcohol	$C_{28}H_{21}O_7N_6$	133	65.8	4.1	8.2	65.4	4.5	8.8	Yellow from alcohol

Tschugaeff Reaction.—The methyl xanthogenate deriving from methyl-(9-phenanthryl)-carbinol was decomposed as usual by boiling for twenty minutes. In the first experiments only polymeric products were obtained, apparently due to traces of iodine, since this difficulty was easily overcome when the crude product before distillation in high vacuum was shaken with molecular silver. In one of the experiments, the distillation (1 mm.) gave a yellow oil, b. p. 150–160°, which oxidized spontaneously. *Anal.* Calcd. for $C_{16}H_{12}$: C, 94.1; H, 5.9. Found: C, 92.1; H, 6.1.

When this 9-vinylphenanthrene (IV, R = H; 0.4 g.) was boiled with maleic anhydride (0.25 g.) in xylene (10 cc.) for five hours, a crystalline condensation product was obtained, which after recrystallization from dioxane–water, melted at 218–220° and according to the analysis was probably the expected *tetrahydrotriphenylene-dicarboxylic acid* (as V, R = H). *Anal.* Calcd. for $C_{20}H_{16}O_4$: C, 75.0; H, 5.0. Found: C, 75.6; H, 5.2.

In other experiments, the distilled oil (b. p. 155° at 0.7 mm.) crystallized immediately; from methyl alcohol, m. p. 66°. This substance, according to its properties and to the m. p. (124°) of its picrate, was *9-ethylphenanthrene*. *Anal.* Calcd. for $C_{16}H_{14}$: C, 93.2; H, 6.8. Found: C, 92.6; H, 7.2. It was identified by the method of mixed melting points.

Tschugaeff "Dehydration" of 9-Phenanthryl-benzylcarbinol.—The carbinol (2.5 g.) was treated with sodium metal (0.35 g.) in xylene (30 cc.); when most of the metal was dissolved, carbon disulfide (3 cc.) and methyl iodide (3 cc.) were added. After some minutes all the volatile products and half of the xylene were driven off *in vacuo*, the remainder shaken for four hours with silver powder, the excess xylene removed and the residue distilled. The resin obtained at 220–230° (0.8 mm.) crystallized on trituration with acetone and methanol; from methanol, clusters of leaflets, m. p. 81.5°.

The 9-(β-phenylethyl)-phenanthrene (XI) was resistant to bromine solution and gave no characteristic color reaction with concd. sulfuric acid. *Anal.* Calcd. for $C_{22}H_{18}$: C, 93.6; H, 6.4. Found: C, 93.6, 93.7; H, 6.6, 6.5.

9-Propenylphenanthrene (IV, R = CH$_3$).—9-Allylphenanthrene (12 g.) in alcohol (25 cc.) was isomerized with an alcoholic potash solution (2.1 g. in 50 cc.) by four hours of boiling. 9-Propenylphenanthrene was a yellowish, mobile oil, b. p. 157° (1.25 mm.), yield, 10 g., which was purified *via* the red picrate. The purest preparation had b. p. 179° (2.5 mm.); $n^{27.5}D$ 1.6928. *Anal.* Calcd. for $C_{17}H_{14}$: C, 93.6; H, 6.4. Found: C, 90.5, 90.4; H, 6.5, 6.4.

Reactions with maleic anhydride are summarized in Table III. They were carried through in boiling solutions for four hours, except in the case of 9-cyclopentenylphenanthrene, which has been referred to.

TABLE III

Hydrocarbon	9-Propenylphenanthrene[a] (IV, R CH$_3$)	9-Isopropenylphenanthrene[b] (VI)	9-Cyclopentenylphenanthrene[c] (XIII)	9-Styrylphenanthrene[d] (VII)
Grams taken	1	2	11	0.5
Anhydride, g.	0.5	1	8	.2
Xylene, cc.	10	10	50	10
M. p., °C.	264	262	275–276	249–250
Yield, mg.	150	400	9000	180
Formula	$C_{21}H_{16}O_3$	$C_{21}H_{16}O_3$	$C_{23}H_{18}O_3$	$C_{26}H_{18}O_3$
Carbon, %:				
Calcd.	79.7	79.7	80.7	82.5
Found	79.3	79.9	80.8	81.8
H, %:				
Calcd.	5.1	5.1	5.3	4.8
Found	5.5	5.1	5.5	5.1

[a] Needles from nitrobenzene or butyl acetate.

[b] Silky needles from xylene.

[c] Clusters of needles from xylene.

[d] Dimorphous crystals from xylene–ethyl benzoate solution.

Experiments with 9-Cyclohexenylphenanthrene (XV). (a) **Oxidation.**—When chromic acid (3.1 g.) in 50% acetic acid (5 cc.) was added to the hot solution of the hydrocarbon (1 g.) in glacial acetic acid (50 cc.), a violent reaction occurred, which was completed by two hours of boiling. On addition of water, phenanthrenequinone (400 g.) precipitated; from propanol as needles, m. p. and mixed m. p. with a pure sample of the quinone, 202°.

(b) **Attempted Cyclization.**—The hydrocarbon (2 g.) in carbon disulfide (20 cc.) was treated with powdered anhydrous aluminum chloride (2 g.) at 0° for twenty-four hours, but was recovered unchanged.

(c) **Dehydrogenation.**—9 - Cyclohexenylphenanthrene (1.2 g.) and selenium (2.4 g.) were heated to 340° for four hours in a sealed tube. The product was extracted with ether and distilled. *9-Phenylphenanthrene* (XVIII) went over at 170–190° (1.25 mm.) as a colorless oil, which exhibited an intense blue fluorescence and crystallized on trituration with acetone and methanol; from propyl alcohol as prisms, m. p. 110°,[28] yield 310 mg. *Anal.* Calcd. for $C_{20}H_{14}$: C, 94.5; H, 5.5. Found: C, 94.4; H, 6.2.

Addition Reactions with Sodium Powder[30]

(a) **1′-(9-Phenanthryl)-1′-phenylethylene (VIII)** reacted with sodium powder in ethereal medium immediately, the color being first green, then blue. The mass was decanted from the excess metal in a nitrogen atmosphere and hydrolyzed by means of alcohol. Most of the product crystallized spontaneously from the ether solution; from a mixture of xylene and ethyl benzoate plates, m. p. 243.5°, of (1′,4′-di-(9-phenanthryl)-1′,4′-diphenylbutane. *Anal.* Calcd. for $C_{44}H_{34}$: C, 94.0; H, 6.0. Found: C, 94.0; H, 6.4.

(b) **9-Styrylphenanthrene (VII)** gave a dark violet addition product (XII), its hydrolysis a fluorescent solution. The residue obtained on evaporating crystallized from alcohol as leaflets, m. p. 81.5°. It was identified as 9-(β-phenylethyl)-phenanthrene by mixed melting point. When treated with dry gaseous carbon dioxide, (XII) was converted into a white sodium salt. Its solution in water, on acidification, gave a microcrystalline powder, which could be recrystallized from 70% acetic acid, m. p. 279°. *Anal.* Calcd. for $C_{24}H_{18}O_4$: C, 77.8; H, 4.9. Found: C, 77.2; H, 5.3.

(c) **9-Phenylphenanthrene (XVIII)** did not react with sodium, but very quickly with lithium metal, which gave a violet solution. Hydrolysis as usual gave an oily substance, which solidified on addition of light petroleum ether (40–60°) and was recrystallized from propyl alcohol; leaflets, m. p. 84°. This 9-phenyl-9,10d-ihydrophenanthrene was identified with a specimen prepared by Bergmann and Bondi.[25]

(d) **9,9′-Diphenanthryl (XIX)** gave immediately a violet-black addition product. Its hydrolysis yielded an ether-insoluble, yellow, fluorescent (green) product and the equivalent amount of the ether-soluble starting material (identification by mixed m. p.). The ether-insoluble product was recrystallized from butyl acetate; long, bent, yellow needles of 10,10′-dihydro-9,9′-diphenanthrylidene (as XX), m. p. 303°. *Anal.* Calcd. for $C_{28}H_{20}$: C, 94.4; H, 5.6. Found: C, 94.2, 94.6; H, 5.2, 5.1. The perbromide was obtained in form of brown-black needles on addition of bromine to a warm chloroform solution of the yellow hydrocarbon; it is rather unstable, therefore giving not very satisfactory analytical results. *Anal.* Calcd. for $C_{28}H_{18}Br_3$: C, 56.6; H, 3.0. Calcd. for $C_{28}H_{18}Br_4$: C, 49.9; H, 2.7. Found: C, 49.4; H, 3.1.

1-Ethynyl-cyclohexanol-(1) and Di-(1-hydroxycyclohexyl-1)-acetylene.—The reaction between monosodium acetylide and cyclohexanone was carried out in ethereal medium; the sodium compound was prepared according to Hess and Munderloh.[31] The two products were separated by distillation *in vacuo*, 40 g. of cyclohexanone giving 10 g. of ethynylcyclohexanol, b. p. 86° (17 mm.), and 9 g. of the glycol, m. p. 160–164° (3 mm.), from light petroleum ether, stout prisms, m. p. 102–103°. They have been obtained by Rupe[32] from cyclohexanone and acetylene in presence of sodamide.

1-Ethylcyclohexanol-(1).—As reported in the theoretical part of this paper, hydrogenation of ethynylcyclohexanol-(1) even under controlled conditions, gave 1-ethylcyclohexanol-(1), b. p. 70–75° (18 mm.). *Anal.* Calcd. for $C_8H_{16}O$: C, 75.0; H, 12.5. Found: C, 75.1, 74.8, 75.3; H, 11.9, 12.2, 12.0. Dehydratation with oxalic acid, therefore, gave *ethylcyclohexene*, b. p. 49° (30 mm.). *Anal.* Calcd. for C_8H_{14}: C, 87.3; H, 12.7. Found: C, 86.5, 86.0; H, 12.2, 12.0.

Undoubtedly the crude hydrogenation product contains some 1-vinylcyclohexanol-(1), since its dehydration gives besides the ethylcyclohexene fraction a viscous oil, b. p. 160°, n^{18}_{D} 1.5348, which according to the analysis is polymeric 1-vinylcyclohexene-(1). *Anal.* Calcd. for $(C_8H_{12})_n$: C, 88.9; H, 11.1. Found: C, 88.7; H, 11.6.

1-Ethynylcyclohexanol-(1), when simply heated (2 g.) with oxalic acid (2.5 g.) at 150° for thirty minutes, was converted into *cyclohexanone*, b. p. 84° (26 mm.). (*Anal.* Calcd. for $C_6H_{10}O$: C, 73.5; H, 10.2. Found: C, 73.6; H, 10.5) and cyclohexenylacetic acid, b. p. 150–160° (25 mm.); n^{21}_{D} 1.4903. (*Anal.* Calcd. for $C_8H_{12}O_2$: C, 68.6; H, 8.6. Found: C, 67.9; H, 9.0.)[33] The latter substance derives from cyclohexenylacetaldehyde, which could have been formed by rearrangement of 1-ethynylcyclohexanol-(1).

Ethyl β-Benzoyl-propionate and Monosodium Acetylide.—When the ester[34] was added to a suspension of dry monosodium acetylide in ether, a vigorous reaction took place, the color changing into a dark yellow-red. The reaction was accomplished by heating, the mass decomposed with ice and dilute sulfuric acid and the neutral and acidic products worked up separately. The neutral fraction consisted of the starting ester, while the acidic one had to be separated mechanically into two substances.

(a) **γ-Phenyl-γ-hydroxy-γ-ethynyl-butyric acid (XXIII)** from 75% acetic acid plates, from dioxane needles, m. p. 242.5°. *Anal.* Calcd. for $C_{12}H_{12}O_3$: C, 70.6; H, 5.9. Found: C, 71.2, 71.2; H, 6.0, 5.9.

(b) **1,4-Dibenzoyl-2,5-dihydroxy-3,6-dihydrobenzene (XXIV)** from butyl acetate as deep orange-red plates, m. p. 200°. *Anal.* Calcd. for $C_{20}H_{16}O_4$: C, 75.0; H, 5.0; mol. wt. 320. Found: C, 74.9; 75.1; H, 4.5, 4.5; mol. wt. (camphor), 300. Phenylhydrazine in boiling alcohol gave a greenish-yellow *bis-phenylhydrazone* from benzene, m. p. 274°. *Anal.* Calcd. for $C_{32}H_{28}O_2N_4$: C, 76.8; H, 5.6; N, 11.2. Found: C, 76.5; H, 5.4; N, 11.0, 11.2. With diazomethane in ethereal suspension, a yellowish *dimethyl ether* was obtained, from benzene-light petroleum, m. p. 204°. *Anal.* Calcd. for $C_{22}H_{20}O_4$: C, 75.9; H, 5.7. Found: C, 75.9, 75.7; H, 5.2, 5.3. This

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[30] *Cf.* Schlenk in Houben-Weyl, "Methoden der organischen Chemie," Vol. IV, Georg Thieme, Leipzig, 1924, p. 959.

[31] Hess and Munderloh, *Ber.*, **51**, 377 (1918).

[32] Rupe, Messner and Kambli, *Helv. Chim. Acta*, **11**, 449 (1928); compare *Chem. Zentr.*, [I] **108**, 2368, 2587, 2685 (1937).

[33] *Cf.* Beilstein, Vol. IX, 1926, p. 46.

[34] Skraup and Schwamberger, *Ann.*, **462**, 135 (1928).

dimethyl ether exhibited no longer the characteristic property of the original substance, to give dark-red solutions in alkali.

Summary

With the exception of α-vinylnaphthalene itself, substituted α- and β-vinylnaphthalenes do not exhibit dienic properties toward maleic anhydride or similar substances.

A number of 9-vinylphenanthrenes have been prepared and their physical and chemical behavior have been studied. Most of them add maleic anhydride forming higher polycyclic systems, as expected. Surprisingly, 9-cyclohexenylphenanthrene and 9,9'-diphenanthryl do not behave like true dienes; this is ascribed to the special steric arrangement of the respective molecules.

The reaction of several substances with alkali metals has been studied.

In two cases, Tschugaeff's classical method for the preparation of ethylenes failed, giving the corresponding saturated systems.

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A Quantitative Discussion of Bond Orbitals

BY LINUS PAULING AND J. SHERMAN

Six years ago, in the course of the development of the quantum mechanical theory of directed valence,[1] a very simple method of discussing the bond-forming power of an atomic bond orbital (one-electron orbital wave function) in its dependence on the angular distribution of the orbital was formulated.[1b,2] The fundamental assumption of the method is that in the case of bond orbitals with the same or nearly the same radial part of the wave function the magnitude of the angular part of an orbital along the bond axis (that is, in the direction of the other atom) is a measure of its relative bond-forming power. The bond-forming power or strength S of an s orbital (normalized to 4π), defined in this way, is 1, that of a p orbital is 1.732, and that of the best bond-forming hybrid sp orbital (called a tetrahedral sp bond orbital) is 2.

In order to obtain information as to the extent to which the bond strength S of an orbital can be considered a qualitative measure of its bond-forming power and also as to the quantitative relation between the energy of a bond and the strengths of the bond orbitals involved in its formation, we have now carried out the thorough discussion of various sp and spd one-electron bonds between identical atoms.

Description of the Method

We discuss a system comprising two atomic nuclei or kernels (nuclei and completed inner shells of electrons), with residual charge $+e$, and one electron, which forms a one-electron bond between the two atoms. The energy integral $E = \int \psi^* H\psi d\tau / \int \psi^*\psi d\tau$ is evaluated for various internuclear distances to give an energy function for each choice of the wave function ψ. This wave function is assumed to be of the form $c(\psi_A + \psi_B)$, ψ_A and ψ_B being similar atomic bond orbitals for atoms A and B and c a normalization constant. The functions ψ_A and ψ_B are formed by linear combination of central-field atomic orbitals. However, in discussing s-p hybridization, we do not use $2s$ and $2p$ hydrogen-like orbitals, inasmuch as these differ somewhat in their radial parts; instead, in order to obtain results bearing directly on the effect of angular distribution of the orbital on its bond-forming power, we use the same radial function for $2s$ as for $2p$. As a result of this simplification of the radial function, the energy of the $2s$ orbital is changed from the hydrogen-like value, a term $l(l+1)/r^2$ being introduced by the kinetic energy operator acting on the radial function, and not canceled by the angular function. In order to achieve sp degeneracy we omit this term, as well as the corresponding term in the sp exchange integrals. In a later section there is then discussed the case in which the s and p orbitals correspond to different energy values. Similarly in discussing M orbitals we use the

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(1) (a) J. C. Slater, *Phys. Rev.*, **38**, 1109 (1931); (b) L. Pauling, THIS JOURNAL, **53**, 1367 (1931).

(2) See also R. Hultgren, *Phys. Rev.*, **40**, 891 (1932), for extended applications of the method, J. H. Van Vleck, *J. Chem. Phys.*, **3**, 803 (1935), for a discussion of the relation between directed bond orbitals and molecular orbitals, and C. A. Coulson, *Proc. Cambridge Phil. Soc.*, **33**, 104 (1937), for a brief discussion of the criterion of maximum overlapping.