

TABLE II
 $R_2C(SCH_2COOC_2H_5)_2$

R	B. p., °C.	Press., mm.	Yield, %	d_{20}^{20}	n_D^{20}	M_D Calcd.	M_D Found	S Analyses, % Calcd.	Found
CH ₃	152-153	1.8	69	1.1368	1.4970	72.26	72.18	22.81	22.92
C ₂ H ₅	162-163	2	65	1.1140	1.4969	81.50	80.80	20.77	20.73
<i>n</i> -C ₃ H ₇	178-179	3	89	1.0758	1.4909	90.74	90.49	19.04	19.06
<i>n</i> -C ₄ H ₉	183-184	3	90	1.0269	1.4862	99.99	99.64	17.58	17.55

separated, washed with water and sodium bicarbonate solution and dried with sodium sulfate. The carbon tetrachloride was evaporated and the residual oil chilled in an ice-bath until it solidified. The sulfones were recrystallized from a mixture of ethanol and water. They were all

colorless crystals. Their properties are summarized in Table III.

Summary

A series of dialkyl *bis*-(carbethoxymethanesulfonyl)-methanes has been prepared by oxidizing dialkyl *bis*-(carbethoxymethylmercapto)-methanes. The latter were obtained by esterification of the corresponding acids which were produced by the reaction between mercaptoacetic acid and the simple ketones. These disulfones possessed no hypnotic activity.

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TABLE III



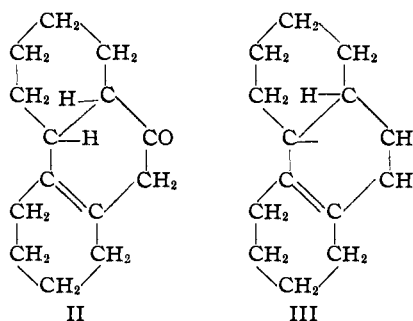
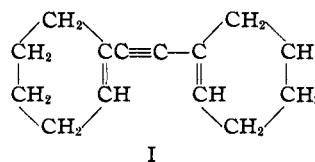
R	M. p., °C. (corr.)	Yield, %	Mol. formula	S Analyses, % Calcd.	Found
CH ₃	84-85	32	C ₁₁ H ₂₀ O ₈ S ₂	18.61	18.79
C ₂ H ₅	73-74	41	C ₁₃ H ₂₄ O ₈ S ₂	17.20	17.08
<i>n</i> -C ₃ H ₇	90-91	37	C ₁₅ H ₂₈ O ₈ S ₂	16.00	15.82
<i>n</i> -C ₄ H ₉	74-75	42	C ₁₇ H ₃₂ O ₈ S ₂	14.95	15.07

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Cyclization of Dienynes. VII.¹ Dehydrogenation of *trans*-Dodecahydrophenanthrene and a Further Study of *trans*-3,4-Dialkylcatalones

BY C. S. MARVEL, RALPH MOZINGO² AND E. C. KIRKPATRICK³

In an attempt to prepare phenanthrene derivatives⁴ it was found that the cyclization of di- Δ^1 -cyclohexenylacetylene (I) gave a ketone described as Δ^{11} -dodecahydro-9-phenanthrone (II), which on Clemmensen reduction yielded a hydrocarbon considered to be Δ^{11} -dodecahydrophenanthrene (III). Attempts to dehydrogenate these compounds with selenium did not give phenanthrene or a phenanthrol. The hydrocarbon (III) was converted by this treatment to a compound which appeared to be identical with the *trans-as*-octahydrophenanthrene (IV) reported by van de Kamp and Mosettig.⁵ Moreover, reduction of the hydrocarbon (III) gave a product with physical properties which checked closely those of tetradecahydrophenanthrene obtained by the hydrogenation of phenanthrene.⁴ These facts seemed to establish the phenanthrene



structure and pointed to the conclusion that selenium does not dehydrogenate fused *trans* ring systems.

Recently, however, Cook, Hewett and Robinson⁶ have shown that van de Kamp and Mosettig's *trans-as*-octahydrophenanthrene contains also the *cis*-isomer (V) and the spiran (VI).

(1) For the sixth communication in this series see Pinkney and Marvel, *THIS JOURNAL*, **59**, 2669 (1937).

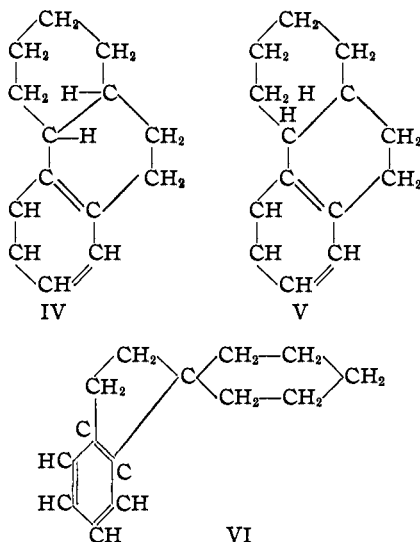
(2) Röhlm and Haas Special Research Assistant in Chemistry, 1937-1939.

(3) Solvay Company Fellow in Organic Chemistry, 1937-1938.

(4) (a) Pinkney, Nesty, Wiley and Marvel, *THIS JOURNAL*, **58**, 972 (1936); (b) Pinkney, Nesty, Pearson and Marvel, *ibid.*, **59**, 2666 (1937).

(5) Van de Kamp and Mosettig, *ibid.*, **58**, 1062 (1936).

(6) Cook, Hewett and Robinson, *J. Chem. Soc.*, 168 (1939).



This result coupled with the fact that all comparisons of physical properties in this series had been made on liquids has made it seem desirable to reconsider the structures which have been assigned previously to compounds II and III.

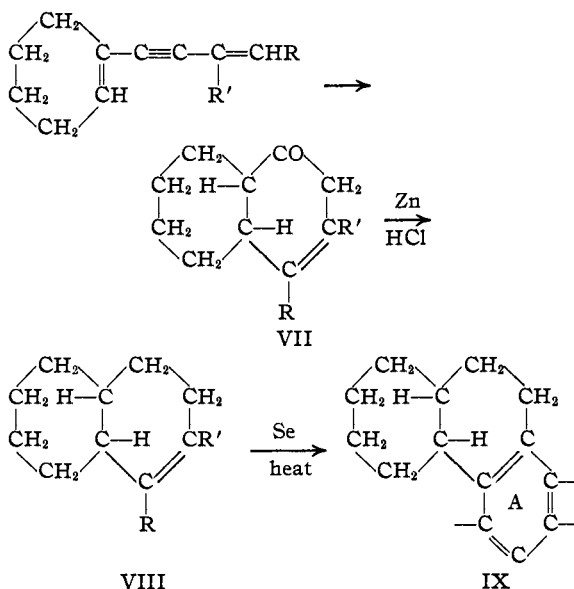
The spiran, cyclohexanespirocyclopentane, has been shown by Clemo and Ormston⁷ to be largely decomposed into unidentified fragments when it is heated with selenium although some of it does yield naphthalene, a completely aromatized compound. Since our hydrocarbon (III) is only partially dehydrogenated and not seriously attacked otherwise when heated with selenium, it obviously cannot be the hydrogenated spiran related to VI.

That our hydrocarbon (III) is a phenanthrene derivative has now been established definitely by dehydrogenation over a platinum on charcoal catalyst⁸ at 300–320° to give phenanthrene as the only product. This leaves only the question of the position of the double union in the hydrocarbon to be determined.

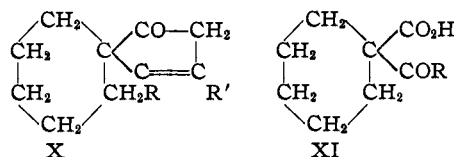
The fact that dehydrogenation of this dodecahydrophenanthrene with selenium gives octahydrophenanthrene indicates that the double union is at the 11-position. Further evidence of this was sought by ozonolysis of the unsaturated cyclic ketone (II). However, only a mixture of products resulted. These results are similar to those reported by Durland and Adkins,⁹ who found that unsaturated hydroaromatic compounds are attacked by ozone–oxygen mix-

tures at other points as well as at the double bond. Confirmation of the 11-position for the double bond was obtained by hydrogenation of the cyclic ketone (II) over Raney nickel.¹⁰ While this hydrogenation has been reported as giving a non-crystalline alcohol^{4b} a solid alcohol has now been obtained. The reduction was more difficult to accomplish than would have been the case if the carbon–carbon double bond had been in an exposed position since a temperature of 185° at 100–200 atmospheres was needed to bring about the addition of hydrogen.

Another case where selenium failed to dehydrogenate a *trans*-bridge has been reported from this Laboratory.¹¹ An octahydronaphthalene derivative (VIII) was prepared by the following reactions. The structure of the intermediate cyclic



ketone (VII, R = *n*-propyl, R' = *n*-butyl) was established by ozonolysis to yield a keto acid which could be distilled at 120–125° (2 mm.), without decomposition. If the ring closure had produced a spiran (X), the product of ozonolysis would have been a β -keto acid (XI) and certainly would have decomposed with the loss of carbon dioxide at this temperature. Hence, the hydrocarbon obtained by the Clemmensen reduction of



(7) Clemo and Ormston, *J. Chem. Soc.*, 352 (1933).

(8) Linstead, Millidge, Thomas and Walpole, *ibid.*, 1146 (1937).

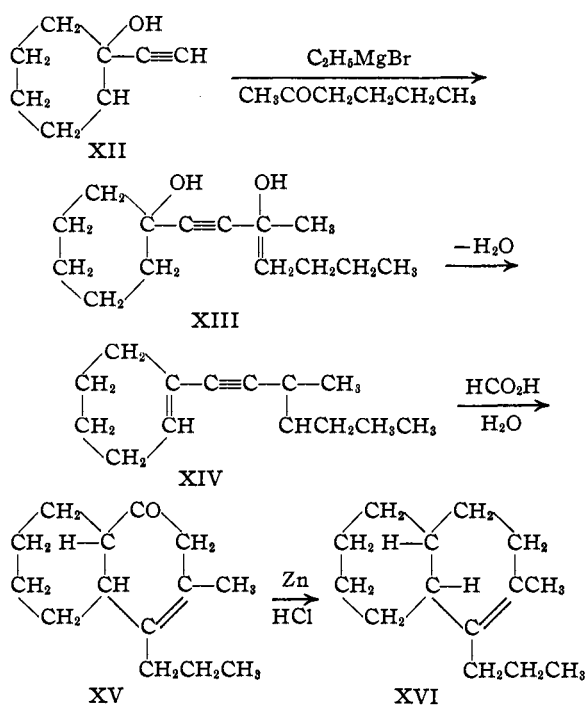
(9) Durland and Adkins, *THIS JOURNAL*, 61, 429 (1939).

(10) Covert and Adkins, *ibid.*, 54, 4116 (1932).

(11) Nesty and Marvel, *ibid.*, 59, 2662 (1937).

the ketone (VII) was assigned the octalin structure (VIII). Attempts to dehydrogenate this hydrocarbon with selenium led to mixtures of hydrocarbons but ultraviolet absorption spectrum evidence indicated no naphthalene derivative. A new aromatic ring (IXA) was apparently formed from the other alkyl groups. It should be noted here that the crude dehydrogenation product was blue in color.

In order more definitely to establish this ring formation from 1,2-dialkyl groups in a Δ^1 -octalin derivative, we have now synthesized the compound corresponding to VIII (in which R is *n*-propyl and R' is methyl) by the following reactions.



When the methyl *n*-propyl octalin (XVI) was heated with selenium, a bluish mixture of hydrocarbons was obtained. Fractional distillation removed the blue color but the colorless product was still a mixture of hydrocarbons. The ultraviolet absorption spectrum of this mixture showed definite bands of the same character and in the same region as the bands shown by tetralin and other hydrocarbons having an alicyclic ring fused to a benzene ring.¹²

Figure 1 shows the ultraviolet absorption curves of the octalin derivative (XIV), its selenium dehydrogenation product and a sample of *trans-as*-

octahydrophenanthrene prepared by the method of van de Kamp and Mosettig.⁵ Figure 2 shows the curves of the selenium dehydrogenation product from the octalin mixture and for tetralin.¹²

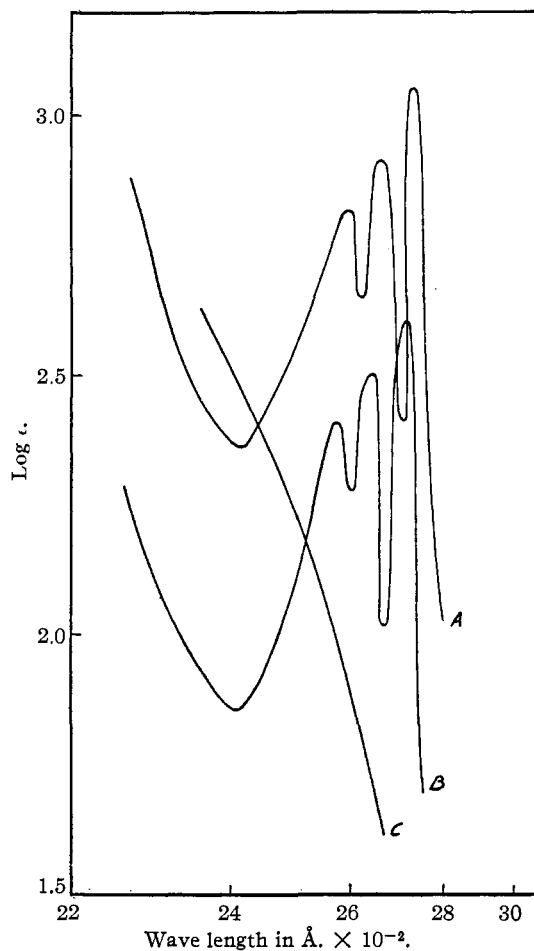


Fig. 1.—A, *as*-octahydrophenanthrene; B, selenium dehydrogenation products; C, octalin derivative (XIV).

The very close similarity between absorption curves B^{12a} and A in Fig. 1 shows that they must be produced by the same basic ring structure calculating from Beer's law, the position of B on the log ϵ axis indicates that the concentration of *trans-as*-octahydrophenanthrene in the dehydrogenation product amounts to about 35–40%.

In order to complete the identification of the supposed octalin (XVI), an attempt was made to dehydrogenate it over a platinum-charcoal catalyst to yield the naphthalene in the same way that the dodecahydrophenanthrene (III) had been converted to phenanthrene. However, this at-

(12a) To calculate the molal concentration to draw this curve, a molecular weight of 186 was used.

(12) Morton and de Gouveia, *J. Chem. Soc.*, 916 (1934).

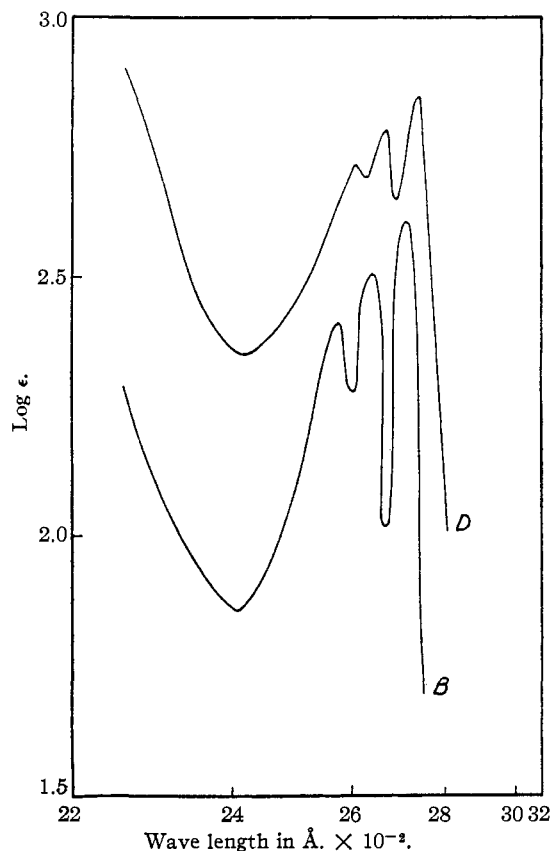


Fig. 2.—B, selenium dehydrogenation product; D, tetralin.¹²

tempt produced a complex blue mixture of hydrocarbons. Fractional distillation of the dehydrogenation mixture gave about a 19% yield of the deep blue hydrocarbon. This hydrocarbon showed absorption in the ultraviolet (Fig. 3) similar to that shown by known azulene derivatives.¹³ The octalin mixture before dehydrogenation gave the characteristic deep blue color with bromine and acetic acid which has been reported for azulene-yielding compounds.¹⁴

The exact structure of this new azulene has not been established. Its formation, however, shows that the supposed octalin (XVI) contains a hydrocarbon which can be dehydrogenated to give the azulene structure in which a seven-membered ring is fused to a five-membered ring with two carbons in common. Since the ozonization of the ketone (XV) gave evidence of the hydro-naphthenone structure, the rearrangement to a seven-five system must have occurred during the

(13) Susz, St. Pfau and Plattner, *Helv. Chim. Acta*, **20**, 469 (1937).

(14) Baber and Smith, "A Research on Eucalypts," Sydney, 1920, p. 417; Haworth, *Ann. Reports*, **34**, 393 (1937).

Clemmensen¹⁵ reduction. It should be pointed out that no azulenes were noted in the dehydrogenation of the dodecahydrophenanthrene (III) and hence the rearrangement during the Clemmensen reduction must not have occurred in the phenanthrene series.

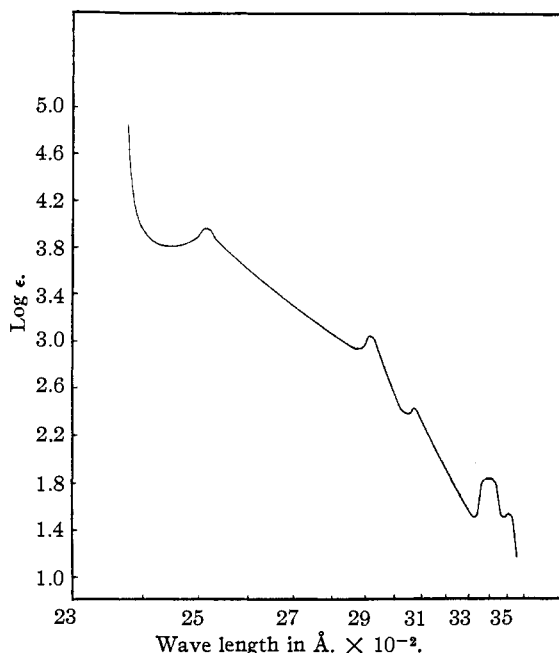


Fig. 3.—Absorption spectrum of blue hydrocarbon.

Experimental

Preparation of 1-Ethynylcyclohexanol.—A modification of the method of Pinkney, Nesty, Wiley and Marvel^{4a} was used. In a 2-liter three-necked flask were placed a solution of 40 g. (1.0 mole) of potassium in 400 ml. of *t*-amyl alcohol and 800 ml. of anhydrous ether. The solution was cooled to -15° and saturated with acetylene. To the stirred solution was added dropwise over ten to twelve hours 300 g. (3.0 moles) of cyclohexanone during which time a rapid stream of acetylene was passed through the reaction mixture which was kept at -15° . The solution was stirred for six hours after the addition of all of the cyclohexanone and the acetylene shut off. The reaction mixture was poured into 90 ml. of concentrated hydrochloric acid and 200 g. of ice. The acetylenic alcohol was extracted from the water with ether and fractionated, after removing the unreacted ketone with sodium bisulfite solution. The pure product, b. p. $77-78^{\circ}$ (17 mm.), n_D^{25} 1.4790, weighed 260 g. (2.1 moles, 69% based on the ketone used).

Preparation of 1-(3-Hydroxy-3-methyl-1-heptynyl)-cyclohexanol.—To the Grignard solution prepared from 79 g. (3.30 gram atoms) of magnesium and 380 g. (3.48 moles) of ethyl bromide in 1.5 liters of anhydrous ether was added with stirring 186 g. (1.50 moles) of 1-ethynylcyclohexanol. The addition was carried out as rapidly as possible without loss of ether and after all the acetylenic

(15) Clemmensen, *Ber*, **46**, 1837 (1913).

alcohol had been added the solution was stirred for one hour at room temperature. To the stirred solution was then added 165 g. (1.65 moles) of 2-hexanone and the mixture stirred for two hours. The reaction mixture was poured into 600 g. of ice to which had been added 150 ml. of concentrated hydrochloric acid. The organic layer was separated and the water layer extracted twice with ether. The ether solution was dried over magnesium sulfate, the ether removed and the product fractionated through a modified Widmer column under reduced pressure. The glycol boiled at 124–126° (1 mm.) and did not crystallize on standing. The yields in two runs were 214 g. (61%) and 207 g. (59%), respectively. Some dehydration during distillation evidently occurred because the analysis was high in carbon.

Anal. Calcd. for $C_{14}H_{24}O_2$: C, 75.00; H, 10.71. Found: C, 75.43; H, 10.76.

Dehydration of 1-(3-Hydroxy-3-methyl-1-heptynyl)-cyclohexanol.—Two hundred and seven grams of the glycol was heated to 190–200° with 20 g. of anhydrous potassium bisulfate for thirty minutes. Most of the water which was produced in the dehydration distilled out as it was produced and the remainder was removed under reduced pressure. The residue was fractionated through a Widmer column under reduced pressure. The 1-(3-methyl-3-hepten-1-ynyl)-cyclohexene boiled at 143–148° (21 mm.) and amounted to 154 g. (89%). On standing in the air this hydrocarbon rapidly absorbed oxygen, which accounts for the poor analysis.

Anal. Calcd. for $C_{14}H_{20}$: C, 89.36; H, 10.64. Found: C, 88.14; H, 10.97.

Cyclization of 1-(3-Methyl-3-hepten-1-ynyl)-cyclohexene.—A mixture of 131 g. (0.7 mole) of the dienyne and 900 ml. of 87% formic acid was refluxed for thirty hours. The dark colored mixture was diluted to 2 liters with water and 100 g. of sodium carbonate added to partly neutralize the formic acid. The organic layer was separated and the water layer extracted with ether in portions until the ether no longer became colored. The ether solution was neutralized with sodium bicarbonate and after removal of the ether the product was fractionated under reduced pressure. The first fraction consisted of the dienyne, b. p. 90–93° (1 mm.), and amounted to 15 g. The ketone distilled at 107–108° (1 mm.). The yield after refractionation was 48 g. (38% based on the dienyne not recovered); n_D^{25} 1.5022.

Anal. Calcd. for $C_{14}H_{22}O$: C, 81.55; H, 10.63. Found: C, 80.77, 80.60; H, 10.75, 10.64.

The 2,4-dinitrophenylhydrazone, prepared according to the method of Brady,¹⁶ melted at 124–125°.

Anal. Calcd. for $C_{20}H_{26}O_4N_4$: C, 62.18; H, 6.73. Found: C, 61.95; H, 6.85.

Clemmensen Reduction of *trans*-3-Methyl-4-propyl-1,2,4a,5,6,7,8,8a-octahydro-1-naphthalenone.—To a solution of 15 g. of the ketone in 250 ml. of acetic acid were added 100 g. of amalgamated zinc and 90 ml. of 18% hydrochloric acid. The mixture was refluxed one hour and then 60 ml. of concentrated hydrochloric acid added in the course of two hours. The solution was refluxed for twelve hours longer. The organic material was extracted

with ether. Fractionation of the ether extract gave 9 g. of hydrocarbon boiling at 115–120° (14 mm.).

Anal. Calcd. for $C_{14}H_{24}$: C, 87.50; H, 12.50. Found: C, 87.20; H, 12.49.

Platinum-Charcoal Dehydrogenation of the Clemmensen Reduction Product.—Four grams of the product from the Clemmensen reduction was passed over platinum-charcoal dehydrogenation catalyst⁸ at 300–320°. After repeated passage of the compound over the catalyst until evolution of hydrogen ceased, the product was washed from the dehydrogenation apparatus and subjected to fractional distillation. The lower boiling portion consisted of 0.66 g. of material boiling at 123–128° (20 mm.). An intermediate fraction amounting to 0.32 g. boiling at 128° (20 mm.) to 111° (2 mm.) was colored blue. The fraction boiling at 111–125° (2 mm.) was very dark blue and amounted to 0.75 g. (19% of the theoretical). A brown residue remained.

Azulene Test.—Three drops of the Clemmensen reduction product was dissolved in 10 ml. of acetic acid and enough bromine added to make the solution faintly yellow. After standing for two hours, an intense blue color developed, indicating the presence of a hydroazulene in the reduction product. The blue color was destroyed by allowing the sample to stand in the air for several days.

A similar positive test for azulenes was obtained when the mixture of hydrocarbons obtained in the dehydrogenation was treated with bromine in acetic acid.

Selenium Dehydrogenation of the Clemmensen Reduction Product.—Four grams of the hydrocarbon was heated with 20 g. of powdered selenium under an air condenser for twenty-eight hours at 390–400°. After this time the evolution of hydrogen selenide became slow. The organic material was removed by extraction with ether. After distillation the product, which boiled at 115–123° (17 mm.), amounted to 2.1 g. No attempt was made to fractionate the material, but comparison of the ultraviolet absorption spectrum with *trans-as*-octahydrophenanthrene⁵ indicated that the mixture contained about 35–40% of this compound.

In another run the hydrocarbon (15 g.) was heated with selenium (30 g.) for forty-two hours at 390–400°. The product was blue and analyzed for a hydrocarbon.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.50; H, 12.50. Calcd. for $C_{14}H_{18}$: C, 90.32; H, 9.68. Found: C, 88.69; H, 11.41.

Ultraviolet Absorption Spectra.—The spectra were taken with a Bausch and Lomb ultraviolet spectrograph. A hydrogen discharge tube operating on 15,000 volts gave a continuous ultraviolet source and the H_{α} , H_{β} , and H_{γ} lines served to calibrate the wave length scale of the spectrograph. The pictures were taken with a slit opening $60\mu \times 5$ mm. and a 1.0 cm. quartz cell. Eastman double coated orthochromatic plates were used with a three-minute exposure. The absorption coefficient was determined by comparison with the blackness of a trace due to a 10^{-4} molar solution of naphthalene. The concentrations used were varied from 10^{-2} to 10^{-5} for each sample. Alcohol was used as the solvent.

Ozonization of 3-Methyl-4-propyl-1,2,4a,5,6,7,8,8a-octahydronaphthalen-1-one.—Two ozonolysis reactions were carried out using 10-g. samples of the ketone in carbon

(16) Brady, *J. Chem. Soc.*, 756 (1931).

tetrachloride solution. In the first the reaction was interrupted after six hours and, in the second, after twelve and a half hours. Both gave acidic fractions boiling from 90–180° (1 mm.), but no pure product was isolated. The boiling point changed continuously. The ozonization was not complete in either case. The acidic fraction amounted to 2.1 g. boiling below 100° (1 mm.) and 3.2 g. boiling from 100–180° (1 mm.) with some residue, when the ozonization was carried out for twelve and a half hours. The acid fraction gave no 2,4-dinitrophenylhydrazone.

Preparation of Δ^{11} -Dodecahydro-9-phenanthrene.—This ketone was prepared by the formic acid cyclization of dicyclohexenylacetylene.^{4a} The ketone was fractionated to give a fraction boiling at 135–136° (2 mm.) with the refractive index n_D^{20} 1.5296. The refractive index of the sample did not vary during distillation.

Hydrogenation of Δ^{11} -Dodecahydro-9-phenanthrene to Tetradehydro-9-phenanthrol.—A solution of 22.2 g. of the ketone in 120 ml. of ethyl alcohol was hydrogenated at 185° under a pressure of 100–200 atmospheres of hydrogen using Raney nickel¹⁰ as the catalyst. Four hours were required for complete reduction to the saturated alcohol. The product from the hydrogenation was filtered and the solvent distilled. The residue was fractionally distilled through a modified Widmer column. The portion boiling at 136–138° (2 mm.) solidified to a waxy solid on standing for a few hours. The product did not give a sharp melting point and it has not been possible to purify it by recrystallization. The wide melting range indicates that the tetradehydro-9-phenanthrol is a mixture of *cis-trans* isomers.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.77; H, 11.54. Found: C, 80.87; H, 11.38.

Δ^{11} -Dodecahydrophenanthrene.—The reduction of Δ^{11} -dodecahydro-9-phenanthrene to the corresponding un-

saturated hydrocarbon was carried out by the method of Clemmensen¹⁵ in the manner previously described.^{4a}

Dehydrogenation of Δ^{11} -Dodecahydrophenanthrene.—Four and two-tenths grams of Δ^{11} -dodecahydrophenanthrene was passed repeatedly over platinum-charcoal catalyst⁹ until the material was solid. The dehydrogenation product was removed from the apparatus with acetone and filtered. On recrystallization of the solid, after evaporation of the acetone, phenanthrene separated. The non-crystalline portion which remained in the solvent was recovered and again dehydrogenated and the product recrystallized. The phenanthrene amounted to 2.3 g. and melted at 97–98°. No other dehydrogenation product was isolated.

Anal. Calcd. for $C_{14}H_{10}$: C, 94.38; H, 5.62. Found: C, 94.20; H, 5.90.

Summary

1. Evidence has been presented to show that the cyclization of di- Δ^{11} -cyclohexenylacetylene yields Δ^{11} -dodecahydro-9-phenanthrene and not a spiran derivative.

2. Further evidence to support the view that cyclization of dienes produces ring systems with the *trans*-configuration has been described.

3. Clemmensen reduction of *trans*-3-methyl-4-propyl-1,2,4a,5,6,7,8,8a-octahydro-1-naphthalenone has been found to cause a partial rearrangement of the carbon skeleton to a seven-five fused ring system which yields azulene derivatives on dehydrogenation.

URBANA, ILLINOIS

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

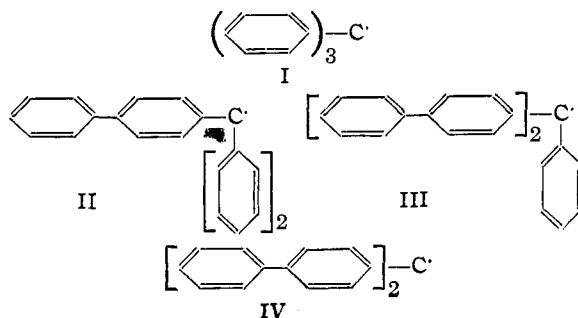
Effect of Substitution on the Dissociation of Hexaarylethanes. VII.¹ Meta and Para Phenyl Groups

By C. S. MARVEL, MAX B. MUELLER AND EMANUEL GINSBERG

A comparison of the degree of dissociation of hexaarylethanes which have phenyl groups substituted for hydrogen atoms in the meta and para positions with respect to their attachment to the ethane carbon atoms is of considerable interest in testing the resonance theory of dissociation of hexaarylethanes.²

It has been pointed out previously² that in triphenylmethyl (I) the odd electron can resonate among ten positions, in diphenyl-*p*-biphenyl-

methyl (II), among thirteen positions, in di-*p*-biphenylmethyl (III), among sixteen positions and in tri-*p*-biphenylmethyl (IV) among nineteen positions.



(1) For the sixth communication in this series see THIS JOURNAL, 61, 77 (1939).

(2) Pauling and Wheland, *J. Chem. Phys.*, 1, 362 (1933); 2, 482 (1934); Wheland, *ibid.*, 2, 474 (1934); Hückel, *Trans. Faraday Soc.*, 30, 40 (1934); see also Gilman, "Organic Chemistry," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1938, p. 1850.