solution was evaporated to a sirup under reduced pressure and dried by repeated distillation from methanol solution to an amorphous solid; yield 6.7 g. This material was acetylated by heating at the boiling point with 3.5 g. of fused sodium acetate and 50 ml. of acetic anhydride. The reaction mixture was then cooled and poured into 300 ml. of ice and water. After the destruction of the acetic anhydride, the mixture was extracted with chloroform, the chloroform solution was washed with water, dried with anhydrous sodium sulfate and evaporated to a sirup under reduced pressure. The five-gram portions of this sirup were chromatographed by placing each on a column (250 × 80 mm., diam.) of Magnesol[9]:Celite[9,12] (5:1 by wt.) and developing with 3500 ml. of benzene:*t*-butyl alcohol (100:1 by vol.). Zones near the middle of the columns produced β-isomaltose octaacetate; yield 1.03 g., m.p. 139–141°, $[\alpha]^{25}\text{D}$ +96.4° (*c* 4, chloroform); after one recrystallization from ethanol, m.p. 145–146°, mixed melting point with an authentic sample of β-isomaltose octaacetate unchanged, $[\alpha]^{25}\text{D}$ +98.4°; yield of crude product based on a quantity of starting material equivalent to 50 g. of D-glucose, 1890 mg. No trace of β-gentiobiose octaacetate could be found.

Reversion Reaction of D-Glucose.—A series of four solutions of D-glucose (concentrations 0.4, 2.0, 5.0, and 10.0%) in 0.082 *N* HCl were heated for 10 hr. in a boiling water-bath, the solution temperature being maintained at 97°. In each case the quantity of D-glucose was 50 g., except the first, in which only 36 g. was used because of the large volume involved. After cooling, the acid was removed from the solutions by means of a Duolite A-4[10] column. Gentiobiose (zone 35–70 mm. from column top) and isomaltose (zone 90–150 mm. from column top) were then isolated as their β-octaacetates from the solutions by the procedure outlined above; all samples of β-gentiobiose octaacetate, m.p. 187 ± 2°, mixed m.p. with authentic sample unchanged, $[\alpha]^{25}\text{D}$ −4.5 ± 0.1° (*c* 2.5, chloroform) where yield was adequate for determination; all samples of β-isomaltose octaacetate, m.p. 144 ± 2°, mixed m.p. with authentic sample unchanged, $[\alpha]^{25}\text{D}$ +86.5 ± 0.5° (*c* 3.0, chloroform) where yield was adequate for determination. Upon further purification of β-isomaltose octaacetate the constants were: m.p. 145–146° $[\alpha]^{25}\text{D}$ +97.1° (*c* 3.0, chloroform). The quantities of each are recorded in Fig. 1.

COLUMBUS 10, OHIO

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

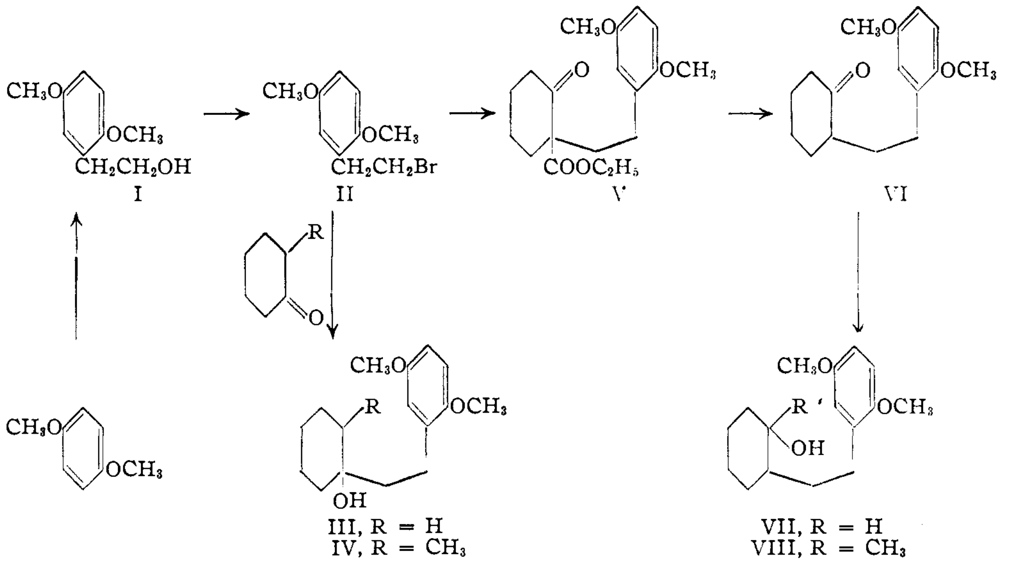
Synthesis of Phenanthrenes. V. A Mechanism for the Cyclization of β-Arylethylcyclohexanols[1]

BY RODERICK A. BARNES

RECEIVED NOVEMBER 22, 1952

The cyclization of four new β-arylethylcyclohexanols has been carried out in order to obtain further information bearing on the mechanism of the reaction. The results obtained fron this study together with previous observations has made it desirable to formulate a reaction path in which a bridged ion is an important intermediate.

When a given β-arylethylcyclohexanol is to be cyclized it would be desirable if a prediction could be made concerning the amounts of spirane and phenanthrene to be expected. Some generalizations could be made from previous experimental results in our own and other laboratories; however, it was difficult to formulate a mechanism which explained all the facts.



The purpose of this work was to study the cyclization of four new alcohols which were chosen in an attempt to decide between the two mechanisms which were originally considered most likely. The four alcohols were synthesized from β-(2,5-dimethoxyphenyl)-ethyl bromide (II) which in turn was prepared from hydroquinone dimethyl ether.

Bromide II was rather unstable and hydrogen bromide was eliminated to some extent even during vacuum distillation; however, satisfactory yields of the desired alcohols could be obtained.

Each of the alcohols (III, IV, VII and VIII) was cyclized with a mixture of 85% phosphoric acid and phosphorus pentoxide. The yield of crystalline

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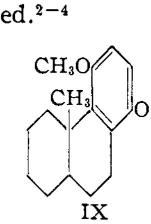
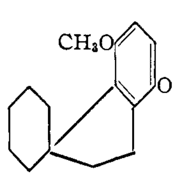
[1] Presented at the 121st Meeting of the A.C.S., Buffalo, New York, March 26, 1952.

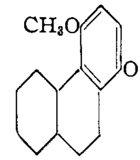
cyclization product from pure secondary alcohol VII was 95%; the yields from the unpurified tertiary alcohols (III, IV and VIII) were lower (60–80%). Both alcohols IV and VIII produced the same cyclization product, 5,8-dimethoxy-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (IX) which was isolated in only one stereoisomeric modification as in similar cyclizations previously reported.[2-4]



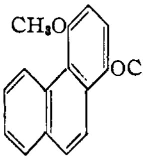
IX



X



XI



XII

Alcohol III produced spirane X as the major product but alcohol VII yielded a mixture of products which could not be separated by fractional crystallization or chromatography on alumina. Dehydrogenation of this mixture produced spirane X (which does not dehydrogenate under the experimental conditions used) and 1,4-dimethoxyphenanthrene (XII). From this result it follows that the mixture before dehydrogenation consisted of spirane X and phenanthrene XI. This was confirmed by comparing the infrared curve of the mixture with the curves for pure X and XI.

A cyclization carried out using alcohol III which had been distilled (and hence largely dehydrated) and phosphorus pentoxide alone at 160° produced mainly XI in one stereoisomeric form.

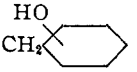
In considering possible mechanisms to explain these and previously observed cyclizations[2-5] the following generalizations must be taken into account.

(1) The cyclization of alcohols similar to IV or VIII (R = CH_3) produces a phenanthrene as the major product.

(2) Alcohols (or corresponding olefins) similar to III and VII yield mixtures of spirane and phenanthrene under usual low temperature cyclization conditions.[5-7]

TABLE I

CYCLIZATION OF ARYL-CH_2CH_2



Aryl group	Yield of spirane, %	Ref.
Phenyl	4	6
p-Methoxyphenyl	(Low)	*a*
4-Hydrindenyl	59	5
m-Methoxyphenyl	69	7
2,5-Dimethoxyphenyl	56	*a*

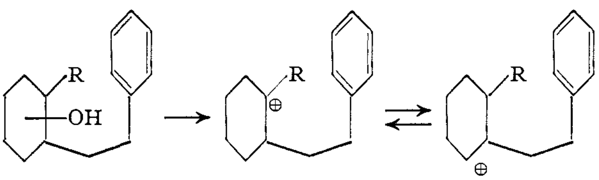
[a] This paper.

(3) The yields of spirane vary depending on the reactivity of the aromatic nucleus at the cyclization position (Table I).

(4) The cyclizations leading to phenanthrenes with an angular methyl group produce one of the two possible stereoisomers as the major product.[2-4,8]

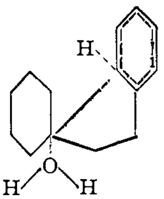
(5) The particular stereoisomer formed by cyclization of an alcohol having an unreactive aromatic nucleus (*o*-chlorophenyl) is not the same as that obtained from the corresponding alcohol having a more reactive nucleus (phenyl).[4]

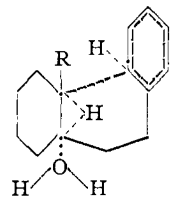
The mechanism first considered[5] involved the formation of a carbonium ion as the intermediate actually reacting with the aromatic nucleus.



This mechanism fails to indicate how the reactivity of the aromatic nucleus can influence the yield of spirane (R = H) or determine which stereoisomer of the phenanthrene (R = CH_3) is formed.

The second possible mechanism was visualized as a concerted process in which the bond with the aromatic ring was formed as the hydroxyl–carbon bond was being broken.





As indicated this kind of process would in some cases also require simultaneous migration of a hydrogen atom. The fact that alcohols IV and VIII (and all other pairs in which R = CH_3 so far examined) both produce the same stereoisomer is contrary to the prediction of the mechanism.

Since both alcohol IV and VIII are prepared by reaction of a Grignard reagent with a 2-alkylcyclohexanone they should have the same stereochemical configuration. It is likely that the entering alkyl group approaches the carbonyl group so that the two alkyl substituents are *trans;* the extent to which this is true will depend somewhat on the size of the groups.[9]

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[2] R. A. Barnes and R. T. Gottesman, THIS JOURNAL, **74**, 35 (1952).

[3] R. A. Barnes, H. P. Hirschler and B. R. Bluestein, *ibid.*, **74**, 4091 (1952).

[4] R. A. Barnes and M. D. Konort, *ibid.*, **75**, 303 (1953).

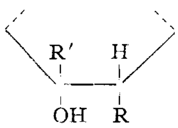
[5] R. A. Barnes and L. Gordon, *ibid.*, **71**, 2644 (1949).

[6] D. Perlman, D. Davidson and M. T. Bogert, *J. Org. Chem.*, **1**, 288, 300 (1936).

[7] J. W. Cook, C. L. Hewett and A. M. Robinson, *J. Chem. Soc.*, 168 (1939).

[8] W. B. Renfrow, A. Renfrow, E. Shoun and C. A. Sears, THIS JOURNAL, **73**, 317 (1951), have carried out a cyclization with anhydrous hydrogen fluoride and obtained at least two (and perhaps more) of the four stereoisomers possible in this example. It is possible that the reaction takes a somewhat different course with this reagent than with sulfuric or phosphoric acid.

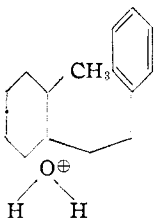
[9] As an example, ethylmagnesium bromide has been found to react with 2-ethylcyclopentanone to yield only *trans*-1,2-diethyl-1-cyclopentanol; see G. Chiurdoglu, *Bull. soc. chim. Belg.*, **42**, 347 (1933); *ibid.*, **44**, 527 (1935).



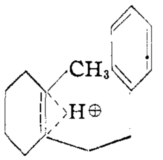
IV, R = CH_3, R' = $CH_2CH_2C_6H_3(OCH_3)_2$
VIII, R = $CH_2CH_2C_6H_3(OCH_3)_2$, R' = CH_3

If the structures for IV and VIII are correct the second mechanism would predict that IV should yield the *cis*-octahydrophenanthrene and VIII the *trans* isomer.

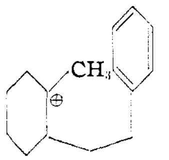
It is now believed that there are three possible intermediates which can be formed under appropriate conditions of acidity and temperature.



XIII



XIV



XV

It is also suggested that bridged ion XIV is of appreciably lower energy than the free carbonium ion XV.[10]

Under mild conditions XIII is present to the exclusion of XIV and XV, but only aryl groups having *extremely reactive* nuclear positions will cyclize. If the aromatic nucleus is *moderately* reactive conditions have to be such that XIV is formed before cyclization can occur. Finally with *unreactive* aryl groups the higher energy carbonium ion must be formed to some extent in order for cyclization to take place.

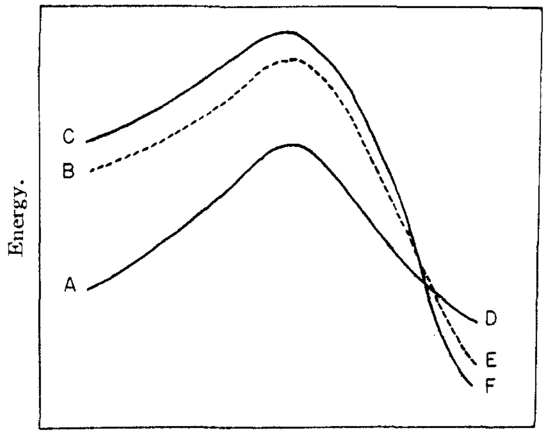
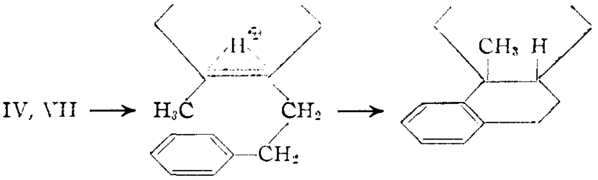


Fig. 1.—A, oxonium ion; B, bridged ion; C. carbonium ion; D. spirane; E, *cis*-octahydrophenanthrene; F, *trans*-octahydrophenanthrene.

Figure 1 illustrates the reaction of the three intermediates each with an aryl group of the appropriate degree of reactivity.

The aromatic nucleus of alcohols IV and VIII is considered to be moderately reactive so that the cyclization intermediate is a bridged ion which leads to the *cis*-octahydrophenanthrene.



This is also believed to be the main reaction path for all other cyclizations so far studied in which R = CH_3, except the example in which the aryl group is *o*-chlorophenyl.[4] In this latter case the free carbonium ion is believed to be the intermediate which yields the *trans*-octahydrophenanthrene.

The planar carbonium ion might form either isomer; however, it would be expected that the frequency with which the aromatic nucleus approached the carbonium ion from one side would be different from the frequency of approach to the opposite side. Depending on the steric factors this difference in rates of reaction could be sufficiently great so that essentially a single isomer would result.

Cyclizations in which R = H may proceed through four intermediates: oxonium ion, bridged ion, tertiary carbonium ion and secondary carbonium ion.[11] Although there is less data available, the existing experimental evidence fits into the general mechanistic scheme which has been proposed if one modification is made. It is suggested that the bridged ion in these cases (bridge between a secondary and tertiary carbon) is intermediate in energy with respect to the free tertiary and secondary carbonium ions.[12]

Thus when the aryl group is moderately reactive (phenyl) cyclization proceeds mainly through the bridged ion to yield the *cis*-octahydrophenanthrene and when the aryl group is more reactive (*m*-methoxyphenyl) the cyclization proceeds largely *via* the tertiary carbonium ion to yield a spirane (Table I).

The cyclization (low temperature) of alcohols III and VII probably involves the formation of the tertiary carbonium ion as the main intermediate. The difference between the two cases indicates that the oxonium ions must participate in the cyclization (the other intermediates are the same for both alcohols). In the higher temperature cyclization of the olefin from III it is likely that enough energy is supplied to form the bridged ion or perhaps the secondary carbonium ion before cyclization can occur. A decision as to which of these intermediates is involved cannot be made until it is determined whether the resulting octahydrophenanthrene XI is the *cis* or *trans* isomer.

This latter experiment suggests that it may be

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(10) K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945), first introduced the idea of a protonated double bond. Later discussions of this kind of ion are by (a) M. J. S. Dewar, *Ann. Repts. on Progress Chem.*, (*Chem. Soc. London*), **48**, 118 (1951); (b) P. D. Bartlett, Twelfth National Organic Symposium of the American Chemical Society, June 1951, Denver, Colorado, and (c) D. J. Cram, THIS JOURNAL, **74**, 2137 (1952).

(11) When R = CH_3 there are actually two tertiary carbonium ions. These are believed to be in equilibrium and of about equal energy but one of them can be disregarded since it can react only to form the relatively higher energy (sterically strained) spirane. P. D. Bartlett, ref. 10b, has discussed a similar equilibrium between two tertiary carbonium ions.

(12) D. J. Cram, ref. 10c, has presented evidence that in the E_1 reactions of the *p*-toluenesulfonates of the isomeric 3-phenyl-2-butanols there is rearrangement to the tertiary carbonium ion. His suggestion that a hydrogen-bridged ion is intermediate in this process is essentially the equivalent of the above statement.

possible to control the stereochemistry of other octahydrophenanthrenes from such cyclizations by proper choice of experimental conditions.

Acknowledgment.—The author wishes to thank the Research Corporation and the Rutgers University Research Council for financial assistance during this investigation.

Experimental[13]

β-(2,5-Dimethoxyphenyl)-ethanol.[14]—*n*-Butyllithium was prepared from lithium (28 g.) and *n*-butyl chloride (180 g.) in dry ether (350 ml.). A solution of hydroquinone dimethyl ether (205 g.) in dry ether (776 ml.) was added in one portion and the solution allowed to stand for 15 hours. The reaction mixture was maintained at 0° while ethylene oxide (130 g.) was passed in as a gas during 3 hours. After standing overnight the reaction mixture was poured into ice-water (2 liters). The organic layer was separated, dried and fractionated. There was obtained 182 g. (68%) of product which boiled at 130–142° at 0.7 mm., $n^{25}\text{D}$ 1.5402.

Anal. Calcd. for $C_{10}H_{14}O_3$: C, 65.91; H, 7.74. Found: C, 65.79; H, 7.69.

This alcohol formed *p*-nitrobenzoate which melted at 73–74°.

Anal. Calcd. for $C_{17}H_{17}O_6N$: C, 61.62; H, 5.18. Found: C, 61.65; H, 5.25.

From the distillation residue (20 g.) 6 g. of a crystalline by-product, m.p. 134–135°, was isolated.

β-(2,5-Dimethoxyphenyl)-ethyl Bromide (II).[14]—A solution of I (66 g.) in benzene (65 ml.) was stirred and cooled in an ice-bath while phosphorus tribromide (30 g.) in benzene (50 ml.) was added dropwise. The solution was kept at 0–5° for two hours and then at 60° for four hours. Ice-water was added to the cool reaction mixture and the organic layer was separated. The benzene solution of crude bromide was washed with ice-cold 5% sodium hydroxide solution, water and dilute hydrochloric acid. Acidification of the sodium hydroxide extract yielded about 20 g. of an oil containing phenolic by-products. The benzene solution was concentrated and the residual crude bromide distilled rather quickly at a low pressure and temperature. There was obtained 48 g. (54%) of II which boiled at 97–110° (0.25 mm.), $n^{24}\text{D}$ 1.5542. There is decomposition of this bromide with distillation and in three separate attempts an analytically pure sample could not be prepared, some loss of hydrogen bromide took place even with evaporative distillation.

Anal. Calcd. for $C_{10}H_{13}O_2Br$: C, 49.00; H, 5.34. Found: C, 51.55, 50.37, 50.09; H, 5.50, 5.59, 5.44.

Ethyl 2-Keto-1-β-(2′,5′-dimethoxyphenyl)-ethylcyclohexane-1-carboxylate (V).—This substance was prepared by a previously described procedure[15] from β-(2,5-dimethoxyphenyl)-ethyl bromide (101.5 g.), ethyl 2-ketocyclohexane-1-carboxylate (94 g.) and potassium (16.6 g.). There was obtained 99 g. (71.5%) of crude product. A portion of this was evaporatively distilled at 0.04 mm. (temp. 150°). The distillate had $n^{26}\text{D}$ 1.5190.

Anal. Calcd. for $C_{19}H_{26}O_5$: C, 68.20; H, 7.80. Found: C, 68.06; H, 7.69.

The 2,4-dinitrophenylhydrazone of this ketoester melted at 131–132° after recrystallization from ethanol.

Anal. Calcd. for $C_{25}H_{30}O_8N_4$: C, 58.35; H, 5.88. Found: C, 58.32; H, 5.89.

2-β-(2′,5′-Dimethoxyphenyl)-ethylcyclohexanone (VI).—The crude ester (25 g.) from the preceding experiment was refluxed for 48 hours with a solution of barium hydroxide (105 g.) in water (735 ml.). The reaction mixture was acidified with 70 ml. of hydrochloric acid and acetic acid (15 ml.) and heated to boiling. It was then extracted with ether. By washing the ether layer with sodium bicarbonate solution the acidic cleavage product (4 g.) was removed; this substance melted at 91–93° but was not further investigated. Evaporation of the ether left the crude ketone which was distilled at 0.20 mm., b.p. 130–140°, $n^{23}\text{D}$ 1.5326, yield 12.6 g. (64%).

Anal. Calcd. for $C_{16}H_{22}O_3$: C, 73.25; H, 8.45. Found: C, 73.12; H, 8.56.

This product formed a semicarbazone which melted at 187–189°.

Anal. Calcd. for $C_{17}H_{25}O_3N_3$: C, 63.92; H, 7.89. Found: C, 63.91; H, 7.89.

2-β-(2′,5′-Dimethoxyphenyl)-ethylcyclohexanol (**VII**).—Powdered lithium aluminum hydride (1 g.) was stirred overnight in anhydrous ether (100 ml.). Then a solution of ketone VI (10 g.) in dry ether (25 ml.) was added dropwise. The mixture was allowed to stand two days with occasional stirring and finally decomposed with cold 20% sodium hydroxide solution. The crude alcohol was purified by evaporative distillation at 140° (0.10 ml.), $n^{25}\text{D}$ 1.5350.

Anal. Calcd. for $C_{16}H_{24}O_3$: C, 72.69; H, 9.15. Found: C, 72.85; H, 9.02.

The infrared curve for VII showed no carbonyl absorption band (ketone VI absorbed strongly at 5.82 μ) indicating that the reduction was complete.

Tertiary Alcohols III, IV and VIII.—These alcohols were prepared by interaction of the appropriate Grignard reagent and ketone.

Alcohol III.—The Grignard reagent prepared from bromide II (12.5 g.), magnesium (1.5 g.) and dry ether (100 ml.) was treated with cyclohexanone (5 g.) at 0°.

Alcohol IV.—The Grignard reagent from bromide II (30 g.), magnesium (3.7 g.) and dry ether (200 ml.) was treated with 2-methylcyclohexanone (13.7 g.).

Alcohol VIII.—Ketone VI (11.5 g.) was added to a solution of methylmagnesium iodide prepared from methyl iodide (13 g.), magnesium (1.9 g.) and dry ether (100 ml.).

An attempt to purify III by evaporative distillation at 100–125° (0.2 mm.) yielded 7.4 g. of a liquid ($n^{24}\text{D}$ 1.5390) which reacted rapidly with a solution of potassium permanganate in acetone (60% yield assuming the product to be pure olefin). No attempt was made to purify the other alcohols except to remove impurities which were volatile at 70° and 0.10 mm.

Cyclizations.—The crude undistilled alcohols were mixed with 85% phosphoric acid (5 ml. per g. of alcohol) and stirred at room temperature for one hour, then phosphorus pentoxide (half of the weight of phosphoric acid used) was added in four equal portions at 20-minute intervals. Finally the reaction mixture was stirred and heated at 85–95° for one hour. The cold reaction mixture was poured onto ice and the product extracted with ether.

From alcohol III (27 g., undistilled) there was obtained 14 g. (56%) of cyclization product X which boiled at 116–120° (0.10 mm.) and melted at 93–107°. Four recrystallizations from absolute ethanol raised the melting point to 113–114°.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.20; H, 8.89.

From alcohol IV (13 g.) there was obtained 7.9 g. (57%) of cyclization product IX which boiled at 108–120° (0.02 mm.) and melted at 56–57.6°. After recrystallization from methanol the pure substance melted at 58–59°.

Anal. Calcd. for $C_{17}H_{24}O_2$: C, 78.42; H, 9.29. Found: C, 78.38; H, 9.27.

From alcohols VII (9 g.) there was obtained 7.9 g. (95%) of crystalline cyclization product which melted at *ca.* 75–85°. After four recrystallizations the melting point was 87–100° but additional recrystallizations did not further improve it. The mixture was chromatographed on alumina using petroleum ether as the eluant but no separation was effected by this procedure.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 78.19; H, 8.71.

From alcohol VIII (12 g.) there was obtained 9.2 g. (81%) of crystalline material which melted at 58–60° after one recrystallization from ethanol. The melting point of a mixture of this substance and the cyclization product from alcohol IV was 58–59.6°.

The olefinic product (7.3 g.) from distillation of alcohol III was mixed with phosphorus pentoxide (10 g.) and heated in a bath to 160°. After 10 minutes at this temperature the reaction mixture was cooled and ethanol (20 ml.) was added. The resulting mixture was refluxed for 30 minutes and then processed as for the other cyclizations. The oily product (4.2 g.) was evaporatively distilled at 100–125° (0.10 mm.) to yield 1.5 g. of volatile material and a poly-

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(13) All melting points are corrected.

(14) Experiment carried out by Doris E. Barnes.

(15) R. A. Barnes, H. P. Hirschler and B. R. Bluestein, THIS JOURNAL, **74**, 32 (1952).

meric residue. The distillate crystallized almost completely on standing and after three recrystallizations melted at 103–104°.

Anal. Calcd. for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00; CH_3O, 25.20. Found: C, 77.87; H, 8.92; CH_3O, 25.09.

One stereoisomer of 5,8-dimethoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (XI) has been previously prepared and reported to melt at 106–107°.[16]

The infrared curves[17] for each cyclization product were compared and found to differ in the region 7–11μ. All of the principal bands of the mixture from cyclization of alcohol VII could be assigned to either spirane X or phenanthrene XI.[18]

Dehydrogenations.—A mixture of the cyclization product (500 mg.), diphenylamine (2 g.) and palladium on charcoal (100 mg., 5%) was heated at 300–315° for six hours while a current of carbon dioxide was passed through the dehydrogenator.[19] The product was washed out with ether, the catalyst filtered and dry hydrogen chloride passed in to precipitate diphenylamine hydrochloride. The ether was evaporated and the crude dehydrogenation product placed on a column of acid-washed alumina (*ca.* 30 g.) with ligroin. Elution with 5% benzene in petroleum ether (80 ml.) removed any starting material and pure benzene (80 ml.) washed out the dehydrogenation product.

Cyclization product X (m.p. 112–113°, from alcohol III) was recovered unchanged in 85% yield.

Cyclization product IX (m.p. 58–59° from alcohols IV and VIII) produced 1,4-dimethoxyphenanthrene (XII) which melted at 123.5–124.5°.[16] Selenium at 360° also formed XII in good yield. The characteristic brown picrate melted at 164–166° in agreement with the reported value.[16]

Cyclization product XI (230 mg.) yielded 157 mg. of 1,4-dimethoxyphenanthrene (m.p. 124–125°) when the dehydrogenation was continued for three hours at 295–305°.

The mixture of product from the cyclization of VII was dehydrogenated to yield spirane X (*ca.* 300 mg.) and 1,4-dimethoxyphenanthrene (*ca.* 100 mg.).

β-(*p*-Methoxyphenyl)-ethyl Bromide.[20]—The procedure was the same as for bromide II. From β-(*p*-methoxyphenyl)-ethanol[21] (75 g., m.p. 24°) there was obtained 67 g. (63%) of bromide which boiled at 133–136° (11 mm.).[21]

1-β-(*p*-Methoxyphenyl)-ethyl-1-cyclohexanol.[20]—Freshly distilled cyclohexanone (6.9 g.) was added to the cold Grignard reagent prepared from magnesium (1.7 g.), dry ether (150 ml.) and β-(*p*-methoxyphenyl)-ethyl bromide (15 g.). When the addition was complete the reaction mixture was refluxed for one hour and then decomposed with ammonium chloride solution. Fractionation of the dried organic layer yielded 6.5 g. (42%) of product which boiled at 164–168° (1 mm.), m.p. 59–60°.

Anal. Calcd. for $C_{15}H_{22}O_2$: C, 76.88; H, 9.46. Found: C, 77.16; H, 9.62.

From the distillation residue there was isolated a crystalline substance believed to be 1,4-di-(*p*-methoxyphenyl)-butane which melted at 78–79° after recrystallization from petroleum ether.

Anal. Calcd. for $C_{18}H_{22}O_2$: C, 79.96; H, 8.20. Found: C, 79.52; H, 8.20.

6-Methoxy-1,2,3,4,4a,9,10,10a-octahydrophenanthrene.[20]—1-β-(*p*-Methoxyphenyl)-ethyl-1-cyclohexanol (5 g.) was treated with 83% sulfuric acid (25 ml.) at −5° for 20 minutes with stirring. The mixture was extracted with petroleum ether to yield 2.5 g. (50%) of cyclization product which boiled at 135–138° (1.5 mm.).

Anal. Calcd. for $C_{15}H_{12}O$: C, 83.28; H, 9.32. Found: C, 82.92; H, 9.05.

A sample of this product was dehydrogenated by using palladium on charcoal at 330° for three hours.[22] During the reaction some material sublimed onto the condenser. This proved to be mainly phenanthrene which melted at 98–100° after recrystallization from methanol and was identical with an authentic sample. From the liquid dehydrogenation product 3-methoxyphenanthrene (m.p. 58–59°) was isolated by forming the picrate (m.p. 125–127°)[23] which was decomposed with ether and dilute ammonia.

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[16] C. A. Grob, W. Jundt and H. Wicki, *Helv. Chim. Acta.* **32**, 2427 (1949).

[17] The infrared spectral measurements were made by Mr. Felix Borek using a Perkin–Elmer double beam model 21 recording spectrophotometer.

[18] Bands in microns for which the transmittance was less than 60% (5% solutions in chloroform): (X)—7.53, 7.60. 8.01. 9.08. 9.30. 9.64. 9.73, 10.37; (XI)—7.98, 8.82, 8.92, 9.23, 9.39: (mixture from alcohol VII)—7.55, 7.98, 8.82, 8.92, 9.08, 9.26, 9.37, 9.63, 9.73. 10.37.

[19] L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, pp. 462.

[20] Experiment carried out by L. Gordon.

[21] K. H. Slotta and H. Heller, *Ber.*, **63**, 3029 (1930).

[22] The aromatization of spiranes to phenanthrenes usually does not occur under these conditions; therefore this experiment is believed to indicate that the octahydrophenanthrene is the major cyclization product.

[23] R. Pschorr and A. Klein, *Ber.*, **34**, 4006 (1901), report the melting point of 3-methoxyphenanthrene as 59° and the melting point of the picrate as 124–125°.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MONTANA STATE UNIVERSITY]

Synthetic Estrogens. I. Derivatives of 1-Phenylphenanthrene

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A number of derivatives of 1-phenylphenanthrene have been prepared. A condensation between 6-methoxy-α-tetralone and anisalacetone was found to be a satisfactory reaction for preparing the hexa- and octahydro- derivatives of 1-phenylphenanthrene. Three of the four compounds tested showed activity in 1 mg. doses.

In view of the high estrogenic activity found by Stuart and co-workers for the four diastereomeric racemates of 2,4-di-(*p*-hydroxyphenyl)-3-ethylhexane[1] (I) it seemed of interest to determine whether hydroaromatic compounds analogous to I, such as II, would have similar activity.

The most convenient approach to II appeared to be the method developed by Rapson and Robinson[2] starting with 6-methoxy-α-tetralone and anisalacetone. The original conditions of the reaction produced only a trace of solid product. However, by adding dimethylamine to the reaction mixture, and by giving the anisalacetone a preliminary treatment with excess dimethylamine in order to form the unstable Mannich base, the yield of solid product was raised to 54%. This compound formed a red dinitrophenylhydrazone, and had an ultraviolet absorption spectrum similar to that of anisalacetone,[3] except for a secondary maximum at

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[1] A. H. Stuart, A. J. Shukis, R. C. Tallman, C. McCann and G. R. Treves, THIS JOURNAL, **68**, 729 (1946).

[2] W. S. Rapson and R. Robinson, *J. Chem. Soc.*, 1285 (1935).

[3] A. L. Wilds, L. W. Beck, W. J. Close, C. Djerassi, J. A. Johnson, T. L. Johnson and C. H. Shunk, THIS JOURNAL, **69**, 1985 (1947).