was washed with 2 *N* aqueous sodium carbonate and with water and was concentrated to a residue which crystallized from 95% ethanol to give the ester in 32% yield, m.p. 141–143°, m.p. 144–145° after a second crystallization.

Anal. Calcd. for $C_{20}H_{18}NO_5$: C, 69.2; H, 3.8; N, 4.0. Found: C, 69.4; H, 3.9; N, 4.0.

(c) **Rearrangement.**—A mixture of 0.079 g. of VIIIβ, 2 ml. of dry benzene, and 0.10 ml. of thionyl chloride was heated on the steam-bath under reflux until a drop of the reaction mixture gave no coloration with alcoholic ferric chloride (25 min.). Removal of solvent and excess thionyl chloride on the steam-bath under reduced pressure afforded 2-chloro-4-phenyltropone as an oil which was rearranged by refluxing with 2 ml. of 10% alcoholic potassium hydroxide for 10 min. on the steam-bath. Removal of ethanol under reduced pressure left material which was dissolved in 2 ml. of water and acidified with 6 *N* sulfuric acid. The filtered precipitate was crystallized from benzene to give 0.060 g. (77% of theory based on VIIIβ) of diphenyl-3-carboxylic acid, m.p. 164–165°. Recrystallization from benzene raised the m.p. to 165–166°. The reported melting points are 161–162°,[27a] and 162–164°.[27b]

Anal. Calcd. for $C_{13}H_{10}O_2$: C, 78.8; H, 5.1. Found: C, 79.1; H, 5.2.

γ-Phenyltropolone (VIIIγ). (a) **Hydrogenation.**—VIIIγ, 0.050 g., absorbed four molar equivalents of hydrogen when hydrogenated in 95% ethanol with platinum oxide catalyst. The residue crystallized after removal of catalyst and solvent. Recrystallization from cyclohexane gave **5-phenyl-1,2-cycloheptanediol** as flat, colorless needles, 0.034 g. (67%); m.p. 93–96°, m.p. 97–98° after two additional recrystallizations from cyclohexane.

Anal. Calcd. for $C_{13}H_{18}O_2$: C, 75.7; H, 8.8. Found: C, 75.6; H, 9.0.

(b) **VIIIγ *p*-Nitrobenzoate.**—This ester, obtained in 71% yield, m.p. 213–215°, was recrystallized from benzene as needles, m.p. 220–221°.

Anal. Calcd. for $C_{20}H_{13}NO_5$: C, 69.2; H, 3.8; N, 4.0. Found: C, 69.6; H, 4.1; N, 3.9.

(c) **γ-Phenyltropolone Methyl Ether.**—Treatment of 0.036 g. of VIIIγ with ethereal diazomethane, followed by evaporation, and crystallization of the residue from benzene, gave the ether as clusters of faintly yellow needles, 0.027 g., m.p. 140–141°. Sublimation at 100° and 4 mm., followed by recrystallization from benzene gave a practically colorless product, m.p. 141°.

Anal. Calcd. for $C_{14}H_{12}O_2$: C, 79.2; H, 5.7; OCH_3, 14.6. Found: C, 79.2; H, 5.5; OCH_3, 14.5.

(d) **2-Chloro-5-phenyltropone.**—A mixture of 0.079 g. of VIIIγ, 2 ml. of dry benzene and 0.10 ml. of thionyl chloride, treated as in the case of the β-isomer above, gave 2-chloro-5-phenyltropone as a yellow solid which crystallized from ethanol in long, light yellow needles, 0.071 g. (83%), m.p. 155–157°. Sublimation at 120–130° and 4 mm., followed by recrystallization from ethanol, raised the m.p. to 158°.

Anal. Calcd. for $C_{13}H_9ClO$: C, 72.1; H, 4.2; Cl, 16.4. Found: C, 72.3; H, 4.1; Cl, 16.3.

(e) **Rearrangement of 2-Chloro-5-phenyltropone with Hydroxide Ion.**—A mixture of 0.071 g. of 2-chloro-5-phenyltropone and 2 ml. of 10% alcoholic potassium hydroxide was rearranged as described above for the β-isomer to give diphenyl-4-carboxylic acid as a yellow precipitate in a yield of 0.057 g. (97%), m.p. 200–210°. Sublimation at 110° and 2 mm., followed by recrystallization from benzene, gave colorless needles; 0.039 g., m.p. 223–224°, m.p. 224.5–226° in admixture with an authentic sample,[28] m.p. 225–226°.

Anal. Calcd. for $C_{13}H_{10}O_2$: C, 78.8; H, 5.1. Found: C, 78.8; H, 5.0.

(27) (a) F. Mayer, *Ber.*, **46**, 2579 (1913); (b) D. H. Hey, *J. Chem. Soc.*, 1966 (1934).

(28) Kindly supplied by Professor Ernst Berliner, Bryn Mawr College, Bryn Mawr, Pa.

KATONAH, N. Y.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, RUTGERS UNIVERSITY]

Synthesis of Phenanthrenes. IV. 8-Chloro-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene

BY RODERICK A. BARNES AND MARK D. KONORT[1]

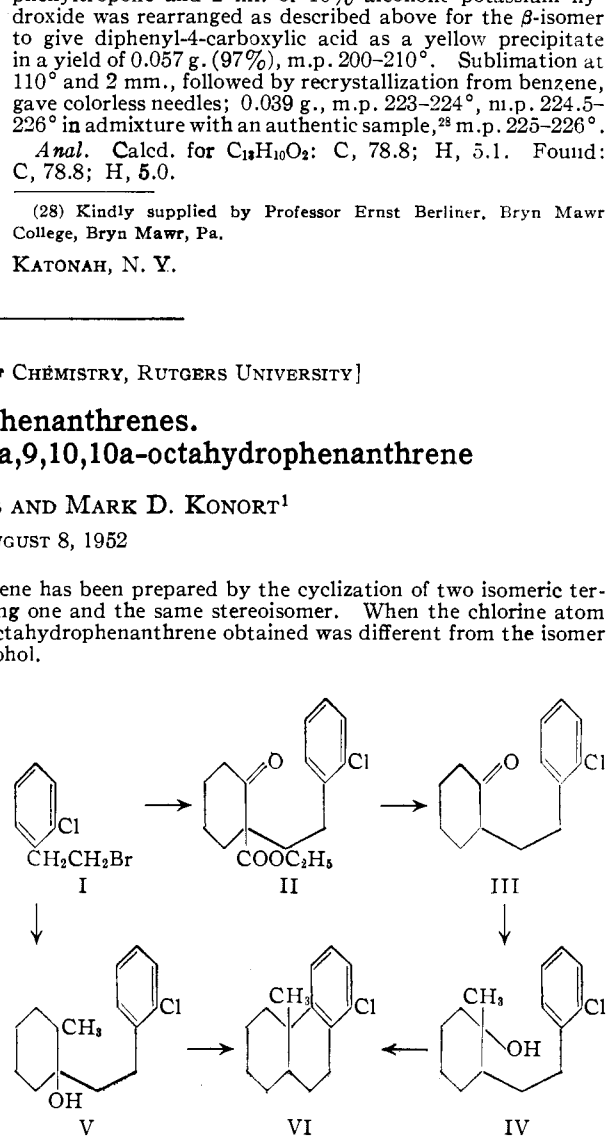
RECEIVED AUGUST 8, 1952

8-Chloro-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene has been prepared by the cyclization of two isomeric tertiary alcohols. Both cyclizations were stereospecific producing one and the same stereoisomer. When the chlorine atom was replaced by hydrogen the 4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene obtained was different from the isomer formed by direct cyclization of the unchlorinated tertiary alcohol.

Previous papers[2,3] have reported the preparation of octahydrophenanthrenes having substituents in both the 5- and 8-positions. The present work was initiated in order to make available an octahydrophenanthrene with a substituent at the 8-position which might be used for building toward a steroid ring system having no functional group in ring C.

Two procedures for preparing 8-chloro-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene were investigated.

A first attempt to prepare β-2-chlorophenylethyl bromide (I) was unsuccessful because the reaction of *o*-chlorophenylmagnesium iodide with ethylene oxide produced only 0–5% yields of the desired alcohol. The reaction of bromine with silver β-2-



(1) Abstracted from a thesis submitted by M. D. Konort to the Graduate Faculty of Rutgers University for the Ph.D. degree, June, 1952.

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

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

chlorophenyl propionate[4] produced I in yields of 60–70%.

The preparation of alcohol V, although a one-step process from I, proceeded in only 22% yield. The low yield is believed to be due to side reactions taking place when I was converted to a Grignard reagent. Considerable amounts of a coupling product, 1,4-di-(*o*-chlorophenyl)-butane and a low boiling fraction were isolated. Alcohol IV was obtained from I in an over-all yield of 25%. The cyclization of both alcohols was effected by 90% sulfuric acid in good yield.

In order to prove the structure of the cyclization products VI the chlorine atom was removed by reduction with sodium and alcohol. The samples of 4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene which resulted were oxidized with chromic acid to 9-keto-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (VII). The two samples of VI both produced the same ketone which was identified as 2,4-dinitrophenylhydrazone VIII (m.p. 209.5–210.5°).

In connection with a study of the reactions of 4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene the 2,4-dinitrophenylhydrazones of both isomers of ketone VII had been obtained.[5] One isomer (IX) was quite pure (m.p. 182.5–184°) and the other obtained by chromatographic separation was sufficiently pure to produce an X-ray powder diagram quite different from that of isomer IX. By modifying the chromatography it has been possible to effect a more complete separation of the 2,4-dinitrophenylhydrazones from the authentic sample of ketone VII[6] and to obtain a pure sample of 2,4-dinitrophenylhydrazone VIII. The melting point, X-ray powder diagram and infrared absorption curve of the two samples of VIII were identical. Therefore it can be concluded that cyclizations of both alcohols IV and V produce one stereoisomer of 8-chloro-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene in which the fusion of the two saturated rings is opposite from that obtained by cyclization of 2-methyl-1-β-phenylethylcyclohexanol.[5]

Experiments are now in progress to determine the stereochemical configuration of the product of these and other cyclizations which have been reported.[3,5] According to a mechanism which will be fully described in a subsequent publication the octahydrophenanthrenes reported in the present work should have the *trans* configuration of the two saturated rings.

Acknowledgment.—We wish to express our appreciation to the Rutgers Research Council for financial assistance which enabled us to complete this research.

Experimental[7]

β-2-Chlorophenylethyl Bromide (I).—β-2-Chlorophenylpropionic acid[8] was converted to the silver salt[4] and dried over phosphorus pentoxide. A solution of bromine (10.8 g.) in dry carbon tetrachloride (30 ml.) was added during one hour to a boiling suspension of the silver salt (19.7 g.) in carbon tetrachloride (80 ml.). The reaction mixture was stirred and refluxed for an additional three hours and then cooled and filtered. The filtrate was extracted with sodium bicarbonate solution; acidification of this extract precipitated 1.5 g. (8%) of the starting acid. The carbon tetrachloride solution was dried, concentrated and the residue vacuum distilled. There was obtained 9.2 g. (63%) of bromide I which boiled at 113–115° (10 mm.), $n^{25}D$ 1.5701.

Anal. Calcd. for C_8H_8ClBr: C, 43.77; H, 3.67. Found: C, 43.45; H, 3.76.

A sample of bromide I was converted to a Grignard reagent and carbonated by pouring onto a slurry of Dry Ice in ether. The acidic product of this reaction was identical with an authentic sample of β-2-chlorophenylpropionic acid, m.p. 93–95°.

Ethyl 2-Keto-1-β-(2′-chlorophenyl)-ethyl-1-cyclohexanecarboxylate (II).—Ethyl cyclohexanone-2-carboxylate (34 g.) was alkylated with bromide I (32.9 g.) using potassium (6.0 g.) and toluene (150 ml.) by the previously described procedure.[2] There was obtained 22 g. (48%) of II which boiled at 178–185° (1.2 mm.), $n^{25}D$ 1.5218.

Anal. Calcd. for $C_{17}H_{21}O_3Cl$: C, 66.12; H, 6.86. Found: C, 66.13; H, 6.79.

A slightly higher yield (55%) was obtained when *t*-butyl alcohol was used as a solvent for the alkylation.[9]

The 2,4-dinitrophenylhydrazone of II melted at 127–128° after recrystallization from ethanol.

Anal. Calcd. for $C_{23}H_{25}O_6N_4Cl$: C, 56.50; H, 5.15. Found: C, 56.26; H, 5.00.

2-β-(2′-Chlorophenyl)-ethylcyclohexanone (III).—This ketone was prepared using the hydrolysis procedure of Renfrow, *et al.*[9] From II (69.9 g.) there was obtained 24.1 g. (45%) of III which boiled at 144–146° (0.8 mm.), $n^{25}D$ 1.5400.

Anal. Calcd. for $C_{14}H_{17}OCl$: C, 71.02; H, 7.24. Found: C, 71.10; H, 7.22.

The 2,4-dinitrophenylhydrazone of III melted at 149.5–150.5° after recrystallization from ethanol–ethyl acetate.

Anal. Calcd. for $C_{20}H_{21}O_4N_4Cl$: C, 57.62; H, 5.08. Found: C, 57.59; H, 5.12.

8-Chloro-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (VI). A.—A solution of methylmagnesium iodide was prepared in the usual manner from magnesium (3.0 g.), methyl iodide (17.2 g.) and dry ether (80 ml.). To this solution cooled in an ice-bath, ketone III (22.6 g.) in anhydrous ether (25 ml.) was added dropwise. When the addition was complete the reaction mixture was refluxed for an hour and then decomposed by pouring into ice-water (140 ml.) containing sulfuric acid (4 ml.). The product was extracted with ether; the ether extracts were washed with water and sodium bicarbonate solution, dried and concentrated. The crude alcohol IV (24 g., 99%) could not be purified without causing dehydration. This substance was cyclized by the dropwise addition of cold 90% sulfuric acid (64 ml.). The temperature was maintained at 5–7° during the addition (3 hours) and for an additional hour. Finally the reaction mixture was stirred at room temperature for 3 hours. The cyclization product was extracted from the sulfuric acid solution with petroleum ether. The extracts were washed with cold concd. sulfuric acid, water and sodium bicarbonate solution. After evaporating the solvent the crude product was vacuum distilled. There was obtained 18.4 g. (82% based on ketone III) of VI which boiled at 126–128° (0.6 mm.), $n^{25}D$ 1.5671.

Anal. Calcd. for $C_{15}H_{19}Cl$: C, 76.74; H, 8.16. Found: C, 76.75; H, 8.18.

B.—β-2-Chlorophenylethyl bromide (34.6 g.) was converted to the Grignard reagent using magnesium (12 g.) and anhydrous ether. A solution of 2-methylcyclohexanone (15.8 g.) in anhydrous ether was added dropwise at 0–5° and then the reaction mixture was refluxed for four hours. Saturated ammonium chloride solution was added to decompose the magnesium complex and crude alcohol V was isolated as in part A.

(4) The chlorine atom deactivates the aromatic nucleus so that ring bromination does not interfere with the normal course for the silver salt–bromine reaction. For further examples see R. A. Barnes and R. J. Prochaska, THIS JOURNAL, **72**, 3188 (1950).

(5) R. A. Barnes and R. T. Gottesman, *ibid.*, **74**, 35 (1952).

(6) Kindly furnished by Prof. M. S. Newman; see M. S. Newman and M. D. Farbman, *ibid.*, **66**, 1550 (1944).

(7) Microanalyses were by W. Manser and J. F. Alicino. Melting points have been corrected.

(8) R. A. Barnes and L. Gordon, THIS JOURNAL, **71**, 2646 (1949).

(9) W. B. Renfrow, A. Renfrow, E. Shoun and C. A. Sears, *ibid.*, **73**, 317 (1951).

Vacuum distillation of the crude alcohol yielded fraction I (b.p. 33–36°, 0.6 mm.) and fraction II (b.p. 97–130°, 0.4 mm.). Fraction I was redistilled at atmospheric pressure, b.p. 169–173°, $n^{23}D$ 1.4790 (*o*-chloroethylbenzene boils at 180°, $n^{25}D$ 1.5187; 2-methylcyclohexanone boils at 166°, $n^{20}D$ 1.4487). Fraction II was seeded with 1,4-di-(*o*-chlorophenyl)-butane and allowed to stand in the refrigerator until recrystallization was complete. The liquid product (7.8 g., 22%) remaining after filtration of the crystals was mainly alcohol V and the corresponding olefin. Cyclization of this material with 90% sulfuric acid (23 ml.) by the procedure used in Part A yielded 6.95 g. (96% based on partially purified alcohol) of VI which boiled at 115–117° (0.22 mm.), $n^{24}D$ 1.5666.

1,4-Di-(*o*-chlorophenyl)-butane. A.—This compound was synthesized in a manner analogous to that used for the preparation of 1,4-diphenylbutane.[10] From β-(2-chlorophenyl)-ethyl bromide (5.53 g.), magnesium (0.69 g.), anhydrous cupric chloride (4.67 g.) and anhydrous ether (40 ml.) there was obtained 0.75 g. (21%) of 1,4-di-(*o*-chlorophenyl)-butane which melted at 51–52° (b.p. 156–162°, 0.5 mm.).

Anal. Calcd. for $C_{16}H_{16}Cl_2$: C, 68.82; H, 5.78. Found: C, 68.87; H, 5.89.

B.—The crystals obtained as a by-product in the preparation of alcohol V were recrystallized from ethanol and had a melting point of 51–52° alone or when mixed with the sample prepared in part A.

4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene.—8-Chloro-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (2.6 g.) was dissolved in absolute ethanol (120 ml.) and to this refluxing solution small pieces of sodium (6.0 g.) were added during 3 hours. The excess alcohol was distilled and the residue treated with ice-water and sufficient acetic acid to make the solution acid. The hydrocarbon was extracted with petroleum ether and after removal of the solvent was vacuum distilled; b.p. 100–103° (0.5 mm.), $n^{25}D$ 1.5453.

Anal. Calcd. for $C_{16}H_{20}$: C, 89.93; H, 10.07. Found: C, 90.09; H, 10.09.

A sample of this hydrocarbon (0.4 g.) was dehydrogenated using palladium-on-charcoal (0.08 g.) at 280–320°. White crystals sublimed onto the condenser of the dehydrogenator during the process. After recrystallization from methanol the dehydrogenated product melted at 97–98° alone or when mixed with an authentic sample of phenanthrene.

9-Keto-4a-methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (VII).—4a-Methyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (1.3 g.) was dissolved in glacial acetic acid (14 ml.) and cooled to 0°. Chromic anhydride (1.7 g.) dissolved in 80% acetic acid was added and the reaction mixture stirred at 0° for 10 hours and then allowed to stand for three days at room temperature. The reaction mixture was diluted with water (175 ml.) and extracted with ether. The ether solution was washed with sodium bicarbonate solution, dried and concentrated. Vacuum distillation of the residue produced 0.5 g. of ketone VII, b.p. 130–132° (0.5 mm.), $n^{25}D$ 1.5675.[11] This was purified by conversion to the 2,4-dinitrophenylhydrazone which was recrystallized from ethanol and ethyl acetate, m.p. 209.5–210.5°.

Anal. Calcd. for $C_{21}H_{22}O_4N_4$: C, 63.94; H, 5.62. Found: C, 64.17; H, 5.70.

Chromatographic Separation of 2,4-Dinitrophenylhydrazones (VIII) and (IX).—The mixture of 2,4-dinitrophenylhydrazones of VII[6] (98 mg., m.p. 166–184°) was placed on a 30-cm. column of acid-washed alumina (10 g.) in a benzene–petroleum ether solution. Fifty fractions were eluted each with 125 ml. of 30% benzene in petroleum ether. The last ten fractions were combined and recrystallized from ethanol–ethyl acetate. The sample of VIII obtained in this way melted at 208–210°.[12] The melting point of a mixture of VIII with the 2,4-dinitrophenylhydrazones prepared from either sample of VI also melted at 208–210°. The ultraviolet absorption spectra of VIII and IX in 95% ethanol were identical with λ_{max} at 385 mμ and λ_{min} at 320 mμ. The infrared absorption curves of the sample of VIII obtained by chromatography and from VI were identical; there were significant differences particularly in the region 8–10 μ between the curves of VIII and IX. The X-ray lattice spacings (d/n) for the two samples of VIII were identical and different from that of IX.[5]

(10) E. E. Turner, *J. Chem. Soc.*, **115**, 559 (1915); E. E. Turner and F. W. Bury, *ibid.*, **123**, 2490 (1923).

(11) M. S. Newman and M. D. Farbman, ref. 6, report the mixture of isomeric ketones to boil at 125–138° (0.5 to 1 mm.), $n^{23}D$ 1.5673.

(12) In the previous separation of these 2,4-dinitrophenylhydrazones ref. 5, the last four fractions of thirty-four yielded a product which melted at 186–190°.

NEW BRUNSWICK, NEW JERSEY

[CONTRIBUTION NO. 268 FROM THE DEPARTMENT OF ORGANIC CHEMISTRY AND ENZYMOLOGY, FORDHAM UNIVERSITY]

Investigations on Lignin and Lignification. XI. Structural Studies on Bagasse Native Lignin[1]

BY GEORGE DE STEVENS AND F. F. NORD

RECEIVED AUGUST 12, 1952

The native lignin from bagasse and the lignin liberated through the action of cellulolytic enzymes present in the wood-destroying mold, *Poria vaillantii*, have been found to be identical in all respects examined. Besides vanillin and syringaldehyde we obtained equivalent amounts of *p*-hydroxybenzaldehyde from each of these lignin preparations on oxidation with nitrobenzene and alkali. Chemical evidence in conjunction with ultraviolet spectroscopic examination indicates that a *p*-hydroxyphenyl ketone is prevalent in bagasse native lignin molecule. The possible presence of a flavanone-type structure in this preparation is considered.

In previous studies on bagasse native lignin it was established that its native lignin fraction is identical with the lignin liberated by the action of enzymes present in wood-destroying molds of the "brown rot" type.[2] The subject matter of this report deals, in part, with the further comparison of these lignin fractions and also with chemical, chromatographical and spectroscopical studies on bagasse native lignin for the purpose of elucidating its structure.

The reactions utilized in the chemical investigations were methylation, acetylation, mercaptolysis, oxidation and hydrogenation. The analytical methods applied were paper chromatography as well as ultraviolet and infrared absorption spectroscopy. Finally, model compounds served to correlate findings pertaining to a possible lignin structure with its chemical and physical behavior.

(1) Presented before the Cellulose Division of the American Chemical Society, Atlantic City, N. J., September, 1952. The data recorded are taken from a part of the dissertation of G. de St. submitted to the Graduate School of Fordham University in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

(2) (a) G. de Stevens and F. F. Nord, THIS JOURNAL, **73**, 4622 (1951); (b) **74**, 3326 (1952).