Compounds of Hexahydroxybenzene and the Toluidines.—When *o*-toluidine, *m*-toluidine and *p*-toluidine were added to hexahydroxybenzene in the same manner that aniline was added, solid products were formed. When these were washed, dried and the nitrogen determined, it was found that two molecules of the toluidines had added to one molecule of hexahydroxybenzene, giving the formula $C_6(OH)_6 \cdot 2NH_2C_6H_4CH_3$ (Table II).

A second compound of *o*-toluidine was formed when the reaction was carried out with exclusion of air. The derivative was buff-colored in the mass, and decidedly crystalline and almost colorless under the microscope, instead of the strikingly colored compound usually obtained. Nitrogen determination showed that the formula of this compound was probably $C_6(OH)_6 \cdot NH_2C_6H_4CH_3$ (Table II).

TABLE II

AROMATIC AMINO COMPOUNDS OF HEXAHYDROXYBENZENE

Reagent	Formula of compound	Color	Form
Aniline	$C_6(OH)_6 \cdot 2NH_2C_6H_5$	Green-red	Plates
o-Toluidine	$C_6(OH)_6 \cdot NH_2C_6H_4CH_3$	Buff	Plates
o-Toluidine	$C_6(OH)_6 \cdot 2NH_2C_6H_4CH_3$	Red	Needles
m-Toluidine	$C_6(OH)_6 \cdot 2NH_2C_6H_4CH_3$	Orange-red	Plates
p-Toluidine	$C_6(OH)_6 \cdot 2NH_2C_6H_4CH_3$	Red	Plates
o-Chloroaniline	Not formed		
m-Chloroaniline	$C_6(OH)_6 \cdot 2NH_2C_6H_4Cl$	Orange-red	Plates
p-Chloroaniline	$C_6(OH)_6 \cdot 2NH_2C_6H_4Cl$	Red	Plates

Summary

1. Tetrahydroxyquinone has been prepared by the action of a mixture of hydriodic acid and hydrochloric acid on disodium tetrahydroxyquinone prepared from oxidized *i*-inositol; yield, 80%.

2. Hexahydroxybenzene has been prepared by the action of hydriodic acid on an alcoholic solution of tetrahydroxyquinone; yield, 70%.

3. Fatty acid esters of hexahydroxybenzene, from the acetate to the normal caprate have been prepared. Hexamonochloroacetate, hexatrichloroacetate and hexabenzoate of hexahydroxybenzene also have been prepared.

4. Aniline, *m*-chloroaniline, *p*-chloroaniline, *o*-toluidine, *m*-toluidine and *p*-toluidine addition compounds with hexahydroxybenzene have been prepared. Two molecules of the amino compound combine with one of the hexahydroxybenzene.

IOWA CITY, IA. RECEIVED JUNE 9, 1943

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Synthesis of 3'-Alkyl-1,2-cyclopentenophenanthrenes

BY BYRON RIEGEL, MARVIN H. GOLD[1] AND MICHAEL A. KUBICO

The importance of thoroughly testing the tumor producing activity of hydrocarbons having the tetracyclic steroid ring structure was pointed out to us by Dr. M. J. Shear of the National Cancer Institute. Since the side chains of the various steroids are attached to the 17-position, the corresponding 3'-position of 1,2-cyclopentenophenanthrene is of particular interest. A few derivatives of 1,2-cyclopentenophenanthrene have been reported, but the methods of preparation are so laborious that sufficient quantities for biological testing have not been prepared.

The most obvious approach to the 3'-alkyl-1,2-cyclopentenophenanthrenes would be through 3'-keto-1,2-cyclopentenophenanthrene which has been prepared by Bachmann and Kloetzel.[2] Low yields, however, prohibited the adaptation of their method, and other attempts at its preparation in this Laboratory involving the cyclization of 2-[β-halopropionyl]-phenanthrenes were unsuccessful.

The series of reactions outlined below proved to be the most successful means of synthesizing the desired compounds. The readily available 2-acylphenanthrenes[3] (I) were reduced by means of aluminum isopropoxide to the corresponding carbinols which were in turn converted to bromides. Condensation of the bromides with sodiomalonic ester followed by saponification and decarboxylation gave the β-[2-phenanthryl]-substituted acids (II). This is an adaptation of the method used by Bachmann and Struve[4] in their synthesis of chrysene derivatives. Ring closure of the corresponding acid chlorides was best effected by means of aluminum chloride in nitrobenzene. Clemmensen reduction of the resulting ketones (III) gave the desired homologs (IV) of Diels' hydrocarbon. The latter part of this synthesis is an adaptation of the method employed for the preparation of 3'-methyl-1,2-cyclopentenophenanthrene by Bergmann and Hillemann[5] who made the acid II

(1) Anna Fuller Fund Research Associate, 1940-1942.

(2) W. E. Bachmann and M. C. Kloetzel, THIS JOURNAL, **59**, 2207 (1937).

(3) B. Riegel, M. H. Gold and M. A. Kubico, *ibid.*, **64**, 2221 (1942).

(4) W. E. Bachmann and W. S. Struve, *J. Org. Chem.*, **5**, 426 (1940).

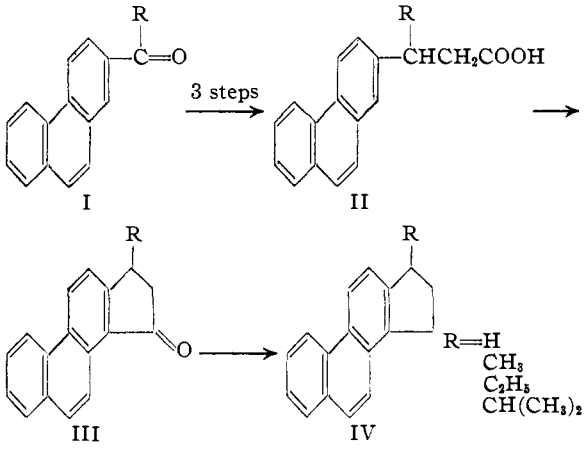
(5) E. Bergmann and H. Hillemann, *Ber.*, **66**, 1302 (1933).

TABLE I

1,2-CYCLOPENTENOPHENANTHRENE DERIVATIVES, M. P., °C.

3'-R	Hydrocarbon	Picrate	1'-Keto	1'-Oxime
H	134.4–135.8	134.5–135[9]	188.6–189.4	235–236 (dec.)
CH_3	126–127[5]	130–131[5]	135–136[5]	α, 169–171 (dec.)
				β, 165–170 (dec.)
C_2H_5	85–86	94.8–96.4	110–111.2	α, 172.5–174.5 (dec.)
				β, 169–170.8 (dec.)
$CH(CH_3)_2$	97.6–98.4	108–113	143.6–144.4	205–211 (dec.)

(R = CH_3) by the Reformatsky reaction between 2-acetylphenanthrene and ethyl bromoacetate followed by dehydration and reduction. The Bachmann and Struve method for the preparation of the acids (II), however, was found to give better results. Difficulty was encountered in the preparation of the acid II where R = $CH(CH_3)_2$.



The low yield here was probably due to ether formation predominating over condensation with sodiomalonic ester. A considerable amount of neutral material was isolated from the reaction mixture which analyzed correctly for α-[2-phenanthryl]-isobutyl ethyl ether indicating that reaction took place between α-[2-phenanthryl]-isobutyl bromide and sodium ethoxide.

To complete the series, the parent hydrocarbon, 1,2-cyclopentenophenanthrene was prepared. By means of the Willgerodt reaction 2-propionylphenanthrene (I, R = C_2H_5) was converted to β-[2-phenanthryl]-propionamide which was hydrolyzed to β-[2-phenanthryl]-propionic acid (II, R = H). Ring closure of the acid chloride gave the ketone (III, R = H) which was reduced to the hydrocarbon (IV, R = H). This is an adaptation of the method used by Bachmann[6] who prepared the acid II by condensing 2-phenanthrylmethyl bromide with malonic ester followed by saponification and decarboxylation.

(6) W. E. Bachmann, THIS JOURNAL, **57**, 1381 (1935).

Purification of the keto compounds (III) was accomplished by converting them to their oximes from which the ketones were regenerated. In some cases *syn* and *anti* isomers of the oximes were obtained. The melting points of the ketones (III), oximes, hydrocarbons (IV), and picrates of the hydrocarbons are recorded in Table I. Highly purified samples of the hydrocarbons were submitted to Dr. M. J. Shear who will report elsewhere on their possible tumor producing activity.

Experimental[7]

3'-Methyl-1,2-cyclopentenophenanthrene (Diels' Hydrocarbon) (IV, R = CH_3).—2-Acetylphenanthrene was prepared by the dehydrogenation[3] of the corresponding 9,10-dihydro derivative. This was then converted to β-[2-phenanthryl]-butyric acid (II, R = CH_3) by the method of Bachmann and Struve.[4] Ring closure gave 1'-keto-3'-methyl-1,2-cyclopentenophenanthrene (III, R = CH_3). When the oxime of this ketone was prepared and crystallized from ethanol, one form separated as thick white plates melting at 169–171° (dec.), and a second isomer, in the form of yellow needles melting at 165–170° (dec.), was obtained by diluting the filtrate with an equal volume of water. The yellow, more soluble, form could be crystallized from dilute ethanol. Rectangular yellow prisms were obtained by crystallization from methanol. The melting points of both forms were obtained by inserting the capillaries in the bath when the temperature had reached 160°.

Anal. Calcd. for $C_{18}H_{15}NO$: N, 5.37. Found: white form, N, 5.46; yellow form, N, 5.40.

2-Phenanthrylethylcarbinol.—Aluminum isopropoxide reduction of 47.5 g. of 2-propionylphenanthrene obtained from the dehydrogenation[3] of the 9,10-dihydro derivative gave 35 g. (73%) of the carbinol, m. p. 85–87°. One treatment with Norit in benzene and two crystallizations from Skellysolve C (petroleum ether, b. p. 85.6–100°) raised the m. p. of the product to 87.4–88.4°.

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.43; H, 6.82. Found: C, 86.61; H, 6.90.

α-[2-Phenanthryl]-propyl Bromide.—From 34 g. of 2-phenanthrylethylcarbinol and 8.5 ml. of phosphorus tribromide in 250 ml. of dry ether was obtained 37.7 g. (87.5%) of the crude bromide, m. p. 80–84°. Seven crystallizations from Skellysolve C gave a product of m. p. 81.5–83°.

(7) All melting points are corrected. Microanalyses by Dr. T. S. Ma, University of Chicago.

Anal. Calcd. for $C_{17}H_{15}Br$: C, 68.24; H, 5.05. Found: C, 68.15; H, 5.28.

β-[2-Phenanthryl]-valeric Acid (II, R = C_2H_5).—Treatment of 35 g. of α-[2-phenanthryl]-propyl bromide with sodiomalonic ester in dry ethanol-benzene gave 27.5 g. (85%) of the crude acid, m. p. 132–135°. Four crystallizations from glacial acetic acid and one from chloroform-petroleum ether (b. p. 30–60°) raised the m. p. of the acid to 134.8–136.2°.

Anal. Calcd. for $C_{19}H_{18}O_2$: C, 82.00; H, 6.44. Found: C, 82.81; H, 6.66.

1'-Keto-3'-ethyl-1,2-cyclopentenophenanthrene (III, R = C_2H_5).—The acid chloride from 18 g. of β-[2-phenanthryl]-valeric acid was dissolved in 75 ml. of nitrobenzene and added dropwise to a solution of 13.5 g. of aluminum chloride in 150 ml. of nitrobenzene and stirred at room temperature for two and one-half hours, then at 80° for an additional hour. After decomposing with ice and hydrochloric acid, the nitrobenzene was removed by steam distillation, the residue was taken up in benzene and decolorized with Norit. Upon concentrating and cooling, 13.3 g. (78.5%) of material, m. p. 105–109°, was obtained. Two crystallizations from acetone–ethanol gave small irregular prisms, m. p. 110–111.2°.

Anal. Calcd. for $C_{19}H_{16}O$: C, 87.67; H, 6.20. Found: C, 88.01; H, 6.36.

Oximes.—A colorless form of the oxime crystallized from 95% ethanol, melting with decomposition at 172.5–174.5°. The second yellow form separated upon diluting the filtrate with an equal volume of water and was crystallized from dilute ethanol, m. p. 169–170.8° (dec.).

Anal. Calcd. for $C_{19}H_{17}NO$: N, 5.09. Found: white form, N, 4.93; yellow form, N, 5.09.

3'-Ethyl-1,2-cyclopentenophenanthrene (IV, R = C_2H_5).—Clemmensen reduction of 8 g. of the 1'-keto-3'-ethyl compound gave 7.08 g. (94%) of the crude hydrocarbon, m. p. 82–84°. The crude material was vacuum sublimed (130–140° at 2–3 mm.), then crystallized twice from acetone–ethanol to give small irregular platelets, m. p. 85–86°.

Anal. Calcd. for $C_{19}H_{18}$: C, 92.65; H, 7.35. Found: C, 92.70; H, 7.55.

Picrate.—The picrate of the 3'-ethyl hydrocarbon, m. p. 94.8–96.4° (dec.), analyzed for two molecules of hydrocarbon per molecule of picric acid.

Anal. Calcd. for $2C_{19}H_{18}\cdot C_6H_4N_3O_7$: N, 5.82. Found: N, 5.50.

2-Phenanthrylisopropylcarbinol.—Aluminum isopropoxide reduction of 72 g. of 2-isobutyrylphenanthrene[8] gave 61 g. (84%) of crystalline material, m. p. 100–102°. Three crystallizations from benzene–Skellysolve C and one from benzene–petroleum ether gave light needles, m. p. 104.4–104.7°.

Anal. Calcd. for $C_{18}H_{18}O$: C, 86.37; H, 7.25. Found: C, 86.75; H, 7.47.

α-[2-Phenanthryl]-isobutyl Bromide.—From 61 g. of 2-phenanthrylisopropylcarbinol and 22 ml. of phosphorus tribromide in 450 ml. of dry ether was obtained 65 g. (85%) of the desired bromide. Three crystallizations from benzene–Skellysolve C gave thick rhombic crystals, m. p. 91–94° (dec.).

Anal. Calcd. for $C_{18}H_{17}Br$: C, 69.02; H, 5.47. Found: C, 69.50; H, 5.81.

β-[2-Phenanthryl]-isocaproic Acid (II, R = $CH(CH_3)_2$).—When 44.3 g. of α-[2-phenanthryl]-isobutyl bromide was treated in the usual manner, *i. e.*, with sodiomalonic ester in dry ethanol–benzene followed by saponification and decarboxylation, 8.6 g. (21%) of acid material was obtained, m. p. 145–147°. Three crystallizations from chloroform–petroleum ether gave fine needles, m. p. 148.8–149.6°.

Anal. Calcd. for $C_{20}H_{20}O_2$: C, 82.16; H, 6.89. Found: C, 81.46; H, 6.82.

In the above procedure the sodiomalonic ester was made from sodium ethoxide and malonic ester. A considerable amount of a neutral material, m. p. 81–83°, was isolated from the above reaction mixture. This compound gave the correct analysis for α-[2-phenanthryl]-isobutyl ethyl ether. *Anal.* Calcd. for $C_{20}H_{22}O$: C, 86.28; H, 7.97. Found: C, 86.50; H, 7.50.

It was decided, therefore, to eliminate sodium ethoxide from the reaction mixture. This was done by preparing the sodiomalonic ester by treating powdered sodium and malonic ester in dry benzene. The bromide in a benzene solution was then added to this suspension of sodiomalonic ester in benzene and the mixture stirred for several days at room temperature, then at 80° for twenty-four hours. However, after working up in the usual manner, the yield of the desired acid was even less than was obtained by the previous method.

1'-Keto-3'-isopropyl-1,2-cyclopentenophenanthrene (III, R = $CH(CH_3)_2$).—Ring closure of 4.3 g. of β-[2-phenanthryl]-isocaproic acid by the method described for the 3'-ethyl compound yielded 2.2 g. (75%) of material, m. p. 139–143°. Two treatments with Norit in acetone–ethanol and two crystallizations from acetone gave needles, m. p. 143.6–144.4°.

Anal. Calcd. for $C_{20}H_{18}O$: C, 87.56; H, 6.61. Found: C, 87.78; H, 6.69.

Oxime.—Fine white needles, m. p. 205–211° (dec.), were obtained by crystallization from ethanol.

Anal. Calcd. for $C_{20}H_{19}NO$: N, 4.84. Found: N, 4.84.

3'-Isopropyl-1,2-cyclopentenophenanthrene (IV, R = $CH(CH_3)_2$).—Clemmensen reduction of 0.711 g. of the 1'-keto-3'-isopropyl compound gave 0.50 g. (73.7%) of crude hydrocarbon, m. p. 87.5–93°. Vacuum sublimation (150–165° at 2 mm.) and two crystallizations from acetone–ethanol gave thin plates, m. p. 97.6–98.4°.

Anal. Calcd. for $C_{20}H_{20}$: C, 92.26; H, 7.74. Found: C, 92.46; H, 7.66.

Picrate.—The picrate dissociated so readily that it was impossible to obtain an analytically pure sample. A few crystals mixed with picric acid, from which they were separated mechanically, were obtained. They melted at 108–113° (dec.).

β-[2-Phenanthryl]-propionic Acid (II, R = H).—This compound was prepared from 2-propionylphenanthrene using the modification of the Willgerodt reaction described by Fieser and Kilmer.[8] A mixture of 4 g. of 2-propionylphenanthrene, 16 ml. of purified dioxane and 20 ml. of am-

(8) L. F. Fieser and G. W. Kilmer, THIS JOURNAL, **62**, 1354 (1940).

monium polysulfide solution (1 g. of sulfur dissolved per 10 ml. of ammonium sulfide made by saturating ammonium hydroxide with hydrogen sulfide) were sealed in a bomb tube and heated at 160° for ten hours. Upon cooling, a yellow precipitate formed which was collected on a filter and washed with a mixture of ammonium polysulfide and dioxane. This crude amide was then refluxed with a mixture of 20 ml. of hydrochloric acid and 50 ml. of acetic acid for four hours. The reaction mixture was then cooled, diluted with water and the resulting precipitate filtered. The precipitate was dissolved in benzene and the acidic material extracted with several washings of dilute sodium bicarbonate. The acid was reprecipitated by acidifying the extract with hydrochloric acid, then collected on a filter. One treatment with Norit in hot benzene followed by two crystallizations from benzene gave 2.4 g. (56.5%) of the acid (nacreous plates), m. p. 177.2–178.4°. Bachmann[6] reports β-[2-phenanthryl]-propionic acid, m. p. 177–177.5°.

1,2-Cyclopentenophenanthrene (IV, R = H).—Ring closure of the acid chloride of β-[2-phenanthryl]-propionic acid, using aluminum chloride in nitrobenzene, gave 1'-keto-1,2-cyclopentenophenanthrene in 92% yield, m. p. 188.6–189.4°. This compound had been reported by Bachmann[6] as melting at 183–184°. The oxime of this ketone was prepared. It crystallized from ethanol–dioxane in fine white needles melting at 235–236° (dec.). *Anal.* Calcd. for $C_{17}H_{13}NO$: N, 5.66. Found: N, 5.65. Clemmensen reduction of the ketone gave 1,2-cyclopentenophenanthrene which after vacuum sublimation (200–210° at 5 mm.) and crystallization from ethanol melted at 134.4–135.8°. With *s*-trinitrobenzene in alcoholic solution the hydrocarbon formed soft yellow needles, m. p. 165–167°. Cook and Hewett[9] gave the following constants for 1,2-cyclopentenophenanthrene: m. p. 134.5–135°; sublimes at 200–220° at 4 mm.; *s*-trinitrobenzene complex, m. p. 166–167° (soft yellow needles from alcohol).

2-[β-Bromopropionyl]-9,10-dihydrophenanthrene.—To an ice-cold solution of 25 g. of 9,10-dihydrophenanthrene and 24.2 g. of β-bromopropionyl chloride in 250 ml. of carbon bisulfide was added 44 g. of aluminum chloride in small portions over a period of fifteen minutes. Stirring was continued for twenty-five minutes and the reaction mixture was decomposed with ice and hydrochloric acid. Some insoluble material was removed by filtration and the carbon bisulfide layer was separated and dried. The solvent was removed under partial vacuum using a bath whose temperature was kept below 50°. The residue was taken up in ether and allowed to crystallize in a refrigerator. The crude material (30.35 g.; 69%) melted at 70–73°. Several crystallizations and treatment with Norit raised the m. p. of the compound to 76–77.3°.

Anal. Calcd. for $C_{17}H_{15}BrO$: C, 64.76; H, 4.80. Found: C, 65.32; H, 4.82.

2-[β-Chloropropionyl]-9,10-dihydrophenanthrene.—From 10.2 g. of 9,10-dihydrophenanthrene and 7.6 g. of β-chloropropionyl chloride in 125 ml. of carbon bisulfide treated as described for the bromo derivative was obtained 7.7 g. (50%) of crude material melting at 58–65°. Crystallization from ether-pentane gave a product melting at 72–73°.

Anal. Calcd. for $C_{17}H_{15}ClO$: C, 75.39; H, 5.59. Found: C, 75.76; H, 5.64.

2-[β-Methoxypropionyl]-9,10-dihydrophenanthrene.—Using 27 g. of β-methoxypropionyl chloride with 36 g. of 9,10-dihydrophenanthrene in the Friedel–Crafts reaction gave 36.35 g. of oil. This material polymerized when a low pressure distillation was attempted. A small portion of this oil finally crystallized from ether, m. p. 73–77°.

This compound was also prepared from the β-chloro and β-bromo derivatives by heating with sodium methoxide in methanol. From the bromo compound a 42% yield was obtained. Crystallization from methanol gave needles melting at 87.8–88.7°. Mixed melting points of the products from the various sources gave no depression.

Anal. Calcd. for $C_{18}H_{18}O_2$: C, 81.17; H, 6.80. Found: C, 81.25; H, 6.87.

Dehydrogenations.—9,10-Dihydrophenanthrene was dehydrogenated by means of chloranil in boiling xylene in 65% yield according to the method of Arnold and Collins.[10] The β-bromo, β-chloro and β-methoxypropionyl-9,10-dihydrophenanthrenes yielded only intractable tars by this method.

2-[β-Bromopropionyl]-phenanthrene.—This compound was prepared in a manner similar to that described above for the 9,10-dihydrophenanthrene derivatives. From 27.5 g. of purified phenanthrene, 28.5 g. of β-bromopropionyl chloride and 42.5 g. of aluminum chloride in 300 ml. of carbon bisulfide was obtained 24 g. (50%) of crude crystalline material, m. p. 85–102°. Fractional crystallizations from ethyl acetate and acetone gave 7.4 g. (15%) of the higher melting isomer, m. p. 117–119°. Final purification was effected by crystallization from chloroform and ether giving a product which melted with decomposition at 118.7–119.8°.

Anal. Calcd. for $C_{17}H_{13}BrO$: C, 65.18; H, 4.19. Found: C, 65.03; H, 4.51.

A small sample of this material was reduced by Clemmensen's method, giving 2-*n*-propylphenanthrene which was distilled at 2 mm. The oily distillate was converted readily to a picrate, m. p. 89–91°.

The bromoketone was treated with 85% sulfuric acid at 90° and at 100°, and with concd. sulfuric acid at 90°, but in all cases polymeric infusible tars were obtained. Sulfuric acid and phosphoric acid were both used in attempting to cause ring closure with the crude chloroketone mixture with similarly unsuccessful results. Still other attempts were made on the more readily purified bromoketone, such as aluminum chloride, stannic chloride, thionyl chloride and liquid hydrogen fluoride. With liquid hydrogen fluoride the starting material was recovered, but with the others only the polymeric material was obtained.

Summary

1. β-[2-Phenanthryl]-propionic acid has been prepared from 2-propionylphenanthrene by means of the Willgerodt reaction. Using reactions that have already been described, this acid was converted to 1,2-cyclopentenophenanthrene.

2. Attempts to prepare 3'-keto-1,2-cyclopen-

(9) J. W. Cook and C. L. Hewett, *J. Chem. Soc.*, 1098 (1933).

(10) R. T. Arnold and C. J. Collins, THIS JOURNAL, **61**, 1407 (1939).

tenophenanthrene from 2-[β-halopropionyl]-phenanthrene were unsuccessful.

3. Diels' hydrocarbon and its ethyl and isopropyl homologs were prepared from the corresponding 2-acylphenanthrene derivatives.

4. Several intermediates and derivatives of the above compounds are described.

EVANSTON, ILLINOIS RECEIVED JUNE 2, 1943

NOTES

Crystalline Bisulfite Addition Compounds of Menadione

BY F. ABLONDI, R. W. PRICE, B. R. BAKER AND G. H. CARLSON

Although Moore[1] stated that addition compounds of 2-methyl-1,4-naphthoquinone formed with metallic and amine bisulfites failed to crystallize, the alkali metal,[2] ammonium and calcium derivatives crystallized under the conditions herewith reported. The salts showed antihemorrhagic activity at a concentration of one microgram per milliliter and were convertible to the S-benzylthiuronium salt already described.[2a]

Experimental

Lithium Salt.—Lithium carbonate (15 g.), suspended in 50 cc. of water at 0°, was treated with sulfur dioxide until effervescence ceased, the solution was shaken with 17.4 g. of 2-methyl-1,4-naphthoquinone, insoluble material was filtered off and the filtrate, diluted to 100 cc. and cooled to 5°, yielded 6 g. of crystalline product which, recrystallized from 6 cc. of water, gave the lithium salt. *Anal.* Calcd. for $C_{11}H_9O_5SLi$: Li, 2.68. Found: Li, (1) 3.29; (2) 2.10.

The salt was obtained in better yield by concentrating the filtered bisulfite solution (prepared from 21.5 g. of lithium carbonate, 1 liter water, 100 g. of quinone and sulfur dioxide) *in vacuo* until solid separated and, after fifteen hours at 0°, 84 g. of product was filtered off which, recrystallized from 60 cc. of water and 250 cc. of isopropanol, gave 42 g. of the pure salt. *Anal.* Calcd. for $C_{11}H_9O_5SLi$: Li, 2.68. Found: Li, 2.91.

Ammonium Salt.—Sulfur dioxide was bubbled into 100 cc. of 28% aqueous ammonia at 5° until fumes were no longer evolved, solid deposited at 0° was filtered off, the clarified solution was shaken at 30° with 17.4 g. of the quinone, undissolved solid was filtered off, the filtrate was concentrated *in vacuo* (bath temperature 50°) to a volume of 75 cc. and the crystalline product (4.5 g.), after recrystallization from 3 cc. of water, yielded the pure salt. *Anal.* Calcd. for $C_{11}H_{13}NO_5S$: N, 5.17. Found: N (1), 5.26; (2) 5.10.

Calcium Salt.—A mixture of the quinone (17.4 g.) and a solution prepared by the action of sulfur dioxide upon a suspension of 3 g. of calcium carbonate in 150 cc. of water was stirred 18 hours in an atmosphere of sulfur dioxide, undissolved solid (0.5 g.) was filtered off and the filtrate was evaporated to dryness *in vacuo* (bath temperature 35–40°). The residue was dissolved in 25 cc. of methanol, 75 cc. of isopropanol was added, the filtered solution was concentrated *in vacuo* until the bisulfite compound separated and the product (9.4 g.) was washed with isopropanol. The air-dried salt sintered and melted at 97–98°, the anhydrous at 115–117° (with decomposition). *Anal.* Calcd. for $C_{22}H_{18}O_{10}S_2Ca$: Ca, 7.33. Found: Ca, 7.29.

LEDERLE LABORATORIES
PEARL RIVER, N. Y. RECEIVED JULY 8, 1943

(1) Moore, THIS JOURNAL, **63**, 2050 (1941).

(2) The crystalline sodium and potassium salts have already been described: (a) Baker, Davies, McElroy and Carlson, *ibid.*, **64**, 1096 (1942); (b) Menotti, *ibid.*, **65**, 1209 (1943).

4,4′-Dicyanobenzaldazine

BY H. J. BARBER AND R. SLACK

In view of continued interest in 4,4′-diamidinostilbene (Stilbamidine), which is finding increasing use for the treatment of Kala-Azar in India[1] and the Sudan,[2] it was considered necessary to investigate the results claimed by Sah,[3] *viz.*, that 4,4′-dicyanostilbene, an intermediate necessary for the production of the drug, could be obtained by thermal decomposition of the corresponding azine. We had already attempted this unsuccessfully in our work on this product,[4] which is most conveniently prepared from 4,4′,α,β-tetrabromodiphenylethane by the action of cuprous cyanide in pyridine.[5]

In no point of detail could his results be confirmed. Three different specimens of *p*-cyanobenzaldehyde (prepared in excellent yield from *p*-

(1) L. E. Napier, P. C. Sen Gupta and G. M. Sen, *Indian Med. Gaz.*, **77**, 321 (1942).

(2) R. Kirk and M. H. Sati, *Ann. Trop. Med. Parasitol.*, **34**, 83 (1940).

(3) Shou-Cheng Fu and P. P. T. Sah, THIS JOURNAL, **64**, 1482 (1942).

(4) S. Bance, H. J. Barber and A. M. Woolman, *J. Chem. Soc.*, 1 (1943).

(5) British Patent 543,204.