TABLE I

Hydroxybenzophenone	Method of prepn.	M. p., °C.[a]	Empirical formula	Analyses, % Calcd. C	Calcd. H	Found C	Found H
3,4-Di-	I	132 (134)	$C_{13}H_{10}O_3$	...	..	...	..
4,4'-Di-	I	210 (210)	$C_{13}H_{10}O_3$	...	..	...	..
3,4,4'-Tri-	I	205	$C_{13}H_{10}O_4$	67.82	4.35	67.70	4.65
2,3,4-Tri-	I	118 (140)[b]	$C_{13}H_{10}O_4$	67.82	4.35	67.66	4.55
2,4,4'-Tri-	I	198 (200)	$C_{13}H_{10}O_4$	...	..	..	..
2',2,4-Tri-	II	138 (134)	$C_{13}H_{10}O_4$	...	..	...	..
2,4',5-Tri-	I	162	$C_{13}H_{10}O_4$	67.82	4.35	67.63	4.56
2',2,5-Tri-	II	98	$C_{13}H_{10}O_4$	67.82	4.35	67.70	4.39
2,3,4,4'-Tetra-	I	219	$C_{13}H_{10}O_5$	63.41	4.06	63.20	3.94
2,4,2',4'-Tetra-	II	180 (193)[c]	$C_{13}H_{10}O_5$	63.41	4.06	63.25	4.07
2,3,4,2',4'-Penta-	II	200 (168) (187)[d]	$C_{13}H_{10}O_6$	59.54	3.82	59.85	3.94
2',4',3,4,5-Penta-	II	253 (200)[e]	$C_{13}H_{10}O_6$	59.54	3.82	59.50	3.94
3',4',2,4,6-Penta-	I	220 (220)	$C_{13}H_{10}O_6$	...	..	...	..
2,3,4,3',4',5'-Hexa-	II	276 (273)	$C_{13}H_{10}O_7$	...	..	...	..
2,3,4,2',3',4'-Hexa-	II	240 (238)	$C_{13}H_{10}O_7$	...	..	...	..

[a] Melting points recorded in literature are enclosed in parentheses. [b] Reported to crystallize with one molecule of water of crystallization.[8] The monobenzoate of pyrogallol is also reported to have a melting point of 140°. [c] Reported to crystallize with 1.5 molecules of water of crystallization.[9] [d] Controversial melting points reported.[10] [e] Heilbron[11] lists this compound as having been reported by Korczynski and Nowakowski,[12] m. p. 242°. These authors reported 3',4',2,4,5-pentahydroxybenzophenone prepared by the Hoesch reaction between protocatechunitrile and 1,2,4-trihydroxybenzene, m. p. 242°.

test piece of skin and a similar piece of skin treated with mimosa tannin under the same conditions. While the piece of skin treated with mimosa tannin was converted to leather, in no case did the samples treated with the polyhydroxybenzophenones show any change. After thorough washing with cold water, and drying in air, these samples were converted to an inflexible, horn-like material characteristic of untreated skin. On storing samples of these test pieces in aqueous media, apparently normal putrefaction occurred.

The data concerning the polyhydroxybenzophenones are presented in tabular form.

(8) Fischer and Rapaport, *Ber.*, **46**, 2393 (1913).
(9) Shoesmith and Haldane, *J. Chem. Soc.*, **125**, 113 (1924).
(10) Atkinson and Heilbron, *ibid.*, 2690 (1926).
(11) Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, 1934.
(12) Korczynski and Nowakowski, *Bull. soc. chim.*, **43**, 335 (1928).

Summary

Fifteen polyhydroxybenzophenones have been prepared and tested for tanning properties. None were found to have the property of converting hide to leather as judged by color, feel, texture, flexibility and fullness, even though one naturally occurring polyhydroxybenzophenone is reported in the literature to cause precipitation of gelatin, a preliminary test for tanning materials.

Four of these compounds have not previously been reported, while physical properties of four others reported in the literature are either controversial or fail to agree with those obtained in this investigation. Analyses are reported for these compounds.

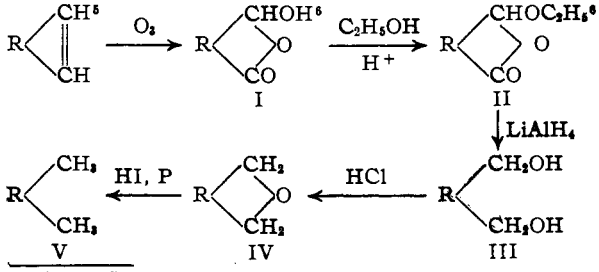
CHAPEL HILL, NORTH CAROLINA RECEIVED MAY 2, 1949

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE OHIO STATE UNIVERSITY]

The Preparation of 4,5-Dimethylphenanthrene[1]

BY MELVIN S. NEWMAN AND HARRY S. WHITEHOUSE[2]

Considerable interest is associated with 4,5-dimethylphenanthrene (V) because of (1) its possible identity with the hydrocarbon,[3] $C_{16}H_{14}$, isolated from the dehydrogenation products of strophanthidin, and (2) its position as the parent hydrocarbon of compounds containing methyl groups in the so-called "impossible" positions.[4] In this paper we describe the preparation of V from pyrene by the steps outlined in the chart.



(1) The material herein presented is taken from the Ph.D. thesis of H. S. W., Ohio State University, December, 1948.
(2) Present address, Procter and Gamble Company, Chemical Division, Ivorydale, Ohio.
(3) Lewis and Biderfield, *J. Org. Chem.*, **5**, 290 (1940); Jacobs and Fleck, *J. Biol. Chem.*, **97**, 57 (1932).
(4) See discussion in Newman, THIS JOURNAL, **62**, 2295 (1940), and Newman and Hussey, *ibid.*, **69**, 3023 (1947).
(5) R, $C_{14}H_8$, represents the phenanthrene nucleus carrying the substituents indicated in positions 4 and 5.
(6) Our reasons for preferring the cyclic structure for these compounds will be set forth in a forthcoming paper.

The ozonization of pyrene was carried out essentially as described previously.[7] The aldehydo acid[6] (I) thus obtained was converted into the ethyl ester[6,8] which was subsequently reduced with lithium aluminum hydride[9] to the diol (III). This diol was converted quantitatively to the cyclic ether (IV) by a variety of acidic reagents. Reduction of IV with hydriodic acid and red phosphorus under very carefully controlled conditions afforded a hydrocarbon, m. p. 76.3–76.9°, which is assigned the structure of 4,5-dimethylphenanthrene (V) on the following counts: (1) analysis of the hydrocarbon, its picrate, and its 2,4,7-trinitrofluorenone[10] (TNF) derivative; (2) cyclodehydrogenation to pyrene; (3) the ultraviolet absorption spectrum and (4) the non-identity of V with any of the fifteen previously described 9,10-unsubstituted dimethylphenanthrenes (there are only sixteen 9,10-unsubstituted dimethylphenanthrenes).

It is interesting to note that V forms a picrate which dissociates very easily in alcohol. This picrate is also lower melting than that of any of the other above mentioned fifteen dimethylphenanthrenes. This behavior is found in other compounds having the same or a similar structural feature.[11]

The ultraviolet absorption spectrum proved similar to that of 1,4,5-trimethylphenanthrene.[11c] The intensity of the absorption, expressed in log units, at the maxima and minima are as follows[12]: 224, 3.91; 230, 3.98; 235, 3.84; 255, 4.56; 285, 3.73; 301, 3.91; 307, 3.82 and 313, 3.92.

One attempt to oxidize V to a quinone was made. As no crystalline quinone was readily isolated, an alcoholic solution of the oxidation product was treated with *o*-phenylenediamine whereupon a yellow crystalline quinoxaline derivative was obtained.

A consideration of the properties of the known dimethylphenanthrenes not containing a substituent in the 9 or 10 position indicates that 4,5-dimethylphenanthrene (V) herein reported is different from any of the others[13] and from the hydrocarbon, $C_{16}H_{14}$, obtained from strophanthidin by Lewis and Elderfield.[8]

Attempts to reduce the aldehyde group of the aldehydo acid (I) to a methyl group are of interest. On Clemmensen reduction 1,2-dihydropyrene[14] was obtained. This ready formation of a carbon–carbon bond between the carbons in the aldehydo acid (I) recalls the fact that on reaction of I with phenylhydrazine 2-phenylazo-1-pyrenol is formed.[7] Treatment of I with alkali and Raney nickel alloy[15] yielded a small amount of the lactone of 5-hydroxymethyl-9,10-dihydro-4-phenanthrenecarboxylic acid, but no acidic material was found. This is surprising in view of the ready hydrogenolysis of carbon–oxygen bonds of the benzyl type usually noted with this reductive system.[15] The lactone ring in VI could be reductively cleaved by refluxing with 47% hydriodic acid, red phosphorus, and 85% phosphoric acid but no pure acid was isolated from the reaction products. The dihydrolactone (VI) was converted into the fully aromatic lactone of 5-hydroxymethyl-4-phenanthrenecarboxylic acid (VII) by heating with sulfur. This lactone (VII) was also formed by refluxing II with toluene and aluminum isopropylate.[16] An attempt to reduce VII with hydriodic acid as with VI failed, VII being recovered quantitatively. Prior to a proposed thioacetal hydrogenolysis,[17] the aldehydo-acid (I) was treated with ethyl mercaptan. Since a compound which we believe to be the CH_3CH_2S-analog of II was obtained further work along this path was discontinued.

The extraordinary ease of cyclization of the dimethanol (III) to the seven-membered cyclic ether (IV) and the resistance of IV to cleavage are noteworthy. Any acidic reagent readily caused the cyclization of III to IV. On passing anhydrous hydrogen bromide through a refluxing solution of IV in toluene, no cleavage was observed, as was also the case on refluxing III with benzene and aluminum bromide. Reaction between hydrogen bromide and fused IV did not set in rapidly until a temperature of 150° was reached, and then a dark tar was formed.

Experimental[18]

Pseudo Ethyl 5-Formyl-4-phenanthrenecarboxylate (II).—A suspension of 8.5 g. of 5-formyl-4-phenanthrenecarboxylic acid,[19] (I) in 50 ml. of alcohol and 100 ml. of benzene containing 5 drops of concentrated sulfuric acid was refluxed on a column with a phase separating head until no further water was obtained. The ester was crystallized from benzene to yield 7.2 g. (76%) of fine silky colorless needles as a first crop, m. p. 177.2–179.2°. The analytical sample melted at 178.8–179.5°. *Anal.* Calcd. for $C_{18}H_{14}O_3$: C, 77.7; H, 5.1. Found[a]: C, 78.0, 77.7; H, 5.5, 5.1.

The same ester was prepared in quantitative yield by treatment of the acid chloride[6] with alcohol in pyridine.

(7) Vollman, *et al.*, *Ann.*, **531**, 1 (1937).

(8) The compound, m. p. 177.5–178°, described by Fieser and Novello, THIS JOURNAL, **62**, 1855 (1940), as the ethyl ester of 4-hydroxymethylphenanthrene-5-carboxylic acid is actually the cyclic ethyl ester of I. We confirmed the identity of these two compounds by a mixed melting point determination with a sample supplied by Dr. L. F. Fieser.

(9) Finholt, Bond and Schlesinger, THIS JOURNAL, **69**, 1199 (1947); Nystrom and Brown, *ibid.*, **69**, 1197 (1947).

(10) Orchin and Woolfolk, *ibid.*, **68**, 1727 (1946).

(11) (a) Cook, *J. Chem. Soc.*, 1592 (1932); (b) Newman and Hussey, THIS JOURNAL, **69**, 3023 (1947); (c) Newman and Wheatley, *ibid.*, **70**, 1913 (1948).

(12) We are indebted to Mrs. Arlene Brooks for these measurements.

(13) "Elsevier's Encyclopaedia of Organic Chemistry," Elsevier Publishing Co., Inc., New York, N. Y., 1946, Vol. 13, p. 800 ff.

(14) E. A. Coulson, *J. Chem. Soc.*, 1298 (1937).

(15) D. Papa, E. Schwenk and B. Whitman, *J. Org. Chem.*, **1**, 587 (1942).

(16) A. L. Wilds in "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, p. 178.

(17) M. L. Wolfrom and J. Karabinos, THIS JOURNAL, **66**, 909 (1944).

(18) All melting points corrected except as otherwise noted. Analyses marked [k] by Mrs. E. H. Klotz, O. S. U., [p] by W. J. Polglase, O. S. U., [a] Arlington Laboratories, Fairfax, Va., [c] H. S. Clark, Microanalytical Laboratory, Urbana, Illinois, and [s] by G. L. Stragand, University of Pittsburgh.

(19) Prepared as described on p. 148 of ref. 7.

4,5-Phenanthrenedimethanol (III).—A warm solution of 5.0 g. of II in 250 ml. of dry sulfur-free benzene was added to a stirred solution containing 0.5 g. of lithium aluminum hydride in 100 ml. of ether. After careful hydrolysis at 0° with water and then dilute sulfuric acid, III was isolated in 90% yield as colorless crystals, m. p. 156–162°. It proved quite tedious to purify this product to its maximum melting point, 164.4–168.8°, by recrystallization from benzene as small amounts of an impurity, evidently the cyclic ether (IV) persisted. III crystallized in rosettes of stout faintly straw-colored elongated prisms. The dibenzoate, dense colorless prisms, m. p. 152.8–154.2°, was prepared in pyridine at 0° using benzoyl chloride and was recrystallized from petroleum ether, b. p. 90–97° (Skellysolve C). *Anal.* Calcd. for $C_{16}H_{14}O_2$: C, 80.7; H, 5.9. Found[a]: C, 80.4, 80.6; H, 6.0, 6.0. Active hydrogen: 2.0. Found (Zerewitinow): 1.8, 1.9. Calcd. for $C_{30}H_{22}O_4$: C, 80.7; H, 5.0. Found[k]: C, 81.3, 80.8; H, 5.1, 5.1.

Cyclic Ether of 4,5-Phenanthrenedimethanol (IV).—Anhydrous hydrogen chloride was passed into a suspension of 2.87 g. of III in 20 cc. of benzene at room temperature for fifteen minutes, during which the glycol disappeared, heat was evolved, and droplets of water were formed. The crude product was vacuum distilled to yield 2.41 g. (90%) of colorless IV, m. p. 72.8–76.2°, b. p. 168–169° at 1 mm. An analytical sample, recrystallized from methanol, melted at 78.5–78.8°. This ether was the main product when the glycol was treated under the following conditions: thionyl chloride in benzene–pyridine; phosphorus pentasulfide in refluxing benzene (on fusion with this reagent a violent reaction took place and no pure product was isolated); anhydrous hydrogen bromide in boiling benzene or with molten III; and *p*-toluenesulfonyl chloride in pyridine at 0°. The TNF[10] complex of IV formed orange elongated prisms, m. p. 194–195° after recrystallization from alcohol–benzene. *Anal.* Calcd. for $C_{16}H_{12}O$: C, 87.3; H, 5.5. Found[p]; C, 87.2, 87.2; H, 5.7, 5.6. Calcd. for $C_{29}H_{17}O_8N_3$: C, 65.1; H, 3.2; N, 7.9. Found[c]: C, 64.9, 65.1; H, 3.3, 3.1; N, 8.1, 8.1.

4,5-Dimethylphenanthrene (V).—In one of the better of many runs a mixture of 3.0 g. of IV, 1.5 g. of red phosphorus, and 30 ml. of 47% hydriodic acid was sealed in a tube and heated at 165° for twelve hours. Vacuum distillation at 1 mm. of the organic reaction product afforded 0.73 g. (26%) of crude V, m. p. 66–72°. There remained a large quantity of viscous non-volatile residue in the distilling flask. The crude product was converted to the TNF derivative[10] which was recrystallized once from ethanol. By chromatography over alumina the TNF derivative was decomposed and the resulting hydrocarbon was recrystallized from methanol to yield 0.47 g. (17%) of V, m. p. 76.0–76.8°. Further recrystallization from methanol yielded the analytical sample, m. p. 76.3–76.9°, as small colorless crystals. The recrystallized TNF derivative formed glistening scarlet needle-shaped crystals, m. p. 120.4–121.4° after several recrystallizations from alcohol. *Anal.* Calcd. for $C_{16}H_{14}$: C, 93.2; H, 6.8. Found[c]: C, 92.9, 92.8; H, 6.8, 6.8. Calcd. for $C_{29}H_{19}O_7N_3$: C, 66.8; H, 3.7; N, 8.1. Found[c]: C, 66.7; H, 3.6; N, 8.2.

The picrate was best formed by dissolving 0.103 g. of V and 0.115 g. of pure picric acid in alcohol. On standing at room temperature orange-red elongated prisms separated. These were collected on a small suction funnel and rinsed with small amounts of ice-cold alcohol. They melted sharply at 109.6–110.2°. *Anal.* Calcd. for $C_{22}H_{17}O_7N_3$: C, 60.7; H, 3.9; N, 9.7. Found[c]: C, 60.6, 60.7; H, 3.9, 3.9; N, 9.8, 10.0.

The separation of unreacted ether (IV) from V was effected most easily by conversion to the TNF derivatives, that of the ether (IV) being much less soluble. Considerable amounts of IV were present in hydriodic reductions which were run at lower temperatures than 165° or at this temperature for less than twelve hours. When reductions were attempted at 180–190° less V and more non-volatile residue were produced.

Conversion of V to Pyrene.—A mixture of 0.20 g. of V and 2 g. of selenium was heated for 18 hours at 300–310°. The mixture was extracted with boiling toluene. After removing the toluene the residue was sublimed and the sublimate treated with TNF to yield 20 mg. of the TNF derivative of pyrene, m. p. 228–234° (4.2%). Recrystallization from 95% alcohol yielded 12 mg. of the TNF derivative of pyrene, m. p., alone and mixed with authentic material,[10] 239–240°.

Oxidation of V.—To a warm (about 40°) solution of 0.5 g. of V in 5 cc. of acetic acid was added dropwise a solution of 1.0 g. of chromic anhydride in 5 cc. of acetic acid. After shaking as long as an exothermic reaction was noticed the reaction mixture was poured on ice. The organic oxidation product was taken into ether–benzene. Removal of the solvent yielded an oil which could not be crystallized. When dissolved in a small amount of alcohol and treated with alcoholic *o*-phenylenediamine, a yellow precipitate separated. After three recrystallizations from alcohol there was obtained 30 mg. of the quinoxaline derivative as yellow crystals, m. p. 171.8–172.8°. *Anal.* Calcd. for $C_{22}H_{16}N_2$: C, 85.7; H, 5.2; N, 9.1. Found[s]: C, 85.4, 85.6; H, 5.1, 5.3; N, 8.6, 8.7.

Reduction of I.—A mixture of 8.0 g. of I, 50 ml. of acetic acid, 50 ml. of concentrated hydrochloric acid, 25 ml. of toluene and 20 g. of amalgamated zinc was heated to reflux for seventy-two hours during which time an additional 36 ml. of hydrochloric acid was added. From the reaction products was obtained 3.8 g. (58%) of 1,2-dihydropyrene, m. p. 127–131°. On recrystallization from alcohol there was obtained pure 1,2-dihydropyrene, m. p. 131.0–132.0°, which formed a picrate melting at 145–147°. These constants agree with those previously reported.[14]

The unchanged starting material was recovered after attempts at high pressure hydrogenation of I or II over copper chromite (37 KAF[20]) in absolute alcohol at 130° and 2000 p. s. i. Similarly, I was recovered unchanged after refluxing with 47% hydriodic acid and 85% phosphoric acid for three days.

When 15.0 g. of Raney nickel–aluminum was added in small portions during one hour to a stirred solution at 90° of 5 g. of I in 200 ml. of 10% sodium hydroxide there was obtained from the neutral product (4.54 g.) 1.59 g. (34%) of the lactone of 9,10-dihydro-5-(hydroxymethyl)-4-phenanthrenecarboxylic acid (VI), m. p. 156.0–156.8°. Attempts at further reduction of VI using the Raney alloy method[15] or the hydriodic–phosphoric acid procedure above described failed to yield crystalline material. *Anal.* Calcd. for $C_{16}H_{12}O_2$: C, 81.3; H, 5.1. Found[p]: C, 81.4, 81.5; H, 4.8, 5.0.

Lactone of 5-(Hydroxymethyl)-4-phenanthrenecarboxylic Acid (VII).—Heating 0.23 g. of VI with 0.03 g. of sulfur at 230–235° for one hour afforded crude VII, m. p. 167–175°, in 66% yield. The analytical sample, purified by alkaline hydrolysis, acidification and recrystallization from alcohol, melted at 177.2–178.0°. The same lactone was obtained in 56% yield on slow distillation of a mixture of 2.78 g. of II, 2.04 g. of aluminum isopropoxide and 150 ml. of toluene until a test[16] for acetone in the distillate was negative. VII was recovered quantitatively from an attempted reduction with hydriodic–phosphoric acids as above described. *Anal.* Calcd. for $C_{16}H_{10}O_2$: C, 82.1; H, 4.3. Found[k]: C, 82.1, 82.1; H, 4.2, 4.3.

Pseudo Ethyl 5-Formyl-4-phenanthrenecarbothiolate.—To a stirred mixture at 0° of 10 ml. of ethyl mercaptan, 1.0 g. of freshly fused zinc chloride and 1 g. of anhydrous sodium sulfate was added, in portions, 0.5 g. of powdered I. After stirring for 14 hours at room temperature the mixture was diluted with ether–benzene and the organic layer washed well with 10% sodium hydroxide, water and saturated salt solution. No acidic material was recovered from the alkaline extract. After removal of the solvent and recrystallization of the residue from alcohol there was obtained a small amount (24%) of the crystalline thioester, m. p. 150.8–152.4°. The analytical sample melted at 152.2–153.0°. No further experiments were carried out on the compound. An attempt to prepare the butyl thio-

(20) R. Connor, K. A. Folkers and H. Adkins, THIS JOURNAL, **54**, 1138 (1932).

ester in a similar manner failed. *Anal.* Calcd. for $C_{18}H_{14}O_2S$: C, 73.4; H, 4.8. Found: C, 73.6, 74.0; H, 5.0, 4.9.

Summary

The preparation of 4,5-dimethylphenanthrene from pyrene is described. The steps involved are: (1) ozonization to 5-formyl-4-phenanthrenecarboxylic acid, (2) esterification, (3) reduction to 4,5-phenanthrenedimethanol, (4) cyclization to the corresponding cyclic ether and (5) reduction to 4,5-dimethylphenanthrene.

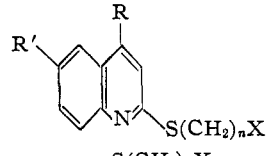
RECEIVED MAY 9, 1949

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

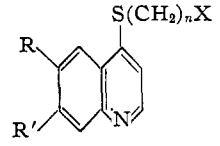
Some Dialkylaminoalkylmercaptoquinolines

BY HENRY GILMAN AND MARY ALYS PLUNKETT[1]

In connection with some studies on the pharmacological activity of certain mercapto quinolines, a series of dialkylaminoalkylmercaptoquinolines has been prepared. It seemed of interest to introduce into nuclei which have chemotherapeutic potentialities certain alkylamino groupings connected directly to the nuclei by a sulfur atom. The quinoline derivatives are of types I and II. Compounds of these types are reported by Bachman, *et al.*,[2] and by Clinton and Suter.[3]

(I) 

Where R is methyl, hydrogen or carboxy; R′ is methoxy or hydrogen; X is diethylamino, N-piperidyl or N-morpholyl; *n* is 2 or 3.

(II) 

Where R is methoxy or hydrogen; R′ is chloro or hydrogen; X is diethylamino, N-piperidyl or N-morpholyl; *n* is 2 or 3.

The compounds reported were prepared by condensation of the appropriate chloroquinoline with the sodium alkyl mercaptide or by condensation of the sodium quinolyl mercaptide with the appropriate alkyl chloride. In general, absolute ethanol was used as solvent for the condensations involving chloroquinolines. In the case of 2-chloro-4-methyl-6-methoxyquinoline it was found that the reflux temperature of methyl cellosolve was necessary for condensation. Reactions using the quinolyl mercaptides were carried out in a 1:1 mixture of ethylene glycol and methyl cellosolve.

In the preparation of 6-methoxy-2-(β-diethylaminoethylmercapto)-quinoline both the quinolyl and the alkyl mercaptides were used. Similar yields were obtained in the two cases. 6-Methoxy-4-methyl-2-(γ-diethylaminopropylmercapto)-quinoline was prepared by treating a mixture of γ-diethylaminopropylisothiouronium chloride hydrochloride and 2-chloro-4-methyl-6-methoxyquinoline in methyl cellosolve with excess sodium ethoxide. The same compound was obtained from the alkyl mercaptide and the chloroquinoline.

In general, the mercaptoquinolines were isolated as the hydrochlorides in yields varying from 23–75%. The compounds prepared are listed in Table I. Details of the preparation of typical compounds are given in the experimental section. The sodium alkyl mercaptides were prepared in accordance with procedures described earlier from the corresponding alkyl chloride[4] or by the isothiouronium salt synthesis.[5]

Most of these compounds have been tested for their pharmacological activity toward malaria-causing plasmodia. Results of these tests will be reported elsewhere.

The authors are grateful to William Meikle for assistance and to Parke Davis and Co. for arranging for the tests.

Experimental

6-Methoxy-2-(β-diethylaminoethylmercapto)-quinoline.—A solution of 5 g. (0.04 mole) of β-diethylaminoethyl chloride and 0.02 mole of the sodium salt of 2-mercapto-6-methoxyquinoline in absolute ethanol was refluxed for four hours. After removal of the solvent the residue was dissolved in ether, dried over anhydrous sodium sulfate and treated with ethereal hydrogen chloride. Recrystallization of the dihydrochloride from absolute ethanol gave a product melting at 168–170° which was identical with that obtained from the reaction of sodium β-diethylaminoethyl mercaptide and 2-chloro-6-methoxyquinoline.[6]

4-Methyl-2-[β-(N-piperidyl)-ethylmercapto]-quinoline.—This compound was prepared by a method analogous to the above procedure from N-β-chloroethylpiperidine[7] and 2-mercapto-4-methylquinoline[8] using a 1:1 mixture of ethylene glycol and methyl cellosolve as solvent. The free base deposited from an ether solution as crystals melting at 75–76°.

The corresponding N-morpholyl compound, as well as the intermediates[9] for the reaction, were prepared in a similar manner.

2-Mercapto-6-methoxyquinoline.—This compound was prepared with some modification, according to the directions of John[10] for the preparation of 4-mercapto-6-methoxyquinoline.

(1) Present address: Vassar College, Poughkeepsie, New York.

(2) Bachman, Welton, Jenkins and Christian, THIS JOURNAL, **69**, 366 (1947).

(3) Clinton and Suter, *ibid.*, **70**, 491 (1948).

(4) Gilman, Plunkett, Tolman, Fullhart and Broadbent, THIS JOURNAL, **67**, 1845 (1945); Gilman and Woods, *ibid.*, **67**, 1844 (1945).

(5) Albertson and Clinton, THIS JOURNAL, **67**, 1222 (1945); L. Fullhart, unpublished studies, Iowa State College.

(6) Magidson and Rubtsov, *J. Gen. Chem. (U. S. S. R.)*, **7**, 1896 (1937) (*C. A.*, **32**, 564 (1938)).

(7) I. G. Farbenindustrie, French Patent 802,416 (1936) (*Chem. Zentr.*, **107**, II, 4255 (1936)).

(8) Rosenhauer, *Ber.*, **62**, 2732 (1929).

(9) Mason and Block, THIS JOURNAL, **62**, 1443 (1940).

(10) John, *J. prakt. Chem.*, [2] **128**, 218 (1930).