hexahydroxy-biphenyltetramethyl ether, obtained by Hayduck[4] on bromination of the diacetate of hydrocedriret and subsequent hydrolysis of that product.

Anal. Subs., 0.1149: AgBr, 0.0924. Calcd. for $C_{16}H_{16}O_6Br_2$: Br, 34.45. Found: 34.22.

OXIDATION OF 3-BROMO-4,5-DICHLOROPYROGALLOL-2,6-DIMETHYL ETHER.—This was effected by dissolving 5 g. of the phenol in 200 cc. of glacial acetic acid and adding 2.5 g. of chromium trioxide. After one-half hour, the solution was poured into about 400 cc. of water, from which 3-bromo-5-chloro-2,6-dimethoxy-*p*-benzoquinone separated; yield, 45%.

3-Bromo-5-chloro-2,6-dimethoxy-*p*-benzoquinone.—This was recrystallized from glacial acetic acid, forming red, scale-like crystals. It melts at 164–165° and is soluble in most organic solvents, save ligroin. It is insoluble in water. It is identical with the substance obtained on chlorination of 3-bromo-2,6-dimethoxy-*p*-benzoquinone, dissolved in chloroform.

Anal. Subs., 0.1743, 0.0942: mixed halides, 0.2050, 0.1102. Calcd. for $C_8H_6O_4BrCl$: Br, 28.46; Cl, 12.45. Found: Br, 28.39, 28.40; Cl, 12.74, 12.60.

Summary

It has been shown that the first substituent bromine atom enters the *meta* position to the hydroxyl in pyrogallol-2,6-dimethyl ether. That is, the combined orienting effect of the two methoxy groups is greater than that of the hydroxyl.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF LOUISVILLE]

CONDENSATION OF 9-METHYLACRIDINE WITH FORMALDEHYDE AND THE PREPARATION OF ACRIDINE-9-CARBOXYLIC ACID

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Introduction

It is known that the methyl group of 9-methylacridine forms condensation products with aldehydes.[1]

The first possible reaction will give a condensation product of the aldol type; the second reaction takes place with elimination of water.

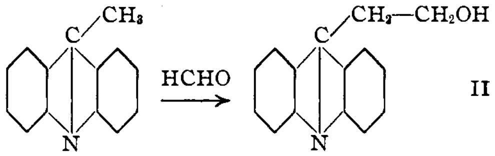
The present investigation was undertaken with a view to prepare condensation products of methylacridine with formaldehyde in order to use these products as starting material in the preparation of acridine-9-carboxylic acid.

Koenig tried to condense methylacridine with formaldehyde but was unable to secure a crystalline product.[1b] The authors chose conditions

[4] Hayduck, *Ber.*, **9**, 929 (1876).

[1] (a) Bernthsen, *Ber.*, **20**, 1541 (1887). (b) Koenig, *Ber.*, **32**, 3599 (1899). (c) Friedländer, *Ber.*, **38**, 2840 (1905). (d) Porai-Koschitz, *Chem. Centr.*, **1907**, [II] 1528. (e) Kaufmann, *Ber.*, **45**, 1737 (1912).

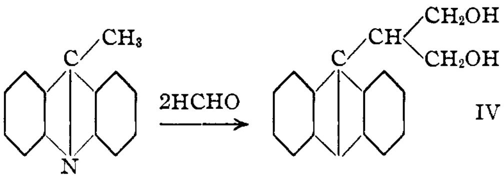
under which the condensation should yield the monomethylol derivative according to Formulas I and II.



I

II

A crystalline product was obtained confirming this composition. Working with an excess of formaldehyde and by longer heating the dimethylol derivative was formed in good yield. This substance Koenig had obtained as only a by-product in his experiments.



III

IV

Attempts to oxidize the condensation products with nitric acid gave only a small amount of the acid derivative; the main products were nitro compounds; but the oxidation with potassium dichromate in sulfuric acid solution gave the acridine-9-carboxylic acid in good yield. This method of preparing the acid should be more convenient than that of Bernthsen.[1a]

Experiments to oxidize 9-methylacridine directly to acridine-9-carboxylic acid yielded only unchanged starting materials.

Further experiments of the condensation of 9-methylacridine with other aldehydes are in progress at the present time.

Experimental Part

Preparation of Acridyl Monomethylol.—Ten g. of 9-methylacridine was treated with 10 cc. of 20% formaldehyde solution and the mixture heated on the water-bath for four hours and allowed to stand overnight. The condensation product which precipitated in a solid form was filtered off and well washed with water. When recrystallized from 75% alcohol, the product precipitated in fine, yellow needles; m. p., 155–156°; yield, 75%. The crystals were insoluble in water and ether, and difficultly soluble in alcohol and benzene.

Anal. Calcd. for $C_{15}H_{13}ON$: C, 80.71; H, 5.83. Found: C, 80.59; H, 6.00.

HYDROCHLORIDE.—This was prepared in alcohol containing some hydrochloric acid and recrystallized from alcohol; it separated in yellow needles; m. p., 240–260°, with decomposition. The yellow needles were soluble in water, difficultly soluble in alcohol and insoluble in ether.

Anal. Calcd. for $C_{15}H_{13}ON.HCl$: Cl, 13.68. Found: 13.77.

PICRATE.—This was prepared in an alcoholic solution with alcoholic picric acid solution. The compound separated from alcohol in golden-brown, short needles; m. p., 186°.

Anal. Calcd. for $C_{15}H_{13}ON.OHC_6H_2(NO_2)_3$: C, 55.74; H, 3.54. Found: C, 55.9; H, 3.66.

BENZOYL DERIVATIVE.—By shaking the acridyl monomethylol with benzoyl chloride in 10% sodium hydroxide solution the benzoyl derivative is formed; this separated from alcohol in silky leaves; m. p., 159°.

Anal. Calcd. for $C_{22}H_{17}O_2N$: C, 80.73; H, 5.20. Found: C, 80.65; H, 5.33.

Preparation of Acridyl Dimethylol.—Four g. of 9-methylacridine was heated with 3 cc. of 40% formaldehyde solution during eight hours on the water-bath. The working up of the condensation product is the same as in the preparation of the mono derivative. It separated from alcohol in fine sulfur-yellow needles; m. p., 194°.

Anal. Calcd. for $C_{16}H_{15}O_2N$: C, 75.89; H, 5.93. Found: C, 75.77; H, 6.08.

HYDROCHLORIDE.—This formed fine, dark yellow needles; m. p., 250–265°, with decomposition.

Anal. Calcd. for $C_{16}H_{15}O_2N.HCl$: Cl, 12.26. Found: 12.35.

PICRATE.—This was prepared in alcoholic solution, and purified by crystallization from alcohol, when it was obtained as short, yellow needles; m. p., 195°.

Anal. Calcd. for $C_{16}H_{15}O_2N.OHC_6H_2(NO_2)_3$: C, 54.77; H, 3.74. Found: C, 54.92; H, 4.02.

Oxidation of Acridyl Monomethylol.—A solution of 2 g. of acridyl methylol in dil. (1:5) sulfuric acid was heated on the water-bath and to it a solution of 2.5 g. of chromium trioxide in 4 g. of concd. sulfuric acid and 10 cc. of water was gradually added. After all of the chromic acid had been added the solution was heated for another hour on the water-bath, then diluted with water and filtered. The precipitate was extracted with diluted sodium hydroxide solution, filtered and the filtrate acidified faintly with acetic acid. The acridine-carboxylic acid precipitated as a yellow powder.

The properties of the acid agree with those stated by Bernthsen.[2]

The acid can be recrystallized from pyridine. It separates in shiny, yellow needles; m. p., 300°, with decomposition to acridine and carbon dioxide.

Anal. Calcd. for $C_{14}H_9O_2N$: C, 75.34; H, 4.04. Found: C, 75.20; H, 4.19.

Summary

A method is given for the preparation of the 9-mono- and dimethylol derivatives of acridine. By oxidation of the monomethylol derivative with chromic acid, acridine-9-carboxylic acid can be prepared in a good yield.

LOUISVILLE, KENTUCKY

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[2] Ref. 1 a, p. 1549.