isolated. When the mixture was heated at 150° for a short time no change occurred, but longer heating at this temperature, or for a few minutes at 153°, gave the 1-phenyl-urazole as the sole product.

Summary.

(1) A study has been made of the progressive action of primary amines on methyl and ethyl allophanate which has resulted in the isolation of aryl allophanic esters, mono- and di-aryl biurets and mono- and di-substituted ureas.

(2) Phenylhydrazine has been found to give 1-phenyl-4-carbethoxy-semicarbazide and 1-phenyl-urazole. The investigation is being continued in this laboratory.

LAWRENCE, KANSAS.

[CONTRIBUTION FROM THE LABORATORY OF WERNER DRUG AND CHEMICAL CO.]

THE METHIODIDES OF THE CONDENSATION PRODUCTS OF SOME CYCLIC ALDEHYDES WITH QUINALDINE AND ALPHA PICOLINE, AND THEIR POSSIBLE VALUE AS INDICATORS IN ACIDIMETRY.

BY LOUIS F. WERNER.

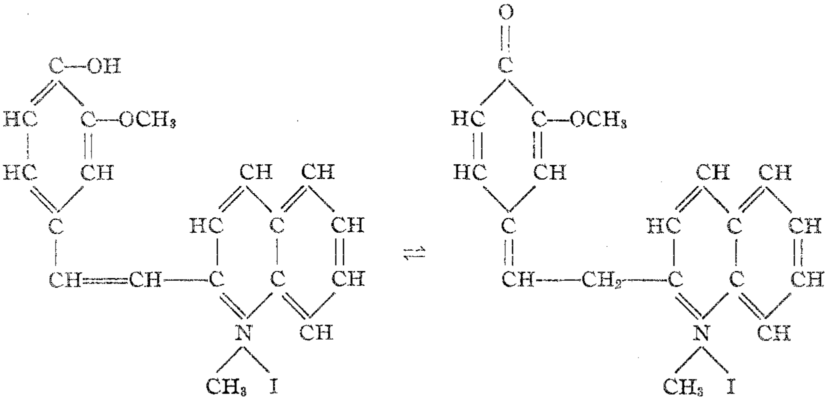
Received July 16, 1920.

The aqueous solution of the methiodide of 2(3-methoxy-4-hydroxy-styryl)quinoline when treated with sodium hydroxide solution was found to give a deep fuchsine-colored fluid, instead of the anticipated precipitate of the quaternary-ammonium hydroxide. As the hydrochloride of 2(3-methoxy-4-hydroxy-styryl)quinoline under like conditions gave but a milky emulsion of the free base, the color noted must be due to the auxochrome effect of the methyl group attached to nitrogen.

Following up these results, the methiodides of the condensation products of various cyclic aldehydes with quinaldine were prepared, and their behavior with sodium hydroxide determined. The methiodides of the condensation products of quinaldine with benzaldehyde, furfural, *o*-hydroxy-benzaldehyde, *p*-hydroxy-benzaldehyde, protocatechuic aldehyde, and also the condensation product of piperonal with α-picoline, were prepared and studied.

The results secured showed that in order that the methiodides of compounds of this type have the properties of an indicator, that there be a phenolic hydroxyl group attached to the neucleus of the aldehyde used in its preparation. Thus in the case of the methiodides of 2-styryl-quinoline, 2(β-furfuryl-vinyl)quinoline, 2(4,3-methylene-dioxyl)pyridine, the yellow-aqueous solutions of these salts were rendered colorless upon the addition of sodium hydroxide solution, but the methiodides of 2(2-hydroxy-styryl)quinoline and of 2(4-hydroxy-styryl)quinoline gave a blood-red coloration, and the methiodide of 2(3-methoxy-4-hydroxy-styryl)quinoline gave a fuchsine-red colored solution, and the methiodide of 2(3,4-dihydroxy-styryl)quinoline gave a grape-colored solution.

The probable effect of the alkali upon those compounds which show this color change is to cause a molecular rearrangement, to give a quinone,



A few preliminary tests carried out to determine the possibility of using these compounds as indicators, indicated that they may be used as such, provided that the hydriodic acid first formed by their hydrolysis in water be neutralized with alkali.

Experimental.

2(β-Furfuryl-vinyl)quinoline, $C_4H_3O.C_2H_2.C_9H_6N$.—Quinaldin, 9 g., and furfural, 6 g., were heated in the presence of 2 g. of anhydrous zinc chloride upon the boiling water-bath for 5 hours. Water, and then a slight excess of hydrochloric acid was added, and steam passed into the mixture until all but tar was dissolved. The solution was filtered hot through a wetted filter, and conc. hydrochloric acid added to the cooled filtrate. The precipitated hydrochloride was filtered out as an orange-colored powder, dissolved in water, filtered, and reprecipitated with hydrochloric acid. The free base was finally secured by dissolving the hydrochloride in water and carefully adding ammonium hydroxide, filtering from the tarry impurities which precipitate first. The free base is recrystallized from ligroin. M. p. (corr.) 56°. The base is soluble in all the ordinary organic solvents.

Subs., 0.3823: 23.4 cc. N (over 30% KOH at 27° and 749 mm.).
Clac. for $C_{15}H_{11}ON$: N, 6.33. Found: 6.69.

2(β-Furfuryl-vinyl)quinoline methiodide, $C_4H_3O.C_2H_2.C_{10}H_9NI$.—This substance was prepared by heating 3 g. of 2(β-furfuryl-vinyl)quinoline with an excess of methyl iodide in a sealed tube in the dark, at a temperature of 140°. It was necessary to heat for 4 to 5 hours, an oil-bath being used. The contents of the tube were then recrystallized from water, and the salt was secured as orange colored needles, having a steel-blue iridescence when viewed in natural light. The substance is soluble in hot alcohol and hot water, but is practically insoluble in the usual organic solvents. M. p. (corr.) 226.2°.

An aqueous solution of this salt is lemon-yellow in color under neutral or acid conditions, and colorless in the presence of alkalies, but the change in color is so slight as to give it no value as an indicator.

Subs., 0.5878; 22.4 cc. N (over 30% KOH at 27° and 746 mm.).
Calc. for $C_{16}H_{14}ONI$: N, 3.86. Found: 4.15.

2(3,4-Methylene-dioxy-styryl)pyridine methiodide, $C_7H_5O_2.C_2H_2.C_6H_8NI$.—2(3,4-Methylene-dioxy-styryl)pyridine[1] and an excess of methyl iodide were heated in a boiling water-bath in the dark for 4 hours. The contents of the bomb tube were then recrystallized from water, the salt being secured as a lemon-colored microcrystalline powder. It is soluble in hot water, alcohol, and acetone, but is but slightly soluble in the usual organic solvents. M. p. (corr.) 276°.

An aqueous solution of this salt is yellow in aqueous acid or neutral solution and colorless in alkaline solution, but the substance has no value as an indicator.

Subs., 0.5029: 19.2 cc. N (over 30% KOH at 27° and 732 mm.).
Calc. for $C_{15}H_{14}O_2NI$: N, 3.82. Found: 4.08.

2-Styryl quinoline methiodide, $C_6H_5.C_2H_2.C_{10}U_9NI$.—2-Styryl-quinoine[2] and an excess of methyl iodide were heated in a sealed tube in the dark for 4 hours in a boiling water-bath. The contents of tube were recrystallized from water, and the salt was secured as acicular bright orange-colored crystals. It is soluble in hot water and alcohol, but only slightly soluble in the common organic solvents. M. p. (corr.) 235.2° with decomposition.

A solution of this substance in neutral or acid aqueous solution is a faint yellow, but is rendered colorless by adding alkali. It is of no service as an indicator.

Subs., 0.5881: 21.4 cc. N (over 30% KOH at 27° and 735 mm.).
Calc. for $C_{13}H_{16}NI$: N, 3.75. Found: 3.91.

2(2-Hydroxy-styryl)quinoline methiodide, $C_6H_5O.C_2H_2.C_{10}H_9NI$. — 2(2-Hydroxy-styryl)quinoline[3] and an excess of methyl iodide were heated in a sealed tube in the dark at 135° to 140°. The contents of the tube were recrystallized from water, and it was thus secured as a bright orange-colored crystalline powder. It is soluble in hot water and hot alcohol, slightly soluble in other organic solvents. M. p. (corr.) 236°.

One cc. of a 0.1% solution in 250 cc. of water was turned to a blood-red

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[1] Thiemich, *Ber.*, **30**, 1578 (1897).

[2] Wallach and Wuesten, *ibid.*, **16**, 2008 (1883).

[3] Dzierzgowski, *ibid.*, **27**, 1980 (1894).

color upon the addition of a drop of 0.1 *N* sodium hydroxide solution but the color reverted to pale lemon upon standing, for a few seconds. Not until 0.4 cc. of the alkali had been added was the blood-red color permanent. This behavior is due undoubtedly to the fact that a certain amount of alkali is needed to neutralize the hydriodic acid formed by the hydrolysis of the salt.[1] It was found that the blood-red color was discharged by 0.12 cc. of 0.1 *N* hydrochloric acid, but it returned upon adding again 0.1 cc. of 0.1 *N* sodium hydroxide solution. To use this substance as an indicator, it would be necessary therefore, to "sensitize" the solution by the addition of the proper amount of sodium hydroxide to overcome this acidity, analogous to the addition of hydrochloric acid to the sodium salt of helianthin (methyl orange).

Subs., 0.6100: 21.1 cc. N (over 30% KOH at 25° and 745 mm.).
Calc. for $C_{18}H_{10}ONI$: N, 3.60. Found: 3.81.

2(4-Hydroxy-styryl)quinoline methiodide, $C_6H_5O.C_2H_2.C_{10}H_9NI$.—Methyl iodide in excess was heated with 2(4-hydroxy-styryl)quinoline[2] in an oil-bath at 140° in the dark. Recrystallized from water, the substance is secured as a bright orange-colored crystalline powder. It is soluble in hot alcohol and hot water, but is only slightly soluble in other solvents. M. p. (corr.) 250.8° with decomposition.

Tested as the preceding compound as to its value as an indicator, it gave similar results, it giving a lemon-yellow solution in presence of acids and in neutral solutions, and a blood-red solution in the presence of alkalies.

Subs., 0.6181: 20.2 cc. N (over 30% KOH at 26° and 743 mm.).
Calc. for $C_{18}H_{16}ONI$: N, 3.60. Found: 3.52.

2(4-Hydroxy-3-methoxy-styryl)quinoline methiodide, 4,3-$OH.OCH_3$.-$C_6H_3.C_2H_2.C_{10}H_9NI$.—This substance was prepared by heating 2(4-hydry-3-methoxy-styryl)quinoline[3] with an excess of methyl iodide in the dark in a boiling water-bath. The product is a brick-red crystalline powder, slightly soluble in hot water and alcohol, practically insoluble in other solvents. It was powdered and purified by extracting 3 times with boiling 95% alcohol to remove tar and any unchanged base. M. p. 267° (corr.) with decomposition.

Upon determining the sensitivity of this compound to acids and bases, it was found that 0.4 cc. of 0.1 *N* sodium hydroxide solution was required to secure a permanent fuchsine-red colored solution, using a mixture of one cc. of 0.1% solution to 250 cc. of water, but only 0.1 cc. of 0.1 *N*

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[1] Compounds of this type, despite the common conception that quaternary ammonium compounds are all strong bases, are on the contrary very weak bases, and those containing no phenolic group are readily precipitated from their strong aqueous solutions of their salts by ammonium hydroxide.

[2] Wallach and Wuesten, *Ber.*, 16, 2009 (1883).

[3] Nencki, *ibid.*, 27, 1974 (1894).

hydrochloric acid was required to turn it to the neutral lemon-yellow color. This dye also would require sensitizing with sodium hydroxide solution before it would serve as an indicator.

Subs., 0.6041: 19.70 cc. N (over 30% KOH at 26° and 749 mm.).
Calc. for $C_{19}H_{18}O_2NI$: N, 3.34. Found: 3.59.

2(3,4-Dihydroxy-styryl) quinoline, $4,3(OH)_2.C_6H_3.C_2H_2.C_9H_6N$.—This was prepared by heating 4.6 g. of protocatechuic aldehyde, 4.8 g. of quinaldin and 2 g. of zinc chloride upon a boiling water-bath until the mass was nearly solid. The paste was then dissolved in water and a little hydrochloric acid, and filtered hot. The hydrochloride was then precipitated by adding an excess of hydrochloric acid, and cooling, and was recrystallized in this manner several times, and the free base secured in a pure condition by adding 5 cc. of glacial acetic acid to the solution, and then carefully adding ammonium hydroxide solution to the appearance of the first permanent turbidity. Upon cooling and agitating well, the tarry impurities were precipitated, and filtered out. The brilliant clear solution was then treated with steam, resulting in the hydrolysis of the acetate, and the precipitation of the free base. This is a very pretty example of progressive hydrolysis, as the bright red color of the acetate rapidly fades as the temperature rises, and is followed by the precipitation of the free base. This last operation is repeated, thus securing the compound in a pure condition. M. p. 244.6° (corr.). The base is slightly soluble in alcohol, acetone and benzol, but not sufficiently to be purified by recrystallization.

Subs., 0.3390: 15.4 cc. N (over 30% KOH at 21° and 746 mm.).
Calc. for $C_{17}H_{13}O_2N$: N, 5.32. Found: 5.32.

2(3,4-Dihydroxy-styryl)quinoline methiodide, $4,3\text{-}(OH)_3.C_6H_3.C_{10}H_9NI$.—This was prepared by heating 2(3,4-dihydroxy-styryl-quinoline in a sealed tube with an excess of methyl iodide at 140° in an oil-bath for 5 hours, protected from the light. The salt was recrystallized from water as a brownish-orange powder, soluble in hot water and alcohol, slightly soluble in cold alcohol and water, and other usual solvents. M. p. 266.8° (corr.) with decomposition.

Upon testing the approximate sensitivity of this salt to alkalies and acids, it was found that to secure a permanent grape-colored solution, 0.4 cc. of 0.1 *N* sodium hydroxide solution was required in a mixture of one cc. of a 0.15% solution in 250 cc. of water, which was converted to the original lemon-yellow colored solution by the addition of 0.1 cc. of 0.1 *N* hydrochloric acid. This indicator would also require sensitizing to fit it for practical use.

Subs., 0.6069: 19.0 cc. N (over 30% KOH at 27° and 749 mm.).
Calc. for $C_{18}H_{16}O_2NI$: N, 3.46. Found: 3.43.

Summary.

The work showed that the addition of a methyl group to the nitrogen atom of the condensation products of the *ortho*- and *para*-hydroxy aromatic aldehydes with quinaldin gave these compounds the properties of indicators, but that compounds not possessing these *ortho*- or *para*-phenol groups did not acquire this property. A little preliminary work was done to determine the suitability of these compounds to serve as indicators in volumetric analysis.

CINCINNATI, O.

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO.]

THE C_4-SACCHARINIC ACIDS. I. THE RESOLUTION OF *dl*-2,3-DIOXYBUTYRIC ACID INTO THE OPTICALLY-ACTIVE COMPONENTS. THE DERIVATIVES OF THESE ACIDS.

BY J. W. E. GLATTFELD AND GEORGE E. MILLER.[1]

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The saccharinic acids are acids which would result from the oxidation of the $H-\underset{|}{C}=O$ group of an aldo-monosaccharide of the formula $C_nH_{2n}O_n$ to the $O=\underset{|}{C}-OH$ group at the expense of one of the $H-\overset{|}{\underset{|}{C}}-OH$ groups which would be reduced to the $H-\overset{|}{\underset{|}{C}}-H$ group. These acids have the same molecular formula as the corresponding aldo-monosaccharides and may thus be looked upon as the results of an internal oxidation-reduction reaction. The saccharinic acids formed from some of the pentoses and hexoses have been the direct subject of study[2] by Nef and his students at various times, and have also entered into consideration in connection with all the sugar-oxidation experiments conducted in this laboratory in recent years. These oxidations were carried out in alkaline solution, under which conditions the production of saccharinic acids was a possibility. In a recent paper from this laboratory[3] there was reported, in the oxidation of maltose in alkaline solution, the production of an acid, the phenylhydrazid of which gave a perfect analysis for that of a 4-carbon-atom saccharinic acid. The properties of the free acid furthermore were those which would be expected of one of these acids. Its configuration could not be reported because of lack of

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[1] The dissertation of which this paper is a condensation was presented by George E. Miller as part fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago. The original dissertation is on file in the University library.

[2] Nef, *Ann.*, **376**, 1–120 (1910).

[3] THIS JOURNAL, **40**, 973 (1918).