TABLE III

SPECTRUM ANALYSES OF DYES

No. of dye	FF[a]	1	2	3	4	Azo
Wave length, millimicrons	540	549	503 514	576	478 514	465 496

[a] The value given for FF (Ref. 8, p. 464) is 540.

The authors acknowledge their indebtedness to Dr. B. Kurrelmeyer, Department of Physics, Columbia University, for his helpful suggestions during the spectrum analyses of these dyes.

Summary

1. A number of new sulfur derivatives were prepared from aminocymene.
2. The position of the chlorine atom introduced into the nucleus during the sulfur chloride condensation of aminocymene hydrochloride was determined.
3. A new azo dye was prepared.
4. Four new thioindigoid dyes containing an isopropyl group were prepared.
5. Fastness tests and spectrum analyses of the dyes were made.
6. The effect of the isopropyl group was found to be a shift of nine millimicrons in the direction of the longer wave lengths.

NEW YORK, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING, COLUMBIA UNIVERSITY]

METHYL ISOPROPYL THIOINDIGOID DYES FROM PARA-CYMENE. II. DYES FROM SODIUM CYMENE SULFONATE[1]

BY A. W. HIXSON AND W. J. CAUWENBERG

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Introduction

The original Heumann synthesis of indigo may be applied to thiophenols for the preparation of thioindigo dyes and this method is now employed in the industry on substituted thiophenols. These compounds are usually prepared by the reduction of the corresponding sulfonyl chlorides or by the action of potassium ethyl xanthate on diazotized amines. After condensing with chloro-acetic acid, the substituted phenylthioglycolic acids are internally dehydrated to the thionaphthene derivatives by chloro-sulfonic or sulfuric acids.

The application of this method to sodium cymene sulfonate would produce thioindigoid dyes which are isomeric with those prepared from amino-

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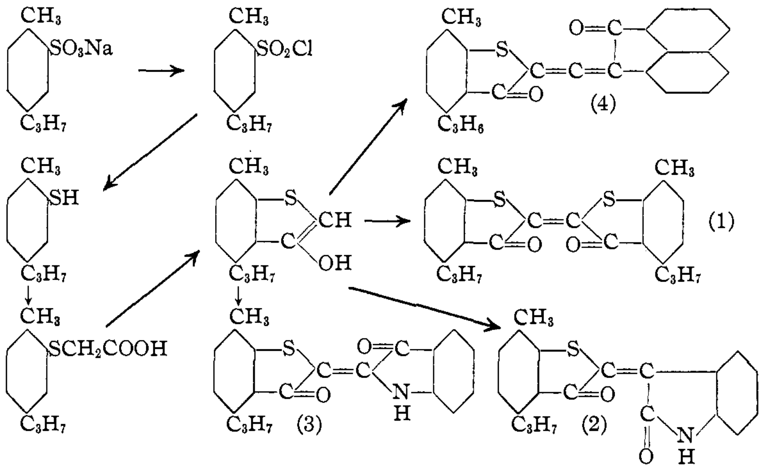
[1] This communication is an abstract of a portion of a thesis submitted by W. J. Cauwenberg in partial fulfilment of the requirements for the Degree of Doctor of Philosophy, to the Faculty of Pure Science of Columbia University.

cymene by the sulfur chloride method.[2] This paper presents the preparation of methyl isopropyl indigoid dyes from sodium cymene sulfonate. 7-Methyl-4-isopropyl-3-hydroxythionaphthene prepared by this method was oxidized to the thioindigo and condensed with isatin and acenaphthenequinone. The relative fastness, properties and spectrum analyses are reported. The method followed in the synthesis of these dyes may be represented as shown in the Flow Sheet.



Flow Sheet

Experimental Part

Preparation of Materials

The sodium cymene sulfonate prepared according to Hixson and McKee[3] was obtained from the Chemical Engineering Laboratory of Columbia University. It was recrystallized twice from alcohol and dried for eighteen hours at 140°.

Cymene-2-sulfonyl chloride was prepared as outlined by Phillips.[4]

Thiocarvacrol.—This compound was first prepared by Flesch[5] from camphor by the action of phosphorus pentasulfide. Roderburg[6] reported the preparation from the sulfonyl chloride. The method used in this work was an adaptation of the thiophenol process of Adams and Marvel.[7]

The wet sulfonyl chloride from 25 g. of sodium cymene sulfonate was added slowly to a mixture of 210 g. of ice and 71 g. of sulfuric acid at −5°. Thirty-six grams of zinc dust was introduced, keeping the temperature below 0°. After stirring the mixture for one and one-half hours at 0°, the ice–salt bath was removed and a reflux condenser connected to the Y-tube. The mass was heated to boiling (no vigorous reaction during the

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[2] Hixson and Cauwenberg, This Journal, **52**, 2118 (1930).

[3] Hixson and McKee, *J. Ind. Eng. Chem.*, **10**, 982 (1918).

[4] Phillips, This Journal, **46**, 686 (1924).

[5] Flesch, *Ber.*, **6**, 478 (1873).

[6] Roderburg, *ibid.*, **6**, 669 (1873).

[7] Adams and Marvel, "Organic Syntheses," John Wiley and Sons, New York, **1921**, Vol. I, p. 71.

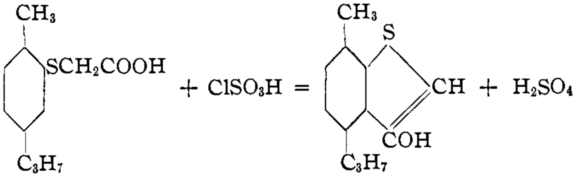
heating) and refluxed for seven hours. The thiocarvacrol was distilled from the reaction mixture with steam and dried over calcium chloride. It was purified by distillation and the fraction boiling at 235–237° was separated. The yield was 49% of the theoretical.

Anal. Calcd. for $C_{10}H_{14}S$: S, 19.27. Found: S, 19.19.

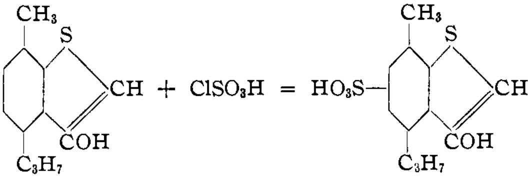
Cymene-2-thioglycolic Acid.—Thiocarvacrol (11 g.) was dissolved in 250 cc. of water containing 20 cc. of a 40% caustic soda solution. After adding a trace of sodium hyposulfite to prevent oxidation, 9 g. of chloro-acetic acid as the sodium salt in 50 cc. of water was added. The solution was heated to 70° and held for thirty minutes. The thioglycolic acid was precipitated by acidifying with hydrochloric acid at 20°. The acid was recrystallized from aqueous alcohol with a yield of 13 g. or 88% of the theoretical. It melted at 97°.

Anal. Calcd. for $C_{12}H_{14}OS$: S, 14.38. Found: S, 14.26.

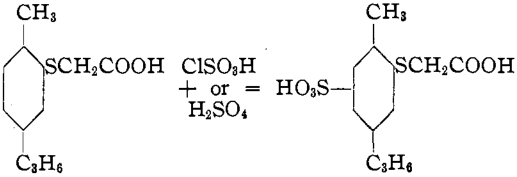
7-Methyl-4-isopropyl-3-hydroxythionaphthene.—The action of chlorosulfonic acid on cymene-2-thioglycolic acid may be represented by the reactions



(1)



(2)



(3)

Reactions 1 and 3 may be considered as consecutive with respect to the liberated sulfuric acid or side by side with respect to the thioglycolic acid. Reaction 2, the sulfonation of the thionaphthene, is consecutive.

A series of experiments was run and the time and yields are given in Table I. The method employed was as follows. Three grams of thioglycolic acid was added in two minutes to 30 g. of chlorosulfonic acid at 0°. The reaction mass was stirred for the time given in the table and poured onto 200 g. of ice. The thionaphthene was obtained as pale yellow plates by steam distillation of the dilution mass. It was purified by redistillation with steam; melting point, 86°.

Anal. Calcd. for $C_{12}H_{14}OS$: S, 15.52. Found: S, 15.41.

Assuming that 72% of the thioglycolic acid is available for conversion to thionaphthene and that this conversion and subsequent sulfonation of the thionaphthene appear as first-order reactions due to the large excess of chlorosulfonic acid (19.3 moles per mole of thioglycolic acid), the velocity constants ratio

$$\frac{K_1}{K_2} = \frac{\text{Rate of formation of thionaphthene}}{\text{Rate of sulfonation of thionaphthene}} = 53.3$$

gave the following results when substituted in the general equation for two consecutive first-order reactions.

$$\text{Yield of thionaphthene at time } \Theta = \frac{C_0K_1}{K_1 - K_2}\, e^{-K_2\Theta}$$

where C_0 is 0.72, K_1 is 64, Θ is time in hours and K_2 is 1.2.

TABLE I

EXPERIMENTAL AND CALCULATED RESULTS

Time in minutes	60	30	7
Experimental yield, g.	27.8	41.5	61.0
Calculated yield, g.	22.0	40.5	63.8

The time at which the yield of thionaphthene is a maximum is given by: $\Theta = I/(K_1 - K_2) \ln (K_1/K_2) = 0.063$ or 3.8 minutes.

The maximum yield of thionaphthene is given by

$$\text{Thionaphthene}_{(\text{max.})} = C_0 \left[\frac{K_1}{K_2}\right]^{\frac{K_2}{K_2 - K_1}} = 0.667 \text{ or } 66.7\%$$

Dyes from 7-Methyl-4-isopropyl-3-hydroxythionaphthene

7,7-Dimethyl-4,4-di-isopropyl-2,2-bis-thionaphthene Indigo. 1.—A solution of 5 g. of thionaphthene in 100 cc. of 5% caustic soda solution was heated to 80°; 2.5 g. of sulfur was added and the heating continued until the dye was completely precipitated. The product was separated by filtration and boiled with 5% caustic soda solution to remove any excess sulfur. The yield was quantitative. It was purified by recrystallization from xylene, from which it separated as fine, dark red crystals.

Anal. Calcd. for $C_{24}H_{24}O_2S_2$: S, 15.70. Found: S, 15.77.

7-Methyl-4-isopropyl-2-thionaphthene-3-indol Indigo. 2.—Thionaphthene (1.5 g.) and isatin (1 g.) were dissolved in 30 cc. of acetic acid and heated to 90°. Two drops of hydrochloric acid was added and the reaction held at 90° for thirty minutes. The dye was filtered, washed with alcohol and recrystallized from xylene. The yield was 1.9 g. or 79% of the theoretical.

Anal. Calcd. for $C_{20}H_{17}NO_2S$: S, 9.55. Found: S, 9.62.

7-Methyl-4-isopropyl-2-thionaphthene-2-indol Indigo. 3.—Isatin chloride formed by adding 1.9 g. of phosphorus pentachloride to 1.35 g. of isatin in 50 cc. of benzene was added to a solution of 1.5 g. of thionaphthene in 200 cc. of benzene at 50°. The benzene was removed with steam and the dye after drying was recrystallized from xylene. The yield was 1.7 g. or 71% of the theoretical.

Anal. Calcd. for $C_{20}H_{17}NO_2S$: S, 9.55. Found: S, 9.63.

7-Methyl-4-isopropyl-2-thionaphthene-acenaphthene Indigo. 4.—This dye was prepared from 0.8 g. of thionaphthene and 0.7 g. of acenaphthenequinone in acetic acid containing two drops of hydrochloric acid at 90°. The product was filtered, washed with alcohol and recrystallized from xylene. The yield was 1.2 g. or 86% of the theoretical.

Anal. Calcd. for $C_{24}H_{18}O_2S$: S, 8.91. Found: S, 8.79.

Thioindigo Dye from Crude Cymene Sulfonate

The production of a thioindigo dye from crude cymene sulfonate was investigated. The intermediates were not purified and the thionaphthene process was modified so as to obtain the maximum yield of dye and to eliminate unnecessary mechanical operations.

Thiocarvacrol was obtained with a yield of 50.8%, which gave a yield of 99.6% of crude thioglycolic acid.

Since the thionaphthene was precipitated by dilution of the reaction mass, it was thought advisable to separate it by filtration and to oxidize it directly. The temperature of the reaction was lowered to −10° and a series of runs was made varying the time.

TABLE II

VARIATION OF YIELD OF DYE WITH TIME

Time in minutes	15	7	4
Percentage yield	26.5	55.0	58.5

A semi-technical batch gave a yield of 51.2% in large-scale equipment.

Properties of Dyes

Solubility.—These dyes are insoluble in water, dilute acids and alkalies and salts with the exception of alkaline hyposulfite.

Fastness.—The relative fastness to light was determined by exposing them for seventy-two hours to an ultraviolet lamp (used less than 200 hours) at a distance of eighteen inches. The fastness to washing was determined by applying the standard test for ninety minutes.

TABLE III

PROPERTIES OF DYES

No. of dye[a]	Color in H_2SO_4	Color of vat	Color in xylene[b]	Wash test	Fastness to light	Color of crystals
FF	Green	Yellow	Pink y	Exc.	Exc.	Red
1	Green	Yellow	Red y	Fair	Exc.	Red
BB	Green	Pale pink	Red y	Fair	Fair	....
2	R violet	Yellow	Pink	Fair	Fair	Red
3	B green	Yellow	Violet	Good	Fair	B black
4	Green	Violet	Yellow y	Good	Fair	Orange

[a] FF is the commercial dye made from *o*-toluidine. BB is the semi-technical batch.

[b] y after color in xylene denotes yellow fluorescence; exc. for excellent.

Spectrum Analyses

The spectrum analyses were made with a Koenig–Martens spectrophotometer using xylene as the solvent.

TABLE IV

SPECTRUM ANALYSES OF DYES

No. of dye	1	BB		2		3		4	
Wave length, millimicrons	559	555	510	520	529	546	575	500	510	521

The authors acknowledge their indebtedness to Dr. B. Kurrelmeyer, Department of Physics, Columbia University, for his helpful suggestions during the spectrum analyses of these dyes.

Summary

1. 7-Methyl-4-isopropyl-3-hydroxythionaphthene was prepared from sodium cymene sulfonate.

2. Four new thioindigoid dyes containing an isopropyl group were prepared.

3. The production of a thioindigo dye from crude sodium cymene sulfonate on a semi-technical scale was made.

4. Fastness tests and spectrum analyses of the dyes were made.

New York, N. Y.

[Contribution from the Department of Research in Pure Chemistry, Mellon Institute of Industrial Research, University of Pittsburgh]

THE ISOLATION AND IDENTIFICATION OF *d*-MANNURONIC ACID LACTONE FROM THE MACROCYSTIS PYRIFERA

By William L. Nelson and Leonard H. Cretcher

Received February 10, 1930 Published May 8, 1930

That alginic acid is a polymer of one or more aldehyde sugar acids was demonstrated by the authors in a previous communication.[1] It was shown at the same time that it is composed, at least in part, of *d*-mannuronic acid. The identity of this uronic acid was established on the basis of the fact that on oxidation it formed a dibasic acid whose diamide and diphenylhydrazide corresponded in properties to the analogous compounds prepared from pure *d*-mannosaccharic dilactone.

At the time of our earlier paper we had not succeeded in obtaining the aldehyde acid in crystalline condition and were consequently unable to publish any data on the physical properties of the new compound. The present paper describes experiments which led to the preparation of crystalline *d*-mannuronic lactone and the determination of its melting point and optical rotation.

The extraction of alginic acid from the fronds of the *Macrocystis*, as well as the method of hydrolysis and subsequent preparation of the barium and cinchonine salts of the hydrolysis product, has been previously described.[1] The yield of pure cinchonine salt was much less than the calculated amount based on the weight of the barium salt from which it was prepared. The mannosaccharic acid formed, in poor yield, after oxidation of the barium salt might, therefore, not have been an oxidation product of the acid whose cinchonine salt we had in hand. In other words, it remained to be proved that the cinchonine salt was that of *d*-mannuronic acid. This is shown to be the case in the present paper. The problem as to whether or not there are other uronic acids present in the algin remains for the future.

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[1] Nelson and Cretcher, This Journal, **51,** 1914 (1929).