The ACETYL DERIVATIVE can be made as already described, dissolving the amine in acetic acid and adding acetic anhydride. This compound melts at 214°, and is obtained from either of the two 3-nitrocarbazoles just mentioned.

The acetyl derivative when dissolved in acetic acid and treated with either sodium or potassium nitrite yields the N-nitroso compound which when crystallized from alcohol melts with decomposition at 162–164°.

Both of these last mentioned compounds had been previously made by Mazzara and Leonardi;[5] though in making the acetyl derivative they heated the mixture of amine and acetic anhydride, while in this work the reaction was found to proceed fairly rapidly in the cold. These two compounds were also made in order to establish the fact that when either nitrocarbazole or one of the intermediate reduction products was reduced in an alkaline solution with zinc dust the amino and not the hydrazo compound was obtained.

Summary

1. From 1-nitro- and 3-nitrocarbazole the corresponding azoxy and azo compounds have been prepared.

2. It has been shown that in an alkaline solution both the 1-nitro- and 3-nitrocarbazole, as well as the corresponding azoxy and azo compounds, are reduced to the amine.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHNS HOPKINS UNIVERSITY]

THE EFFECT OF SULFUR ON THE COLOR OF TRIPHENYLMETHANE DYES

BY H. S. HOLT AND E. EMMET REID[1]

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Introductory and Historical

Within the last several years, a considerable amount of work has been done in this Laboratory on the auxochrome effect of alkyl-linked sulfur, more particularly in the field of azo dyes.[1a]

The present investigation is a further extension of this idea into the field of triphenylmethane dyes. A search through the literature showed few triphenylmethane dyes containing alkyl-linked sulfur.

Brand and Stallmann[2] have studied the auxochrome effect of alkyl mercapto groups on the phenol ethers of triphenylmethane. They have prepared compounds of the type $(C_6H_5)_2C(OH)C_6H_4SCH_3$ (*o*) and $C_6H_5C(HO)(C_6H_4SCH_3)_2$ (*o*) and have shown that such compounds in acetic acid or alcoholic solution when treated with strong sulfuric or hydrochloric acid, develop color. These cannot be classed as true dyes although they do show the auxochrome effect of the —SCH_3 group.

[5] Mazzara and Leonardi, *Gazz. chim. ital.*, [2] **21**, 385 (1891).

[1] From the Doctor's dissertation of H. S. Holt, 1924.

[1a] (b) Waldron and Reid, THIS JOURNAL, **45**, 2399 (1923). (c) Foster and Reid, *ibid.*, **46**, 1936 (1924).

[2] Brand and Stallmann, *Ber.*, **54**, 1578 (1921).

The Present Investigation

The Grignard reagents were prepared from the alkyl ethers of *o*- and *p*-bromo-thiophenol and made to react with Michler's ketone:[3] $RS.C_6H_4MgBr + [(CH_3)_2NC_6H_4]_2CO \longrightarrow [(CH_3)_2NC_6H_4]_2C(OH)C_6H_4.SR$. The desired *o*- and *p*-bromo-thiophenol ethers were obtained from the corresponding amine compounds by the Sandmeyer reaction.

The dyes so made are derived from malachite green by the substitution of —SR in the *ortho* or *para* position in the third ring. The groups used were methyl, *iso*propyl and *iso*amyl in the *para* position and methyl in the *ortho*. Dyes containing the phenyl and benzyl sulfide or methylsulfone groups could not be prepared, since the reaction between magnesium and the bromophenyl-thio-ethers appears to be confined to the simpler members of the series for neither *p*-bromophenyl-benzyl sulfide nor *p*-bromophenyl methylsulfone could be made to attack the magnesium. In the case of *p*-bromophenyl-thiophenol a reaction did take place after long heating but a brown solid immediately precipitated which did not react with Michler's ketone. Insufficient material was available to enable us to study this reaction further.

For comparison, dyes were made containing the methyl and methoxy groups in the same positions by the action of the Grignard reagents from *o*- and *p*-tolyl iodide and *o*- and *p*-iodo-anisole.

Wool skeins were dyed in the usual way using 1% of the dye, 3% of sulfuric acid and 10% of Glauber's salt. The colors[4] are given in Table I.

TABLE I

COLORS OF SUBSTITUTED MALACHITE GREENS ON WOOL

Substituent	Ortho	Para
None	Yellowish-green	Yellowish-green
$—CH_3$	Dull bluish-green (weak)	Bright yellowish-green
$—OCH_3$	Dull yellowish-green (weak)	Dull yellowish-green
$—SCH_3$	Bluish-green (turquoise)	Dull reddish-blue
$—SCH(CH_3)_2$	....	Dull blue-gray (weak)
$—SC_5H_{11}$(*iso*)	....	Dull yellowish-green (weak)

The introduction of sulfur in the *para* position has a pronounced deepening effect on the color and the shift is toward the blue, that is, the shorter wave length. This effect is especially noticeable with the lower members of the series.

As the molecular weight of the alkyl group attached to the sulfur atom increases, a peculiar slate gray results, making it difficult to determine the color. Certainly some of the auxochrome effect is lost.

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[3] Baeyer and Villiger, *Ber.*, **36**, 2789 (1903). Ehrlich and Sachs, *Ber.*, **46**, 4296 (1903). Votocek and Matejzka, *Ber.*, **46**, 1756 (1913).

[4] Thanks are due Dr. R. E. Rose of E. I. du Pont de Nemours and Co. for the color designations.

In the *ortho* position all of the substituents diminish the intensity of the dye and all shift the color towards the blue, the —SCH_3 group showing the greatest effect.

Experimental Part

Preparation of *p*-Nitro-thiophenol.—The procedure of Waldron and Reid was modified slightly, as more consistent results were obtained and less time was required. It was found to be unnecessary to acidify the reaction mixture and then redissolve the free mercaptan. The procedure was as follows.

One gram molecular weight of *p*-nitro-chlorobenzene (157 g.) was treated with sodium disulfide as described by Waldron and Reid. The reaction mixture was poured into about 300 cc. of water and the mixture filtered at once into saturated sodium hydroxide solution, precipitating most of the sodium salt of the mercaptan and some disulfide. This mixture was filtered through cloth and the mercaptan removed by treating with warm water containing a little sodium sulfide. When saturated sodium hydroxide is added to this solution the product is precipitated quite pure.

The disulfide may be collected and reduced with sodium sulfide in strongly alkaline solution (for 125 g. of disulfide, 35 g. of sodium sulfide and 35 g. of sodium hydroxide in 150 cc. of water are required). This reaction mixture is treated exactly as above. The success of the preparation depends on the length of time the reaction mixture is allowed to boil before pouring into water and this is best determined by a few trials. The yields were about 60% on the first step.

Ethers of *o*- and *p*-Bromo-thiophenol, $RS.C_6H_4Br$.—The ethers of *o*- and *p*-amino-thiophenol were made according to the methods of Waldron and Reid and of Foster and Reid. The amino groups in these were replaced by bromine as follows.

A solution of 25 g. of the hydrochloride of the aminophenyl thio-ether in about 300 cc. of water containing 40 g. of concd. hydrochloric acid was cooled to 0° and diazotized in the usual manner. The diazo solution was then poured into a suspension of 22 g. of cuprous bromide and 25 g. of potassium bromide in a little water at 80°. After evolution of nitrogen had ceased, 100 cc. of concd. hydrochloric acid was added and the mixture steam distilled. The distillate was made strongly alkaline to remove any phenol and the bromo compound extracted with benzene. It was distilled in a vacuum after it had been dried and the solvent evaporated. As the phenyl and benzyl ethers were not volatile with steam the reaction mixture, after diazotizing and decomposing as before was extracted with benzene. The benzene solution was shaken with 10% alkali, separated, dried and the solvent evaporated. This left the bromo compounds mixed with considerable tarry material. From this mixture they were distilled under reduced pressure and further purified by redistilling.

***p*-Bromophenyl-Methylsulfone.**—A solution of 22 g. of *p*-aminophenyl methylsulfone, in 300 cc. of water containing 40 g. of concd. hydrochloric acid was diazotized in the usual manner. The diazo solution was poured into a suspension of 20 g. of cuprous bromide and 25 g. of potassium bromide in 50 cc. of water at 80°. This solution was heated to boiling and filtered hot. The bromosulfone crystallizes from the filtrate in yellow needles. By extracting the residue on the filter with hot water and evaporating to small volume, more product can be obtained.

The yields, properties and analyses of the new compounds prepared are given in Table II. Analyses for sulfur were made with the Parr bomb and densities were determined with the Ostwald pycnometer.

TABLE II

PROPERTIES AND ANALYSES OF *o*- AND *p*-BROMOPHENYL THIO-ETHERS, $RS.C_6H_4Br$

Group	Position	B. p. or m. p. °C.	Density 25/25	Sulfur Calcd. %	Sulfur Found %	Yield %
$—SCH(CH_3)_2$	*o*	b. p., 130–135 (11 mm.)	1.2804	13.85	13.59	35
$—SC_6H_5$	*o*	b. p., 175–177 (12 mm.)	1.3733	12.09	12.17	50
$—SCH_3$	*p*	m. p., 27	....	15.76	15.71	55
$—SCH(CH_3)_2$	*p*	b. p., 120 (11 mm.)	1.2338	13.85	13.62	60
$—SCH_2CH(CH_3)_2$	*p*	b. p., 140–143 (15 mm.)	1.1467	12.35	12.23	37
$—SCH_2C_6H_5$	*p*	m. p., 48	....	11.47	11.38	50
$—SO_2CH_3$	*p*	m. p., 97.5	....	13.61	13.79	50

Preparation of the Dyes

The following procedure was used in all cases. About 10 g. of the bromo thio-ether in absolute ether was treated with magnesium turnings and a crystal of iodine. The magnesium dissolved slowly in all cases and it was necessary to heat the mixture at 35° overnight. The calculated quantity of Michler's ketone in dry benzene was then added, precipitating an orange-colored solid which turned green on contact with air. This mass was separated from the solvent by filtration or decantation and dissolved in 1:1 hydrochloric acid. After the mixture had been filtered, saturated zinc chloride solution was added and the dye precipitated by the addition of solid sodium sulfate.

The reaction with *o*-bromophenol-thiophenyl.—To 8.2 g. of this compound and 0.75 g. of magnesium turnings was added 15 cc. of ether and a crystal of iodine. The mixture was heated at 35° overnight. Solution of the magnesium suddenly took place after 24 hours and a brown solid precipitated. More ether was added, followed by the calculated amount of Michler's ketone in dry benzene. The precipitate which formed did not turn green on exposure to air, and on dissolving in hydrochloric acid only colorless products were formed. No dye could be obtained.

Method of Dyeing

One-tenth g. of dye was dissolved in about 500 cc. of warm water containing 1 g. of sodium sulfate and 0.3 g. of sulfuric acid. After solution of the dye, any insoluble material was removed by filtration. A 10 g. skein previously soaked in hot water was then immersed and the solution gradually brought to boiling, the total time of immersion being one-half hour in each case. The skein was then removed, washed with water and air-dried.

Summary

1. A number of new bromophenyl thio-ethers have been prepared. On coupling with Michler's ketone these gave dyes in which the auxochrome effect of the alkyl mercapto groups could be observed.

2. Sulfur in the *para* position has a decided auxochrome effect on the color and the shift is toward the blue. Sulfur in the *ortho* position has a similar effect but to a less degree. Increasing the molecular weight of the alkyl groups results in a loss of some of the auxochrome effect. In general the auxochrome effect of the various groups is in the order $—SCH_3 > —OCH_3 > —CH_3$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE JOHN HOPKINS UNIVERSITY]

THE EFFECT OF SULFUR ON THE COLOR OF CERTAIN PHTHALEINS[1]

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Introductory and Historical

It has been shown[2] that the introduction of sulfur into triphenylmethane dyes causes a decided shift in color, this change being toward the shorter wave length. This idea has been extended into the field of phthaleins, the problem in general being the synthesis of a series of phthaleins containing alkyl-linked sulfur and observation of the auxochrome effect.

No mention of phthaleins containing alkyl sulfur could be found in the literature although compounds such as phenolsulfonephthalein and its derivatives have been known for some time.[3]

The Present Investigation

The method of attack first suggesting itself was the fusion of phthalic anhydride with phenols containing sulfur substituents, $RS.C_6H_4.OH$, the procedure being similar to that used in the preparation of phenolphthalein. These phenols were made from the corresponding amines[4] by the diazo reaction: $RS.C_6H_4.NH_2 \longrightarrow RS.C_6H_4.OH$.

It was found, however, that when one mole of phthalic anhydride is fused with two moles of *o*-hydroxyphenyl methyl sulfide at 180° in the presence of fused zinc chloride, hydroxymethyl-mercapto-anthraquinone is formed. That is, although two moles of thio-ether were used only one reacted: $C_6H_4(CO_2)O + RS.C_6H_4.OH \longrightarrow C_6H_4(CO)_2C_6H_2(OH)SR$. No attempt was made to determine the position of the hydroxyl or methyl mercapto groups.

o-Hydroxyphenyl-thiophenol, $HO.C_6H_4.SC_6H_5$, does not react with phthalic anhydride under similar conditions.

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[1] From the dissertation of H. S. Holt, 1924.

[2] THIS JOURNAL, **46**, 2329 (1924).

[3] Remsen, *Am. Chem. J.*, **20**, 263 (1898).

[4] Foster, THIS JOURNAL, **46**, 1936 (1924).