hydride, and it has been ascertained that a methyl group in Position 4 condenses less readily with the anhydride than one in Position 2 and that the course of the reaction is not the same in the two cases.

3. The reaction with the 2-methyl-quinazoline led to the phthalone; that with the 2,4-dimethyl- to a monophthalone. The nature of the products obtained from the 4-methyl- and from the 2-phenyl-4-methyl remains to be determined.

4. By warming these condensation products with fuming sulfuric acid, sulfo acids were obtained which dyed silk golden-yellow to brown. Although of considerable tinctorial strength, these dyes appeared to be decidedly inferior to Quinoline Yellow.

NEW YORK, N. Y.

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

THE INFLUENCE OF SULFUR ON THE COLOR OF AZO DYES FURTHER INVESTIGATIONS

BY DUNCAN GRAHAM FOSTER[1] AND E. EMMET REID

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In a previous paper from this Laboratory[2] a study has been made of the influence of sulfur in the *para* position upon the color of azo dyes. The purpose of the present investigation has been to show the effect of the sulfur atom and the sulfone group, as before, but in the *ortho* instead of the *para* position. We have made no attempt to duplicate the many dyes previously prepared, a large proportion of which were obtained simply by coupling the same bases with different standard intermediates, but have merely selected those bases which seemed to be representative, prepared the *ortho* analogs and coupled them with the intermediate which had, in the *para* series, given the best-defined color differences, namely with R-salt. By this means we have confirmed in some respects the results found with the *para* compounds, and have uncovered some interesting and unexpected facts connected with the relative influence of the sulfur atom in the two positions.

As in the previous investigation, we have prepared intermediates of two classes.

1. A series of mono-amines,—CH_3,—OCH_3,—SCH_3,—SO_2CH_3, containing the methyl group, methoxyl, thio-ether and sulfone groups in the *ortho* position to the amino group. In the same class falls a series of alkyl thioethers from methyl to *iso*-amyl: $NH_2C_6H_4.S.R$, including the phenyl

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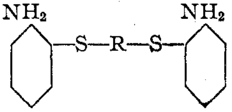
[1] From a dissertation by Duncan Graham Foster, 1923.

[2] Waldron and Reid, THIS JOURNAL, 45, 2399 (1923). Wherever, in this article, we refer "to the previous paper" or to "the methods employed with the *para* series" detailed descriptions of procedures will be found in this reference.

and also two derivatives, the allyl and cyclohexyl, not previously prepared in the *para* series. Of these two we have made also the *para* isomers.

2. A series of diamines derived from the *ortho* analog of benzidine, *o,o'*-diamino-diphenyl, with various groups between the rings,



comprising the series, $—SCH_2S—$, $—SC_2H_4S—$, $—SC_3H_6S—$, and finally the base from mustard gas: $H_2NC_6H_4SC_2H_4SC_2H_4SC_6H_4NH_2$.

The general method of preparing the *para* intermediates was to obtain the nitro bodies by condensing an alkyl halide or an alkylene dihalide with the sodium salt of *p*-nitro-thiophenol or *p*-nitrobenzyl bromide with the sodium compound of a mercaptan. One portion was then reduced to the amine with iron powder and acetic acid and the other portion oxidized to the sulfone with chromic acid and then reduced to the amino-sulfone. All were diazotized, coupled and dyed according to accepted methods.

These procedures were quite readily extended to the *ortho* analogs without any extensive change in the methods, using *o*-nitro thiophenol prepared from *o*-nitro-chlorobenzene instead of the *para* compound.

Materials

The sodium salt of *o*-nitro-thiophenol cannot be salted out as can the *para* compound. The free *o*-nitro-thiophenol we found, in agreement with Wohlfahrt,[3] to be quite stable. Lecher[4] has prepared *o*-nitro-thiophenol from *o,o'*-dinitro-diphenyl-disulfide, $O_2NC_6H_4S\text{-}SC_6H_4NO_2$, by reducing the latter with glucose. Wohlfahrt prepared it either by reduction with sodium sulfide or with sodium hydrosulfide, from the isolated and purified disulfide. We have prepared it by all three of these methods, and finally adopted a combination of two of them. The *o,o'*-dinitro-diphenyl-disulfide we prepared by the method of Wohlfahrt.

A solution of sodium sulfide in alcohol was made by dissolving 24.4 g. of the dry salt, with heating, in a quantity of water equivalent to its water of crystallization, cooling and adding 150 cc. of alcohol. This solution was refluxed until all of the sodium sulfide had disappeared. It was filtered free from precipitated iron sulfides and mixed with 4.8 g. of finely powdered sulfur. After a short time the sulfur dissolved and the solution turned red-brown. It was then added slowly to a boiling solution of 32 g. of *o*-nitro-chlorobenzene in 50 cc. of alcohol. After all the sodium sulfide had been added the solution was refluxed for two hours or more until the dark red color had disappeared and a light yellow precipitate of the disulfide had formed. This was filtered out, washed with water to remove sodium chloride, and dried in the oven at 100°.

A mixture of 30 g. of this disulfide with 100 cc. of alcohol was then prepared and refluxed for a short time. To the boiling suspension was added from a dropping funnel 50 cc. of a solution containing 2.5 g. of sodium hydroxide which had been saturated with hydrogen sulfide, and to which had been added, after saturation, 8 g. more of sodium hydroxide. The addition of this solution should take exactly 15 minutes. The dark

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[3] Wohlfahrt, *J. prakt. Chem.*, [2] **66**, 551 (1902).

[4] Lecher and Simon, *Ber.*, **55**, 2426 (1922).

red reaction mixture was poured hot into about four times its volume of cold water, and this mixture filtered free from any cloudy precipitate, and poured into a mixture of 75 cc. of concd. hydrochloric acid and ice, which was mechanically stirred. The acid solution must be kept cold by the continued addition of ice, and should be immediately filtered as soon as all of the solution of sodium *o*-nitro-thiophenolate has been added. It was sucked as dry as possible on the filter and put at once into a vacuum desiccator containing potassium hydroxide and sulfuric acid. The whole of this reaction should be run through as rapidly as possible and still allow it to proceed to completion, and the product allowed to stand in contact with air as little as possible, particularly in alkaline solution, because the sodium salt of the mercaptan oxidizes very rapidly to the disulfide in contact with the atmosphere.

To purify, we dissolved the product in the minimum quantity of a mixture of one part of carbon tetrachloride and two parts (by volume) of petroleum ether (b. p., 50–70°), a mixture which has a specific gravity of 0.990–0.995. The separated water layer was drawn off and the solution refluxed for a few minutes over calcium chloride, filtered and allowed to cool. The product crystallizes in yellow needles melting at 57–58°. We utilized it as the sodium salt by dissolving in the calculated quantity of alcoholic sodium hydroxide solution.

The alkyl halides used in this work, when they could not be readily obtained on the market, were made by the method of Norris.[5]

o,o'-Diamino-diphenyl, $H_2NC_6H_4\text{-}C_6H_4NH_2$, which we used as a reference point for the dyes of the benzidine series, we prepared by the method of Täuber.[6]

I. Alkyl and Aryl *o*-Nitrophenyl Thio-Ethers of *o*-Nitro-thiophenol

In making this class of intermediates, we followed in part the general procedure of the earlier paper, but have varied the details to a certain extent. We dissolved 13 g. of *o*-nitro-thiophenol in 3.4 g. of sodium hydroxide in 50 cc. of alcohol and filtered the solution free from precipitated disulfide. To the dark red solution thus obtained we added 0.1 mole of alkyl halide (in the case of the methyl thio-ether, the iodide; in all other cases the bromide) and refluxed the whole until the red color of the sodium salt had disappeared, which took in most cases about 10–15 minutes. When solids were formed, they usually crystallized on cooling and were filtered off and recrystallized from alcohol or 80% acetic acid. When, as was usually the case, they were liquids, the bulk of the alcohol was distilled and the residue either reduced to the amine directly, or taken up with water, the solution extracted with ether, the ether dried over calcium chloride, distilled and the residue subjected to vacuum distillation. The latter process is extremely tedious, and since a large number of intermediates had to be prepared, we adopted the practice of merely distilling off the alcohol, reducing the impure product immediately to the amine, and identifying it as the amine hydrochloride. As a result, therefore, we have isolated only five of the thio ethers, the ethyl and the *n*-propyl, which are liquids, and the allyl, methyl and phenyl, which are solids, and of which the last two have been prepared by other workers.

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[5] Norris, *Am. Chem. J.*, **38**, 640 (1907).

[6] Täuber, *Ber.*, **23**, 795 (1890); **24**, 198 (1891).

o-Nitrophenyl-phenylsulfide, $O_2NC_6H_4SC_6H_5$, was prepared in 80% yield by the method of Mauthner.[7]

$$O_2NC_6H_4SNa + RBr = O_2NC_6H_4SR + NaBr \qquad (1)$$

$$O_2NC_6H_4Cl + NaSC_6H_5 = O_2NC_6H_4SC_6H_5 + NaCl \qquad (2)$$

The preparation and properties of these thio-ethers are given in Table I. All the compounds were yellow.

TABLE I

PREPARATION, PROPERTIES AND ANALYSES OF ALKYL AND ARYL *o*-NITROPHENYL THIO-ETHERS

$R—S—C_6H_4—NO_2$

R	$NO_2C_6H_4SH$ G.	Halide G.	Yield G.	Yield %	M. p. or b. p. °C.	Properties	% Sulfur Calcd.	% Sulfur Found
Methyl[8]....	10	9.1	7	50	m. 59–60	Plates	..	..
Ethyl......	10	7	7	46	b. 149–150 (15 mm.)	Oil	17.5	17.1
Propyl.....	20	16	15	64	b. 172–174 (7 mm.)	Oil	16.4	16.6
Allyl......	10	8	5	32	m. 54	Needles	16.4	17.3[9]

The two *para* derivatives were prepared by the method employed with the *para* series. Their properties are given in Table II.

TABLE II

PREPARATION, PROPERTIES AND ANALYSES OF ALKYL *p*-NITROPHENYL THIO-ETHERS

$R—S—C_6H_4—p\text{-}NO_2$

R	$NO_2C_6H_4SNa$ G.	Halide G.	Yield G.	Yield %	M. p. °C.	Properties	% Sulfur Calcd.	% Sulfur Found
Allyl............	17	12	12	65	38–39	Plates	16.4	17.1[9]
Cyclohexyl......	17	16	6	50	56–57	Needles	13.5	13.8

Alkyl and Aryl *o*-Aminophenyl Thio-Ethers

$RSC_6H_4NH_2$

Since the object of this investigation was to produce amine salts capable of being diazotized and coupled with suitable intermediates, we did not consume any more time than was absolutely necessary on the purification of the nitro bodies, but reduced most of them immediately to the corresponding amines, in which form they could readily be identified as the hydrochlorides or the sulfates.

The most satisfactory method of accomplishing this reduction, as exemplified by previous experience with the *para* series, is to stir the nitro compound with about ten times its weight of water, an equal quantity of fine iron dust, and a trace of acetic acid, following the general scheme

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[7] Mauthner, *Ber.*, **39**, 3597 (1906).

[8] Brand, *Ber.*, **42**, 3466 (1909).

[9] We were unable to get good results with the allyl derivatives, all of our analyses showing too much sulfur. This is doubtless due to the fact that they melted lower than the boiling point of the solvent and hence could not be properly purified.

of the commercial production of aniline. After about ten hours the reduction is complete, and the amine may be isolated by making alkaline with soda, filtering and extracting both iron residue and filtrates with benzene.

The methods employed with our *ortho* compounds were exactly the same except that we found the sulfates of the amines much more soluble in water than their *para* analogs. Instead, therefore, of evaporating the benzene and pouring the oily amine into dil. sulfuric acid, we dried the benzene extracts over calcium chloride and passed in dry hydrogen chloride until the mixture fumed strongly. In nearly every case the white, granular hydrochloride precipitated immediately, leaving the bulk of the impurities in the benzene. If it did not, we cooled the solution in ice, upon which crystallization took place without any difficulty. These solids were filtered, washed with ether and dried over sulfuric acid in a vacuum desiccator.

Usually this process gave compounds sufficiently pure for analysis. If not, the solid was dissolved in a very little alcohol, filtered, cooled and ether added until precipitation just began. Further cooling caused the salts to crystallize in beautiful, white needles, which were filtered out, dried and analyzed.

All the amines of this series are oils that decompose below their boiling points, even under diminished pressures. The hydrochlorides are white, crystalline solids, soluble in water or alcohol and insoluble in ether or benzene. They are characterized by very rapid and complete hydrolysis in water. Even in the presence of a large excess of acid, the insoluble amine separates from water solution as a brown oil, which can be redissolved only by heating or the addition of a very large excess of acid indeed.

The analysis of these salts was effected by the very simple procedure of dissolving a weighed sample in water, adding 5 cc. of concd. nitric acid and then an excess of 0.2 *N* silver nitrate solution. The silver chloride formed was collected on a Gooch filter and weighed in the usual manner.

$$\mathrm{R{-}S{-}C_6H_4{-}NO_2 + 6H = R{-}S{-}C_6H_4NH_2 + 2H_2O} \qquad (3)$$

The preparation and analyses of these salts are outlined in Table III. The yields given are of the hydrochlorides and all were calculated from the weight of alkyl halide used, the nitro bodies not being purified. The yields of compounds derived from the five nitro bodies appearing in Table I were calculated on the basis of different runs from those in that table, the intermediate losses due to purification thus being eliminated, and the values appearing correspondingly larger.

Table IV contains data on the two *para* derivatives which were prepared in the same way from *para* nitro bodies, but were isolated as the sulfates

TABLE III

PREPARATION OF *o*-AMINO HYDROCHLORIDES OF ALKYL AND ARYL PHENYL THIO-ETHERS

$R—S—C_6H_4—NH_2—HCl$

R	Alkyl halide	Yield		Analysis for chlorine	
	G.	G.	%	Calcd.	Found
Methyl[10]	12	11	74	..	..
Ethyl	12.6	16	73	18.7	18.7
Propyl	7.9	7	54	17.5	17.4
*iso*Propyl	7.7	12.5	99	17.5	17.8
Butyl	9.2	8	55	16.3	16.7
*iso*Butyl	9.2	10.5	72	16.3	16.4
iso-Amyl	9.4	11	71	15.3	15.4:15.5
Cyclohexyl	5.4	5	32	14.6	14.6
Allyl	8	10	75	18.3	18.1
H(mercaptan)[10]	10	6	58	..	..
Phenyl[10]	10	10	70	..	..

and analyzed by precipitation from acid solution with barium chloride. The sulfur of the sulfate radical only is determined.

TABLE IV

PREPARATION OF SULFATES OF ALKYL *p*-AMINOPHENYL THIO-ETHERS

$(R—S—C_6H_4—p\text{-}NH_2)_2—H_2SO_4$

R	Nitro body	Yield		Analysis for sulfur	
	G.	G.	%	Calcd.	Found
Allyl	5	5	45	8.0	7.9
Cyclohexyl	5	9.9	93	6.2	6.3

II. *o,o'*-Dinitro-diphenyl Derivatives with Various Groups between the Rings

$$O_2N—C_6H_4—S—R—S—C_6H_4NO_2$$

In this series, the derivatives of *o,o'*-dinitro-diphenyl, fall three compounds with various alkylene groups between the rings. We include also, with the series of disulfides, a derivative of mustard gas because its preparation and properties are exactly similar to the series proper, although it is itself a trisulfide: $O_2N—C_6H_4—S—C_2H_4—S—C_2H_4—S—C_6H_4—NO_2$.

All four of these compounds were prepared by the general method of adding alkylene dihalides to the sodium salt of *o*-nitro-thiophenol, following the procedure used in the preparation of the mononitro derivatives. They are all yellow solids, characterized by extremely low solubility in organic and inorganic solvents. In fact, the only solvent we were able to use at all was glacial acetic acid, and even in this they are very sparingly soluble. The alkylene dihalides used were methylene iodide, ethylene dibromide, trimethylene dibromide and mustard gas.

The method adopted in the preparation of these bases was exactly similar to that used in the production of the thio ethers. In all cases the color of the sodium salt disappeared after refluxing for 10–15 minutes and

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[10] Prepared by other workers.

the product crystallized almost completely even while hot. The crystals were filtered off and recrystallized from glacial acetic acid for analysis. The mustard gas derivative alone did not crystallize immediately, but on the evaporation of most of the alcohol and the addition of a little water, the compound set to a yellow crystalline solid.

We purified only sufficient of these compounds for analysis, since, on account of their slight solubility, excessively large amounts of acetic acid were required for recrystallization. The crude products were reduced to the diamines directly.

$$2NO_2C_6H_4SNa + Br\text{-}R\text{-}Br = O_2NC_6H_4\text{-}S\text{-}R\text{-}S\text{-}C_6H_4NO_2 + 2NaBr \qquad (4)$$

The data on these compounds and their analyses are contained in Table V.

TABLE V

PREPARATION, PROPERTIES AND ANALYSES OF *o,o'*-DINITRO-DIPHENYL ALKYLENE DISULFIDES

$O_2NC_6H_4—S—R—S—C_6H_4NO_2$

R	$NO_2C_6H_4SH$ G.	Halide G.	Yield G.	Yield %	M. p. °C.	Properties	% Sulfur Calcd.	% Sulfur Found
$—CH_2—$	13	11	9.5	71	170	Needles	19.9	19.5
$—(CH_2)_2—$	13	8	7	50	205	Needles	19.0	18.4
$—(CH_2)_3—$	13	8.5	10	67	140	Needles	18.3	18.0
$—(C_2H_4)S(C_2H_4)—$	13	6	12	80	107–108	Plates	24.4	23.9

o,o'-Diamino-diphenyl Derivatives with Various Groups between the Rings

$H_2NC_6H_4—S—R—S—C_6H_4NH_2$

Iron and acetic acid readily effect the reduction of these dinitro disulfides to the corresponding diamines. We found, as had been the case with the *para* isomers, that these amines are insoluble in benzene and ether, but are slightly soluble in water and may be extracted from the iron with hot alcohol. Here again the sulfates are too soluble to use as a means of purification. By evaporating the water and alcohol filtrates to dryness, extracting the water residue with alcohol, filtering off the inorganic material remaining undissolved, and again evaporating, the amines were obtained as brown oils. These were converted to the hydrochlorides by mixing with concd. hydrochloric acid and evaporating the excess acid on the steam-bath. With the exception of this procedure, the methods of reduction were exactly the same as those previously employed with the mono-amines.

These diamine hydrochlorides do not crystallize from alcohol and ether mixtures. They were obtained in a doubtful state of purity for analysis by precipitating with ether from solution in alcohol. Here again hydrolysis is very rapid and complete, and in two cases we had to filter the strongly acid solution free from oily amine before it was possible to precipitate the chloride with silver nitrate.

The preparation and analyses of these diamines are given in Table VI. The yields given are based on the weight of hydrochloride obtained.

TABLE VI

PREPARATION AND ANALYSES OF *o,o'*-DIAMINO-DIPHENYL ALKYLENE DISULFIDES

$HCl—H_2NC_6H_4—S—R—S—C_6H_4NH_2—HCl$

R	Nitro compound G.	Yield G.	%	Analysis for chlorine Calcd.	Found
$—CH_2—$	5	5	91	21.2	21.1
$—(CH_2)_2—$	5	3	21	18.3	18.0
$—(CH_2)_3—$	5	5	89	19.6	19.8
$—(C_2H_4)S(C_2H_4)—$	10	10	90	17.4	17.6

III. The Sulfones

It had been our original intention to prepare the sulfones of all our nitro bodies, both the thio-ethers and the disulfides. We found, however, upon coupling and dyeing the intermediates from the mono-amines, that the effect of the alkyl groups is as slight in the *ortho* series as it is in the *para*. There was nothing to be gained, therefore, in multiplying the number of sulfones, since all we wished to demonstrate was the effect of the sulfone group as compared with the sulfur atom alone. The effect of the sulfone group in the *para* series had already been established, and we have shown that the effect of increase in molecular weight in the *ortho* series is exactly the same as in the *para*. It was necessary, then, only to select one sulfone from each series of bases to show the influence of oxidized sulfur in the *ortho* position, since increase in molecular weight has been shown to have nearly the same influence with sulfones that it does with the simple thio-ethers. We chose the methyl sulfone to complete our series: $—CH_3$, $—OCH_3$, $—SCH_3$ and $—SO_2CH_3$. Later we found that the *n*-propyl sulfone, $O_2NC_6H_4SO_2C_3H_7$, is more easily prepared than either of the two lower ones, so we chose this and the one most nearly corresponding to it in the series of diamine disulfides, the sulfone from the trimethylene disulfide: $O_2NC_6H_4SO_2(CH_2)_3SO_2C_6H_4NO_2$. Unfortunately, the dye from the latter is still lacking because, as we shall see later, reduction attacks the sulfone group as well as the two nitro groups.

For some reason, we could not prepare the ethyl sulfone, $O_2NC_6H_4SO_2C_2H_5$, several trials leading to the disappearance of all the materials we had used and giving nothing from the reaction mixture either by evaporation or extraction. It may have gone, as has sometimes been observed to be the case with such compounds, to the very soluble sulfonic acid, which would be extremely difficult to isolate from such a reaction mixture, on account of the large amount of acetic acid and chromic salts present.

We dissolved 5 g. of nitro compound in 100 cc. of 80% acetic acid (except in the case of the trimethylene derivative, whose low solubility necessitated the use of glacial acetic acid) and oxidized with saturated chromic acid solution, as described in the earlier paper. All products were white crystalline solids, crystallizing well from ethyl alcohol.

$$3NO_2C_6H_4SR + 4H_2CrO_4 + 12HAc = 3NO_2C_6H_4SO_2R + 4CrAc_3 + 10H_2O \quad (5)$$

Table VII summarizes the preparation, properties and analyses of these three compounds.

TABLE VII

PREPARATION, PROPERTIES AND ANALYSES OF THE SULFONES

Formula	Sulfide G.	Yield G.	Yield %	M. p. °C.	Properties	% Sulfur Calcd.	% Sulfur Found
$O_2NC_6H_4SO_2CH_3$	10	7	65	104–105	Plates	15.9	16.6
$O_2NC_6H_4SO_2C_3H_7$	5	5	86	50	Short needles	14.0	14.3
$(O_2NC_6H_4SO_2CH_2)_2CH_2$	15	13	72	156–157	Plates	15.5	15.7

The Sulfone Amines

$H_2NC_6H_4SO_2R$

By reduction with iron and acetic acid the simple alkyl sulfones were readily converted to the amines. The trimethylene derivative, however, gave an oil which, upon conversion to the hydrochloride, appeared by analysis to be not the amine of the sulfone, $NH_2C_6H_4SO_2(CH_2)_3SO_2C_6H_4NH_2$, but the amine of the thio-ether, $NH_2C_6H_4S(CH_2)_3SC_6H_4NH_2$. Reduction of the sulfones of this series seems to attack not only the nitro groups but also the sulfone groups, converting them back to the original disulfides. This fact was also noticed with one of the sulfones of the *para* series.

There was no variation from the usual procedure of reduction. The methyl amine was obtained by extraction with benzene in the usual manner and precipitated as the hydrochloride. The propyl was simply filtered hot and the amine extracted from the iron with hot water. As the filtrates cooled it crystallized and was filtered off and recrystallized from alcohol.

Table VIII gives the data on these two compounds.

TABLE VIII

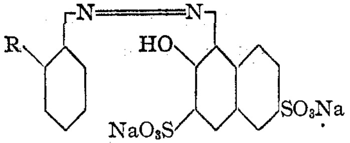
PREPARATION, PROPERTIES AND ANALYSES OF THE SULFONE AMINES

$H_2NC_6H_4SO_2—R$

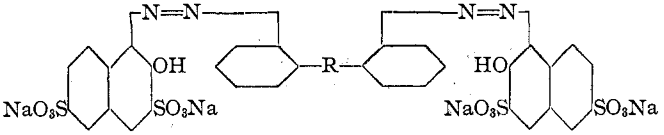
R	Sulfide G.	Yield G.	Yield %	M. p. °C.	Properties	Analyses Calcd.	Analyses Found
Methyl.....	7	5	69	..	Oil	Cl, 16.7	16.9
Propyl......	15	8	53	50	White needles	S, 16.1	16.1

Preparation and Application of the Dyes

In the preparation of the dyes proper we have followed in every respect the procedure of the earlier paper. Our amine hydrochlorides and sulfates were diazotized according to standard methods in acid solution with sodium nitrite and then immediately coupled with R-salt, to give azo dyes of the general structure,



With the diamines these dyes assume the structure,



Only one of the amines, the free mercaptan, HCl—$NH_2C_6H_4SH$, failed to couple and give a dye. This base, although it contained the calculated amount of chlorine and was evidently the compound we supposed it to be, gave a gummy, insoluble diazonium salt and only a faint color with R-salt. Upon salting out, hardly enough color appeared to stain the filter paper through which it was filtered. This is very likely due to the low solubility of the diazonium salt.

The dyes from our bases were all red, orange and yellow shades, and were acid dyes toward animal fiber, dyeing wool and silk from an acid bath. Two per cent. dyeings on 10 g. woolen skeins were made, using 15% sodium sulfate and 4% sulfuric acid, based on the weight of the skein, to aid in dyeing. The methods described in the previous paper were followed in every detail.

Colors of the Dyes[11]

Mono-amine Bases. Dyes from Bases of Tables III and IV and from Table VIII

Table IX shows the *o*-aminophenyl thio-ether and its corresponding sulfone, diazotized and coupled with R-salt and compared with the dyes from *o*-toluidine and *o*-anisidine similarly prepared, all dyed on wool. In the *para* series such a comparison shows the SCH_3 group to be strongly bathochromic compared to the OCH_3 group. The dye from *para* toluidine was tangerine, those from the thio ethers very deep red, and the one from *p*-anisidine intermediate between the two; while with the sulfone the effect was almost completely destroyed, these dyes running toward the orange shades. In the *ortho* series the effect is not nearly so marked. *o*-Toluidine itself gives a dye much lighter in shade than its *para* analog. *The methoxyl group appears more strongly bathochromic than the thio ether.* It will be noted, however, that while the sulfur-free dyes are in general reddish, all those containing sulfur move the characteristic wave length up the scale and appear distinctly yellowish, giving orange shades. This

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[11] Thanks to Dr. R. E. Rose, the color designations here given are from the technical laboratory of E. I. du Pont de Nemours and Co.

is particularly true of the sulfone, in which the red color is almost completely lost and the dye appears a brilliant orange.

TABLE IX

DYES FROM MONO-AMINE BASES COUPLED WITH R-SALT

Auxochromes			
$—CH_3$	$—OCH_3$	$—SCH_3$	$—SO_2CH_3$
Deep salmon	Carmine	Yellowish-red	Orange

Table X shows the effect of increase in molecular weight of the groups attached to the sulfur atom. It comprises the series of thio-ethers from methyl to *iso*-amyl, together with the allyl and the cyclohexyl, and the single representative of the aromatic series, the phenyl derivative; also the methyl and propyl sulfones and the two *para* derivatives not described in the earlier paper. Here, as in the *para* series, the sulfur atom has a distinctly bathochromic effect compared to methyl, but so much less so than the *para* that it actually appears hypsochromic compared to the methoxyl group. The relation of the members of the series to one another appears more clearly than in the *para* series. In general, increase in the molecular weight has a slight hypsochromic effect, reaching its maximum in the phenyl derivative, which is much lighter in shade than any of the dyes containing aliphatic residues. There appears, however, a periodicity in color such as that noticed in the boiling and melting points of some of the aliphatic homologous series. Unfortunately, in the tables published herewith, we have had to substitute for our dyed skeins more or less indefinite color designations, so that this periodicity has completely disappeared, although it is quite marked when the colors themselves are available for comparison. The increase in intensity of the color is slight with the methyl derivative, quite marked with the ethyl, lighter again with the propyl, marked again with the *n*-butyl, and again lighter at the end of the series, the *iso*-amyl. These slight variations in color we do not believe are due to accidental differences in the strength of the dyeing, because we found that differences in the concentration of the dye bath as great as 100% cause a scarcely perceptible difference in the intensity of the color on the skein, and our accuracy was much greater than this.

The cyclohexyl group is aliphatic in its influence, falling in place alongside the *iso*-amyl group rather than with the phenyl. A double linkage apparently has little effect, the allyl group giving a color indistinguishable from the *iso*propyl.

In the series of sulfones, our two representatives show that increase in molecular weight exerts a hypsochromic effect, and more markedly so than with the thio-ethers or the *para* sulfones. It is interesting to note that these sulfones are almost identical in color with their *para* isomers, oxidized sulfur having almost exactly the same influence in the *ortho* that it does in the *para* position.

TABLE X

DYES FROM MONO-AMINE BASES COUPLED WITH R-SALT. EFFECT OF INCREASE IN MOLECULAR WEIGHT

Auxochrome	Color	Auxochrome	Color
$—CH_3$	Deep salmon		
$—OCH_3$	Carmine		
$—SCH_3$	Yellowish-red	$—SO_2CH_3$	Orange
$—SC_2H_5$	Bright scarlet		
$—SC_3H_7$, *n*	Very dull yellow-scarlet.	$—SO_2C_3H_7$, *n*	Orange
$—SC_3H_7$, *iso*	Dull very yellowish-scarlet		
$—SCH_2CH{=}CH_2$	Yellowish-scarlet	$—SCH_2CH{=}CH_2$ (para)	Bluish-red
$—SC_4H_9$, *n*	Scarlet		
$—SC_4H_9$ *iso*	Scarlet		
$—SC_5H_{11}$ *iso*	Scarlet		
$—SC_6H_{11}$ cyclo	Yellowish-scarlet	$—SC_6H_{11}$ cyclo (para)	Bluish-red
$—SC_6H_5$	↓ Yellowish-scarlet		

Regular periodic decrease in intensity of color in direction of arrow.

Diamine Bases. Dyes from Bases of Table VI

Table XI shows the effect of introducing groups containing sulfur between two benzene rings, these groups being in the *ortho* position to the azo group. They are compared to the dye made by coupling tetrazotized *o,o'*-diamino-diphenyl with R-salt. This latter differs markedly from the corresponding benzidine dye, which was a purple shade bordering on deep blue. The peculiar properties of the benzidine dyes have been completely lost, both as to color and in the fact that none of these ortho dyes are direct dyes on cotton. Unfortunately, in making a similar comparison in the *para* series, the intermediates were not coupled with R-salt, but only with salicylic acid, giving mustard-yellows. In general, however, the color relation in the *ortho* and *para* series seems to be the same, although the *para* dyes were very irregular in their effect. Our *ortho* dyes are much more regular. Two sulfur atoms separated only by a methylene group exert a slightly hypsochromic effect. Further separation has a bathochromic influence, still further increased by the introduction of a third sulfur atom, as in the grouping of the atoms in the dye from mustard gas. It is difficult to say, however, whether the effect among the higher members of the series is bathochromic or hypsochromic with respect to the dye from *o,o'*-diamino-diphenyl. Certainly, the sulfur colors are very much brighter shades of red, but whether this is due to the presence of more of the yellow rays in the light transmitted by these colors or the fact that the diamino-diphenyl dye transmits a small proportion of the blue or green, giving it a duller hue, can hardly be seen by simple inspection.

As to the color relations between the sulfur-containing dyes of these diamine bases, it would seem that the bathochromic effect of the sulfur is in some way neutralized, the closer the sulfur atoms in the chain approach each other. This is the only way in which the results can be explained, because we know from our study of the simple thio-ethers that increasing the length of a chain has the opposite (hypsochromic) effect.

TABLE XI

DIAMINE BASES COUPLED WITH R-SALT

	Auxochromes			
(*o*,*o*′-Diamino diphenyl)	—SCH_2S—	—$S(CH_2)_2S$—	—$S(CH_2)_3S$—	—$S(CH_2)_2S(CH_2)_2S$—
Very red-brown	Weak scarlet	Scarlet	Scarlet	Scarlet

Slight regular deepening of the color in this direction →

Summary and Conclusions

1. *o*-Amino thio-ethers may readily be prepared by condensing sodium *o*-nitro-thiophenolate with alkyl halides and reducing the nitro body with iron and acetic acid. Diamines with sulfur between the rings are prepared in the same way from sodium *o*-nitro-thiophenolate and alkylene dihalides. The thio-ethers may be oxidized to the sulfones with chromic acid. All the procedures are similar to those used in preparing the *para* analogs.

2. Dyes prepared from these intermediates by diazotizing and coupling with R-salt, compared with similar sulfur-free dyes from known intermediates, show the following influences of sulfur in the *o*-position.

a. In the simple thio-ethers, a bathochromic effect much less marked than with sulfur in the *para* position, and hypsochromic with respect to the oxygen ethers.

b. In the simple thio-ethers, increase in the molecular weight of the alkyl group attached to the sulfur produces a general hypsochromic effect, showing a periodicity in color similar to that shown in the melting points, etc., of aliphatic homologous series.

c. In the diamines with two sulfur atoms between the rings, a hypsochromic effect with reference to the sulfur-free dye when the two atoms are separated only by one carbon atom. Increasing separation and the introduction of a third atom of sulfur show a bathochromic influence with respect to the other sulfur dyes of the series, the color relation to the sulfur free dye being difficult to place.

BALTIMORE, MARYLAND