4. The mechanism of the reaction involved in the formation of 1-mercapto-benzothiazoles by the action of sulfur on disubstituted thioureas is fully discussed. Experimental evidence is offered in support of the view that this reaction takes place by virtue of direct sulfurization of the *cis*-mercapto form of thiocarbanilide and subsequent loss of the aryl amine to form the mercapto-benzothiazole. It is also pointed out that sulfurization of the *trans*-mercapto form of thiocarbanilide and loss of hydrogen sulfide explains the simultaneous formation of anilido-benzothiazole.

5. Direct sulfurization and subsequent elimination of the corresponding hydrosulfide is offered as the best explanation of the formation of mercapto-benzothiazoles by the action of sulfur on the aryl dithiocarbamic acids and their salts.

6. Six substituted mercapto-benzothiazoles are described together with four of the corresponding disulfides.

7. Methods are given for the preparation of the zinc, normal lead and basic lead salts of the 1-mercapto-benzothiazoles and in three cases such salts are described.

COLUMBUS, OHIO

THE INFLUENCE OF SULFUR ON THE COLOR OF AZO DYES

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The purpose of the present investigation was to study the effect of the sulfur atom and of the sulfone group, in various positions, on the color of azo dyes.

Brand[2] and coworkers found the —SCH$_3$ group to be strongly bathochromic as compared with —OCH$_3$ when introduced into azobenzene or into triphenyl carbinol, but they did not prepare any real dyes except to tetrazotize the dimethylether of o,o'-dimercapto-benzidine and couple it with salicylic acid, which gave a direct yellow on cotton, and with H-acid which gave a blue shade.

Several workers[3] have mentioned that various amines containing sulfur give red dyes when diazotized and coupled with β-naphthol. The importance of thio-indigo and other dyes containing sulfur appeared to warrant a thorough investigation of the influence of sulfur in azo dyes.

Two classes of dyes have been considered. (1) Those derived from mono-amines, particularly those from p-thio-anisidine, $CH_3SC_6H_4NH_2$, and its sulfone, $CH_3SO_2C_6H_4NH_2$, which have been contrasted with the corresponding dyes from p-toluidine and p-anisidine, thus showing the

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[1] From a dissertation by W. R. Waldron, 1922.

[2] Brand, (a) *Ber.*, **42**, 3463 (1909). Brand and Wirsing, (b) *Ber.*, **45**, 1757 (1912); (c) **46**, 820 (1913). Brand and Stallmann, (d) *Ber.*, **54**, 1578 (1921).

[3] Nietzki and Bothof, (a) *Ber.*, **27**, 3262 (1894). Claasz, (b) *Ber.*, **45**, 1027 (1912).

relative effects of the groups CH_3-, CH_3O-, CH_3S- and CH_3SO_2- as auxochromes. The bases containing sulfur and the sulfone group have been prepared, diazotized and coupled with a number of standard intermediates, such as R-salt and chromotropic acid, and the resulting dyes compared with the corresponding known dyes containing methyl and methoxyl groups. In addition to the bases containing the CH_3S- group, a number have been made containing other radicals in place of methyl joined to sulfur, but the influence of the sulfur atom overshadows that of the radical. Methoxyl is a much stronger auxochrome than methyl; the CH_3S- group has been found to be stronger still, while oxidation of this group to the sulfone CH_3SO_2- destroys this effect entirely, the group actually appearing as hypsochromic. (2) Those derived from diamines, which may be regarded as benzidine with various groups interposed between the two rings. A number of bases containing such groups as $-S-$, $-SO_2-$, $-CH_2S-$, $-SCH_2S-$, etc., between the two rings were made and dyes prepared by diazotizing and coupling with standard intermediates. The bases most extensively compared were benzidine, thio-aniline, thio-aniline sulfone and one derived from mustard gas, $NH_2C_6H_4SCH_2$-$CH_2SCH_2CH_2SC_6H_4NH_2$. It was hoped that the dyes from these new bases would resemble those from benzidine, but it appears that the peculiar properties of benzidine dyes are lost when the two rings are separated. On the contrary, a base such as $NH_2C_6H_4SCH_2CH_2SC_6H_4NH_2$ resembles $2NH_2C_6H_4SCH_3$. The $-S-$ and $-SO_2-$ groups have the same effects in the diamino as in the mono.

In all the dyes made, the sulfur atom has a decided bathochromic effect, provided it is joined directly to the ring carrying the azo chromophore group, but it has little effect when it is separated from the ring by even a methylene group. In the dyes derived from the two isomeric bases, $NH_2C_6H_4SCH_2C_6H_5$ and $NH_2C_6H_4CH_2SC_6H_5$, the sulfur has a decided effect in the first case and practically none in the second.

As intermediates, a large number of new compounds have been prepared, along with some that have been previously described. The general method has been to obtain the nitro compound by condensing a halide with the sodium salt of p-nitro-thiophenol, or p-nitrobenzyl bromide with the sodium compound of a mercaptan. One portion of the product has been reduced to the amino-sulfide and the other portion oxidized to the sulfone and then reduced to the amino-sulfone. The details of the numerous preparations are given in tables. The diazotizing, coupling and dyeing were according to accepted methods.

Materials

The p-nitrobenzyl bromide used in this work was prepared following the method of Brewster[4] with slight modifications. p-Nitro-toluene was brominated in the sunlight

4 Brewster, THIS JOURNAL, **40,** 406 (1918).

in Pyrex glass at the boiling point of carbon tetrachloride which was used as solvent, a trace of iodine being used as a bromine carrier. When the amount of solvent recommended by Brewster is reduced to half, the most of the p-nitrobenzyl bromide crystallizes on cooling to 5°, leaving the oily by-products in solution. By one recrystallization from three parts of alcohol the compound was obtained in long needles, m. p., 99°. By removing the carbon tetrachloride first, the product was contaminated with oils which necessitated two or three recrystallizations before it was obtained pure; yield, 55–65%.

p-Nitro-thiophenol was first prepared by Willgerodt.[5] The preparation has been studied and improved by Mayer,[6] Kehrmann and Bauer,[7] Brand[8] and Blanksma.[9]

In the following work the sodium salt of the mercaptan was prepared following in part the methods of Wohlfahrt,[10] Mayer,[11] and Brand.[12] Brand states that this salt is not stable above 100° and that its solution oxidizes rapidly in the air. We isolated the salt readily in a very pure state, dried it at 60°, and found that it keeps indefinitely without apparent change.

One gram-mole of p-nitrochlorobenzene is suspended in 150 cc. of alcohol, to which is added slowly with mechanical stirring 1 mole of sodium disulfide (100% excess) in 600 cc. of water. The reaction is exothermic and the mixture boils by the time all of the disulfide has been added. After the charge has been stirred for 5 minutes it is poured into 2 liters of cold water. By this time practically all of the p-nitrochlorobenzene has reacted; the solution contains a mixture of the sodium salt of the mercaptan and the disulfide. After dilution, the disulfide is filtered off and the red solution acidified, precipitating the impure free mercaptan. This is filtered off at once and dissolved in 500 cc. of boiling 5% sodium hydroxide solution. The hot alkaline solution is filtered to remove any disulfide or impurities carried by the mercaptan. It is allowed to cool and saturated sodium hydroxide solution is added causing an almost complete precipitation of the sodium salt in large red plates. The disulfide residue obtained is reduced with sodium hydroxide and sodium sulfide, following the procedure of Brand, and the solution containing the sodium salt is treated in the same way as described above. The yields obtained average 60%, being equally divided between the two steps in the process.

The p-nitrotoluene, p-nitrochlorobenzene and a large number of naphthalene intermediates used in this work were obtained through the courtesy of E. I. du Pont de Nemours and Company. We are also indebted to them for much information as to carrying out various processes.

I. (a) Alkyl and Aryl para-Nitro-thiophenyl Ethers, $RSC_6H_4NO_2$

The methyl,[13] ethyl[14] and benzyl[15] compounds had previously been made, the first two by the same method as used here.

The alkyl derivatives (including benzyl) were made by dissolving 0.1 mole of the halide in 75 cc. of 95% alcohol and adding 0.105 mole of sodium

[5] Willgerodt, Ber., **18**, 331 (1885).

[6] Mayer, Ber., **42**, 3050 (1909).

[7] Kehrmann and Bauer, Ber., **29**, 2362 (1896).

[8] Brand, Ber., **42**, 3463 (1909); **45**, 1757 (1912); Ger. pat. 228,868.

[9] Blanksma, Rec. trav. chim., **20**, 138 (1901).

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

[11] Mayer, Ber., **42**, 3050 (1909).

[12] Ref. 2c, p. 822.

[13] Blanksma, Rec. trav. chim., **20**, 400 (1901). Ref. 11.

[14] Blanksma, Ref. 13, p. 403.

[15] (a) Fromm and Wittmann, Ber., **41**, 2267 (1908). (b) Kulenkampff, Inaug. Dissertation, Freiberg, 1906.

p-nitro-thiophenate made into a thick paste with water. The mixture is stirred vigorously for 5 minutes and then heated to boiling on a water-bath. The reaction is soon complete, the solution remaining reddish on account of the slight excess of sodium mercaptide. The less soluble solid products separate as the solution is cooled to 0°. The oils were obtained by distilling most of the alcohol, washing the residue with water and dil. alkali and finally drying with calcium chloride. The solids are best recrystallized from 50–80% acetic acid.

The details of the preparations together with the properties of the products are given in Table I. Methyl iodide, benzyl and phenacyl chlorides were used and the bromides of all of the other alkyls.

TABLE I

PREPARATION AND PROPERTIES OF ETHERS OF *para*-NITRO-THIOPHENOL, $RSC_6H_4NO_2$

Alkyl	$NO_2C_6H_4SNa$ G.	Halide G.	—Yield— G.	%	M. p. ° C.	d_{25}^{25}	Properties
Methyl[a]	17.7	14.2	12	71	72	....	Yellow needles
Ethyl[a]	8.9	7.8	7	76	44	....	Yellow needles
*iso*Propyl	17.8	12.3	15.5	76	44.5	....	Yellow needles
Propyl	17.8	12.3	14	71	..	1.1963	Brown oil
*iso*Butyl	35.5	27.4	33	78	..	1.1573	Brown oil
Butyl	17.8	13.7	15	71	..	1.1625	Brown oil
*iso*Amyl	17.8	15.1	15	70	..	1.1335	Brown oil
Benzyl[a]	17.8	12.6	18	73	123	....	Yellow plates
Phenacyl	6	5.2	9	98	118	....	Yellow plates
Hydroxyethyl	35.5	16.2	33	82	59	....	Yellow needles

[a] Previously prepared, the melting points given in the literature are: methyl 67° and 71–72°, ethyl 40° and benzyl 123°.

Four of the thio-ethers are oils having slight but peculiar odors. They could not be distilled even at 5 mm. pressure on account of decomposition. All of the compounds are insoluble in water.

Sulfur analyses were made according to the method of Parr.[16]

*iso*Propyl	$NO_2C_6H_4SCH(CH_3)_2$	Calc. 16.27	Found 16.25
Phenacyl	$NO_2C_6H_4SCH_2COC_6H_5$	11.76	11.88
Hydroxyethyl	$NO_2C_6H_4SCH_2CH_2OH$	16.08	16.28
Bromo-ethyl	$NO_2C_6H_4SCH_2CH_2Br$	12.23	12.94

Fromm and Wittmann[17] obtained *p*-nitrophenyl-thioglycolic acid by condensing the mercaptide with sodium chloro-acetate. This and the corresponding amine have also been prepared by Friedlaender and Chwala.[18] They made the acid from *p*-nitro-chlorobenzene and thioglycolic acid with sodium hydroxide. We obtained it from *p*-nitro-thiophenol and chloro-acetic acid in the presence of alkali.

The same reaction took place with glycol-chlorohydrin and sodium

[16] Parr, *J. Ind. Eng. Chem.*, **11**, 230 (1919).

[17] Ref. 15a, p. 2273.

[18] Friedlaender and Chwala, *Monatsh.*, **28**, 274 (1907).

p-nitro-thiophenolate, forming the thio-ether of monothioglycol as yellow plates; m. p., 59°. On refluxing this compound with hydrobromic acid for several hours the bromide $NO_2C_6H_4SCH_2CH_2Br$ was obtained in 86% yield as yellow plates; m. p., 58°.

The phenyl derivative was readily prepared in 95% yield from p-nitro-chlorobenzene and the sodium salt of thiophenol in alcoholic solution. It had previously been made by Kehrmann and Bauer[19] by eliminating the amino group from p-nitro-p'-amino-diphenyl sulfide.

Esters of p-Nitro-thiophenol

Esters were readily obtained by using benzoyl chloride, phosgene and thiophosgene. These were recrystallized from about 50% acetic acid as they are too soluble in strong acetic acid. Sulfones could not be obtained by oxidizing these esters. On reduction, only the p-nitrophenylthiol-benzoate (6 g.) gave the desired amine (4 g.; 75%); m. p., 115°. The calculated percentage of sulfur was 14.01; that found, 14.10.

PREPARATION AND PROPERTIES OF ESTERS OF $para$-NITRO-THIOPHENOL

					Sulfur		
Formula	$NO_2C_6H_4SNa$ G.	⌐Yield⌐ G.	%	M. p. ° C.	Calc. %	Found %	Properties
$NO_2C_6H_4SCOC_6H_5$....	17.7	14	54	123.7	12.39	12.42	Yellow plates
$(NO_2C_6H_4S)CO$......	18	11	64	174.5	19.04	19.46	Yellow powder
$(NO_2C_6H_4S)CS$.......	18	10	55	141	27.28	27.10	Buff powder

The chlorides of p-toluene-sulfonic and m-nitrobenzene sulfonic acids were used in the same way but the desired esters could not be obtained.

(b) Alkyl and Aryl $para$-Amino-thiophenyl Ethers, $RSC_6H_4NH_2$

The methyl[20] compound had been prepared by the reaction of p-aceto-amino-thiophenol on methyl sulfate with the subsequent removal of the acetyl group, and the ethyl,[21] phenyl[22] and benzyl[15h] compounds by the reduction of the corresponding nitro compounds with tin and hydrochloric or acetic acid. We considered that reductions with iron and a trace of acetic acid, though much slower, would obviate the danger of splitting the molecule at the sulfur atom. The method with iron was found to be quite satisfactory.

To 5 g. of the nitro compound is added 15 g. of iron dust, 0.1 cc. of concd. acetic acid and 100 cc. of water, and the charge is stirred for 10 hours at 85–90°. At the end of this time the mixture is made alkaline with sodium carbonate and filtered. The filtrate is shaken with benzene to obtain the oil and the iron residue extracted four times with hot benzene. The combined extract is distilled on a water-bath, the last traces of benzene being removed by applying a vacuum. The oil is then added to 100 cc. of 5% sulfuric acid and the difficultly soluble sulfate so obtained is recrystallized from boiling

[19] Kehrmann and Bauer, $Ber.$, **29**, 2364 (1896).

[20] Zincke and Jörg, $Ber.$, **42**, 3368 (1909); b. p., 140° (15 mm.)

[21] Monier-Williams, $Soc.$, **89**, 278 (1906); b. p., 280–281°.

[22] Ref. 19; m. p., 93°; acetyl, 146°.

water, a small amount of diatomaceous earth being added to remove any tar.   The yields in all cases are 85–90%.

All of these bases except the phenyl are oils with practically no odors; they darken rapidly in the light and the solubility of the sulfates decreases rapidly with increase in molecular weight, the sulfate of the benzyl compound being almost insoluble in boiling water.   The hydrochlorides are much more soluble and may be obtained by saturating the benzene solution of the base with dry hydrogen chloride.

Details of the preparations and the properties of the compounds are given in Table II.   The sulfates of the bases were analyzed by dissolving in hot water and adding barium chloride solution, the figures given being the sulfur in the sulfate ion.

TABLE II

PREPARATION AND PROPERTIES OF *para*-AMINOPHENYL ALKYL OR ARYL SULFIDES, $NH_2C_6H_4SR$

Alkyl or aryl	Nitro compound G.	Yield G.	%	M. p. ° C.	d_{25}^{25}	Sulfur Calc. %	Found %
Methyl[a]	10	8	97	..	1.1425	..	..
Ethyl[a]	5	4	95	..	1.1010	..	..
isoPropyl	10	7	82	..	....	7.41	7.45
Propyl	10	7.5	88	..	....	7.41	7.30
isoButyl	10	8	93	..	1.0421	6.96	7.08
Butyl	10	8	93	..	....	6.96	7.08
isoAmyl	10	8	92	..	....	6.57	6.62
Phenyl[a]	18.5	10	62	95.8	....	..	..
Benzyl[a]	12	8.5	81	..	1.1321	..	..
Phenacyl	9	7	87	111.5	....	13.19	13.59

[a] Prepared by other authors; the phenyl is given as melting at 93° and 95°.

(c) Alkyl and Aryl *para*-Nitrophenyl Sulfones, $RSO_2C_6H_4NO_2$

Three sulfones of this series have been prepared previously; the methyl[15b] and benzyl[23] by the oxidation of the corresponding sulfides with chromic acid and the phenyl[24] by the reaction of *p*-nitro-chlorobenzene on benzene sulfinic acid under pressure.   The chromic acid method was used in this work.

Ten g. of the sulfide is dissolved in 100 cc. of 80% acetic acid and the mixture heated to boiling, then a saturated solution of chromic acid in water is added a little at a time until an orange coloration denotes the presence of an excess.   After boiling for 15 minutes, an equal volume of water is added and the solution allowed to cool.   The sulfone separates and is recrystallized from 50% acetic acid to remove chromium compounds. The sulfones are obtained as white plates or needles which are recrystallized to constant melting point.

The sulfones are white solids, crystallizing very well from acetic acid or alcohol.   They are very stable towards oxidizing agents, as none of them

[23] Ref. 15a, p. 2270.   Ref. 15b.
[24] Ullmann and Posdermadjian, *Ber.*, **34,** 1154 (1901).

shows any tendency to break at the sulfur atom forming sulfonic acids. The oxidation with chromic acid is exothermic; at the same time the product is purified by oxidation of any disulfides present to soluble sulfonic acids. The sulfones with low melting points separate from the oxidizing mixture as oils but solidify after standing for several hours. The yields are about 85%.

Details of the preparations are given in Table III together with properties of the products. The analyses were made by the method of Parr.

TABLE III

PREPARATION AND PROPERTIES OF para-NITROPHENYL ALKYL OR ARYL SULFONES, $NO_2C_6H_4SO_2R$

Alkyl or aryl	Nitro sulfide	Yield G.	%	M. p. ° C.	Sulfur Calc. %	Found %	Form
Methyl[a]	10	10	84	142.5	15.97	16.02	Needles
Ethyl	10	9	76	138.5	14.91	14.98	Plates
isoPropyl	8	8	86	115.3	14.01	14.41	Plates
Propyl	10	10	86	114	14.01	14.32	Plates
isoButyl	10	10	87	73	13.20	13.25	Needles
Butyl	15	12	70	56.4	13.20	13.28	Plates
isoAmyl	15	12	70	62.5	12.49	12.55	Plates
Phenyl[a]	22.5	22.5	88	142	...	...	Plates
Benzyl[a]	5	5.5	97	172	...	...	Plates

[a] Prepared by other authors who give the melting point of the methyl as 136°, the phenyl 143°, and the benzyl 169°.

(d) Alkyl and Aryl para-Aminophenyl Sulfones, $RSO_2C_6H_4NH_2$

Two of this series of amino sulfones have been prepared previously, the methyl[15b] and phenyl[25] derivatives by the reduction of the nitro bodies with tin and hydrochloric acid.

We have prepared others by reduction from the corresponding nitro compounds described above.

Five g. of the nitrophenyl sulfone is reduced, following the same procedure as used in the case of the nitrophenyl sulfides. When the reduction is finished the charge is diluted with two volumes of water, heated to boiling and filtered hot. In the case of the first 7 products, the iron residue is extracted twice more with 500 cc. of hot water, but with the last two alcohol is used, since they are not very soluble in water. The water or alcohol extracts are cooled to 0°, at which a large percentage of the product crystallizes; but in the case of the methyl and ethyl derivatives it is necessary to evaporate to a small volume before any solid is obtained. The yields are about 90%, being low in the case of the methyl and ethyl compounds on account of their greater solubility.

The amino sulfones are white, odorless solids, and are much more soluble than the corresponding amino sulfides, the solubility decreasing with increase in the size of the radical. The first 4 numbers of the series melt lower than the corresponding nitro compounds while the last 5 melt higher. The methyl and ethyl compounds darken considerably on standing in light and air but the others remain white.

[25] Ref. 24, p. 1155.

Details of the preparations are given in Table IV.

TABLE IV

PREPARATION AND PROPERTIES OF *para*-AMINOPHENYL ALKYL OR ARYL SULFONES,
$RSO_2C_6H_4NH_2$

Alkyl or aryl	Nitro sulfone G.	Yield G.	Yield %	M. p. °C.	Sulfur Calc. %	Sulfur Found %	Form
Methyl[a]	10	6	70	133	18.74	19.13	Plates
Ethyl	10	4	46	89.3	17.33	17.29	Plates
*iso*Propyl	10	7	80	122	16.10	16.29	Needles
Propyl	15	12	92	97	16.10	16.37	Needles
*iso*Butyl	10	8	91	83.7	15.06	15.52	Plates
Butyl	10	8	91	109	15.06	15.28	Needles
*iso*Amyl	11	9	92	110	14.12	13.97	Needles
Phenyl[a]	10	8	90	176	...	...	.....
Benzyl	5	4	89	218.5	12.99	13.11	Needles

[a] Prepared by other authors who give the melting point of the methyl as 137°, and the phenyl 176°

II. (a) Alkyl and Aryl *para*-Nitrobenzyl Sulfides, $NO_2C_6H_4CH_2SR$

No *para* derivatives of this class have been made though *ortho*[26] and *meta*[27] nitrobenzyl-methyl sulfides have been prepared and also the corresponding amines. In these cases the sodium salt of the nitrobenzyl mercaptan was used with methyl iodide. As the *para* mercaptan[28] is rather difficult to prepare, it was thought that the *para* sulfide could be obtained by the reaction of *p*-nitrobenzyl bromide on the sodium salt of the various mercaptans.

The methyl and ethyl derivatives could not be prepared in this way as, on adding a solution of the theoretical quantity of sodium ethylate saturated with an excess of the mercaptans to *p*-nitrobenzyl bromide, *p,p'*-dinitro-dibenzyl sulfide,[29] m. p., 159°, resulted, though the butyl, *iso*amyl and phenyl derivatives were thus obtained, using the mercaptans.

One-tenth g.-mole of *p*-nitrobenzyl bromide is dissolved in 100 cc. of alcohol and heated to 60°. To this is added 0.1 mole of sodium mercaptide made by adding an alcohol solution of 0.1 mole of sodium ethylate to the mercaptan. This is added slowly with rapid agitation at 60° and after 15 minutes the alcohol is distilled and the excess of mercaptan distilled with steam. The oil is washed with water and dried with calcium chloride. In the case of the phenyl compound which is solid it is recrystallized from alcohol. Details are given in Table V.

The mercaptan salt has no apparent reducing action on the nitro group when *p*-nitrobenzyl bromide is still present in excess, but beyond this point it reduces the sulfide to a red substance which is probably an azo compound. Excess of the free mercaptan has no effect, the sodium salt being

[26] Gabriel and Stelzner, *Ber.*, **29**, 163 (1896).

[27] Lutter, *Ber.*, **30**, 1070 (1897); m. p., 31°.

[28] Waters, *Inaug. Dissertation*, Munich (1905).

[29] Otto Fischer, *Ber.*, **28**, 1337 (1895).

necessary for the reduction.   The reaction seems best at 60–70°, for at room temperature the p-nitrobenzyl bromide is rather insoluble in alcohol. The phenyl compound is solid and may be purified by crystallization from alcohol or acetic acid.   The butyl and *iso*amyl derivatives are

TABLE V

PREPARATION AND PROPERTIES OF *para*-NITROBENZYL ALKYL OR ARYL SULFIDES, $NO_2C_6H_4CH_2SR$

Alkyl or aryl	G.	RSH G.	Na G.	Yield G.	%	M. p. °C.	d_{25}^{25}	Sulfur Calc. %	Found %	Form
Butyl...	77.7	43.2	8.28	62	76.6	..	1.1462	14.25	...	Oil
*iso*Amyl	32.4	16.2	3.45	33.7	94	..	1.1513	13.41	...	Oil
Phenyl..	17.2	8.8	1.84	14.5	74.3	79	....	13.10	13.26	White plates

higher-boiling oils which decompose on distillation at 5 mm. pressures. They have an odor similar to the corresponding oils in the previous series. The yields are about 75%.

(b) Alkyl and Aryl p-Aminobenzyl Sulfides, $NH_2C_6H_4CH_2SR$

These compounds are prepared in the same way as the amino sulfides of the previous series, and resemble them in properties, the phenyl compound being solid also, but having a lower melting point.   The oils were isolated as the slightly soluble sulfates which were recrystallized to remove p-aminobenzoic acid.

TABLE VI

PREPARATION AND PROPERTIES OF *para*-AMINOBENZYL ALKYL OR ARYL SULFIDES, $NH_2C_6H_4CH_2SR$

Alkyl or aryl	Nitro sulfide G.	Yield G.	%	M. p. °C.	d_{25}^{25}	Sulfur[a] Calc. %	Found %
Butyl................	13	10	89	..	1.0321	6.66	6.75
*iso*Amyl..............	10	8	41	..	1.0307	6.20	6.28
Phenyl................	7.25	6	94	72	....	14.91	35.13

[a] The first two of the series are oils, and the analyses were therefore made on the sulfates of the bases, only the sulfur in the sulfate ion being determined.   These sulfates are obtained as curdy precipitates, very slightly soluble in cold water, something like 1 g. per liter.   On recrystallization from hot water, they separate in flocculent form.

(c) Alkyl and Aryl $para$-Nitrobenzyl Sulfones

The sulfones of this class are prepared in the same way as those of the previous series.   They are crystalline solids, and are formed with a good yield,—about 75%.   The butyl and *iso*amyl compounds are contaminated with 5–10% of p-nitrobenzoic acid, which lowers their melting points and which it is practically impossible to eliminate by crystallization.   It is removed by agitating several times with a large volume of 5% solution of sodium carbonate.   The sulfones may be recrystallized from acetic acid or alcohol.   They are very slightly soluble in water; when the oxidation is carried out with a water suspension of the sulfide a poor yield of sulfone

contaminated with tar is obtained. Hot 20% sodium hydroxide solution decomposes the sulfones, giving a red solution and a yellow precipitate (m. p., 195°) which contains no sulfur and is probably a compound of the formula $NO_2C_6H_4CH:CHC_6H_4NO_2$ (m. p., 210–216°).

A similar ·decomposition[30] has been noted with sulfone esters.

TABLE VII

PREPARATION AND PROPERTIES OF *para*-NITROBENZYL ALKYL OR ARYL SULFONES, $NO_2C_6H_4CH_2SO_2R$

Alkyl or aryl	Nitro sulfide G.	—Yield— G.	%	M. p. ° C.	Sulfur Calc. %	Found %	Form
Butyl	33	19	50	139.5	12.49	12.40	Plates
*iso*Amyl	36.5	31	75	117	11.83	11.81	Plates
Phenyl	7.2	7.2	88	209.5	11.58	11.51	Plates

(d) Alkyl and Aryl *para*-Aminobenzyl Sulfones, $NH_2C_6H_4CH_2SO_2R$

The amino sulfones are prepared in the same way as those of the former series, starting with material free from *p*-nitrobenzoic acid, and have similar properties. They are removed from the iron residue by extraction with alcohol. They were recrystallized by dissolving in hot alcohol, adding water cautiously to incipient separation and cooling.

TABLE VIII

PREPARATION AND PROPERTIES OF ALKYL OR ARYL *para*-AMINOBENZYL SULFONES, $NH_2C_6H_4CH_2SO_2R$

Alkyl or aryl	Nitro sulfone G.	—Yield— G.	%	M. p. ° C.	Sulfur Calc. %	Found %	Form
Butyl	8	6	85	95	14.11	13.9	Needles
*iso*Amyl	11	7	71	126	13.30	13.32	Needles
Phenyl	7.2	4	62	180	13.00	13.20	Needles

III. (a) p,p'-Dinitro-diphenyl Derivatives with Various Groups between the Two Rings, $NO_2C_6H_4.X.C_6H_4NH_2$

In this series of compounds, p,p'-dinitro-diphenyl may be considered the simplest member, the more complicated ones consisting of various radicals containing sulfur between the two rings, X in the above formula standing for the following groups: $-S-$, $-CH_2S-$, $-CH_2SCH_2-$, $-SCH_2S-$, $-SC_2H_4S-$, $-SC_3H_6S-$, $-SC_2H_4SC_2H_4S-$, $-SC_2H_4SO_2-C_2H_4S-$.

Nietzki and Bothof[3a] prepared dinitro-diphenyl sulfide by treating *p*-nitro-chlorobenzene with sodium sulfide. This reaction was rather slow and did not go to completion. p,p'-Dinitro-benzylphenyl sulfide was formed from *p*-nitrobenzyl bromide and sodium *p*-nitro-thiophenol. p,p'-Dinitro-dibenzyl sulfide was prepared by Fischer[29] from *p*-nitrobenzyl chloride and ammonium sulfide. Others of the series containing two or more separated sulfur atoms we obtained from two molecules of sodium *p*-nitro-thiophenolate with the following halides, methylene iodide, ethyl-

[30] Michael and Comey, *Am. Chem. J.*, **5**, 349 (1883–84).

ene bromide, trimethylene bromide, benzal chloride, mustard gas and mustard gas sulfone. In all cases the reaction took place at once with the separation of the new compound. Methylene chloride did not react at all because of its low boiling point and the inactivity of the chlorine atoms; hence, the iodide was used. In the case of ethylene bromide the reaction took place on warming to 70°, but when one ethylene hydrogen has been replaced by methyl, as in propylene dibromide, the reaction is much slower and the resulting compound was contaminated with a large amount of disulfide, produced by oxidation of the mercaptan either by the nitro group or by air. This takes place only to a very limited extent when the reaction is rapid. This was borne out by the fact that using butylene dibromide, in which two ethylene hydrogen atoms have been replaced by methyl, the desired reaction was so slow that the product obtained consisted almost entirely of disulfide.

Mustard gas and its sulfone both react immediately with the mercaptide, their chlorine atoms being much more active.

These nitro sulfides are yellowish, odorless solids which crystallize well from acetic acid, and are insoluble in water and only slightly soluble in alcohol. The yields average about 85%.

Inasmuch as the different compounds are made, using several intermediates, and the preparation is self-explanatory from Table IX, following, it will suffice to describe one completely, the others being made in the same way.

One-tenth g.-mole of methylene iodide is dissolved in 100 cc. of alcohol and 0.21 mole of sodium p-nitro-thiophenolate, with enough water to produce a thick paste, is added. The mixture is stirred while being heated on a water-bath to 65–70°. After a few minutes at this temperature, the reaction is complete and the solid sulfide partly precipitates. On cooling to 0°, practically all of the sulfide separates and is filtered off. It is purified by boiling with a 1% sodium carbonate solution and recrystallized from 80% acetic acid in which it is fairly soluble hot, and very slightly so cold; the latter treatment removes any dinitro-diphenyl disulfide formed.

TABLE IX

PREPARATION AND PROPERTIES OF p,p'-DINITRO-DIPHENYL COMPOUNDS, $NO_2C_6H_4$—X—$C_6H_4NO_2$

X	Mercaptide G.	Halide G.	Yield G.	Yield %	M. p. °C.	Sulfur Calc. %	Sulfur Found %	Properties
—S—[a]	7.8	31.5	10	36	154	...	...	Orange plates
—CH₂S—	17.8	21.6	27.4	94	108	11.07	10.99	Pale yellow plates
=(CH₂)₂S[a]	9.6	17.28	11.5	95	159	...	...	Yellow needles
—SCH₂S—	35.4	26.7	23.5	83	179	19.88	19.83	Olive plates
—S(CH₂)₂S—	17.7	9.4	10	60	136	19.06	19.11	Yellow plates
—S(CH₂)₃S—	35.4	20.2	32	91	110	18.29	18.33	Yellow plates
—SCH(C₆H₅)S—	35.4	16.1	30	75	150.5	16.09	16.03	Yellow needles
=(SCH₂CH₂)₂S	17.7	8	15	76	86.5	24.28	24.29	Yellow plates
=(SCH₂CH₂)₂SO₂	27.7	14.5	25	77	170	22.48	22.48	Pale yellow plates

[a] Previously known, the melting points being given as 154° and 159°, respectively.

(b) p,p'-Diamino-diphenyl Compounds $(NH_2C_6H_5)_2X$

Two amines of this group have been made previously. Nietzki and Bothof[3a] prepared thio-aniline by reducing the dinitro derivative, while Mertz and Weyth[31] prepared it by a fusion of aniline with sulfur. O. Fischer[32] reduced dinitro-dibenzyl sulfide to the corresponding diamine with tin and hydrochloric acid. We have prepared these and the other amines of this group by reducing the dinitro compounds just described with iron and acetic acid as outlined above. Benzene was used for extracting the amines from the iron residue. On concentrating and cooling the benzene solutions, the amines were usually obtained as crystals. One of them is an oil.

The amines are very slightly soluble in water, more soluble in alcohol and very soluble in benzene. The solubility in all cases decreases rapidly with increase in molecular weight.

TABLE X

PREPARATION AND PROPERTIES OF p,p'-DIAMINO-DIPHENYL COMPOUNDS, $NH_2C_6H_4$—X—$C_6H_4NH_2$

	Nitro comp.	—Yield—		M. p.	Sulfur Calc.	Found	
X	G.	G.	%	°C.	%	%	Properties
—S—[a]	..	..	..	108	...	...	Needles
—CH₂S—	10	6	76	93	13.92	14.10	Flat needles
=(CH₂)₂S[a]	5.5	3	68	105	...	...	White plates
—SCH₂S—	10	7.5	92	99	24.43	24.47	Red needles
—S(CH₂)₂S—	10	7.25	88	111	23.20	23.28	Red needles
—S(CH₂)₃S—	5.5	4	87	...	8.26[b]	7.97	Oil
—SCH(C₆H₅)S—	10	7.5	88	131	18.93	18.40	White needles
=(SCH₂CH₂)S	6	4.5	88	93	28.60	28.54	Red needles
=(SCH₂CH₂)SO₂	6	5	97	149	26.12	26.22	White needles

[a] Previously prepared, the melting points being given as 108° and 105°, respectively.
[b] In the sulfate ion of the sulfate.

(c) Sulfones from the Dinitro-diphenyl Compounds

Fromm and Wittmann[33] prepared dinitro-diphenyl sulfone by oxidizing the sulfide dissolved in acetic acid with chromic acid. Following the procedure described above for preparing mononitro sulfones, we obtained disulfones in all cases except from p,p'-dinitro-diphenyl-dithiomethane, where the two sulfur atoms are separated only by a CH_2 group and oxidation breaks the molecule, yielding •only soluble sulfonic acids. Various oxidizing agents were tried with the same result. In the case where the two sulfur atoms were separated by two CH_2 groups, no difficulty was encountered even when three sulfur atoms are present.

The sulfones are insoluble in water, slightly soluble in alcohol, and

[31] Mertz and Weyth, Ber., 3, 978 (1870).
[32] Ref. 29, p. 1338.
[33] Ref. 15a, p. 2270; m. p., 282°.

fairly soluble in boiling 80% acetic acid, the last member, however, being insoluble in this, as the solubility of the series decreases markedly with the increase in molecular weight. They are white solids with high melting points, and are obtained in yields averaging 75%.

TABLE XI

PREPARATION AND PROPERTIES OF SULFONES FROM p,p'-DINITRO-DIPHENYL COMPOUNDS, $NO_2C_6H_4.X.C_6H_4NO_2$

	Nitrosulfide G.	—Yield— G.	%	M. p. °C.	Sulfur Calc. %	Found %	Form
$-SO_2-$	12	11	82	282	...	...	Needles
$-CH_2SO_2-$	13.7	13.7	90	195	9.95	10.03	Plates
$=(CH_2)_2SO_2$	6	5	75	260	9.54	9.49	Needles
$-SO_2(CH_2)_2SO_2-$	10	9	75	235 dec	16.02	16.16	Needles
$-SO_2(CH_2)_3SO_2-$	12.5	7	47	208	15.48	15.59	Needles
$=(SO_2CH_2CH_2)_2SO_2$	12	11	80	235 dec	19.54	19.68	Needles

(d) Reduction Products of p,p'-Dinitro-diphenyl Sulfones

The preparation of diamino sulfones is much more difficult than that of the mono-amine sulfones in Classes I and II. Fromm and Wittmann[34] obtained diamino-diphenyl sulfone by reducing the corresponding nitro-sulfone with tin and acid. This reduction also took place with iron and acetic acid but on carrying it to the next member of the series, p,p'-dinitro-benzylphenyl-sulfone, a compound was obtained which seemed by analysis to be a nitro-amino sulfone and could not be reduced further by this means; m. p., 215° (decomp.). Analysis: Calc. for S, 10.98. Found: 11.26. Dinitro-dibenzyl sulfone yielded a white, tarry substance.

These last two reductions were readily effected by using tin and hydro-chloric acid in alcohol, the tin double salt separating on cooling. From this the desired base was obtained.

In the case of the di- and tri-sulfones, neither method of reduction was satisfactory. According to the analyses of the compounds isolated, both nitro groups had been reduced, and also one sulfone group to a sulfide; or both sulfone groups to sulfoxide, this being the case with the di- and tri-sulfones. Various methods of reduction were tried but the desired compounds were not obtained; according to the analyses, $NO_2C_6H_4SO_2$-

TABLE XII

PREPARATION AND PROPERTIES OF p,p'-DIAMINO-DIPHENYL SULFONES, $NH_2C_6H_4.X.C_6H_4NH_2$

	Nitro compound G.	—Yield— G.	%	M. p. °C.	Sulfur Calc. %	Found %	Properties
$-SO_2-$[a]	4	2.5	78	176.5	...	...	Yellow needles
$-CH_2SO_2-$	10	7	86	216	12.22	12.28	White plates
$=(CH_2)_2SO_2$	5	3	73	187.5	11.60	11.91	Yellow needles

[a] Previously prepared.

[34] Ref. 15a, p. 2270; m. p., 174°.

$C_2H_4SO_2C_6H_4NO_2$ reduced to the compound $NH_2C_6H_4SO_2C_2H_4SC_6H_4NH_2$; calc.: S, 20.75; found, 20.87; m. p., 206° (chars).

Preparation and Application of the Dyes

1. From Mono-amines. See Tables II, IV, VI and VIII

One-hundredth g.-mole of the base (in case it is liquid the equivalent quantity of the sulfate) is dissolved in two equivalents of hydrocloric acid in 75 cc. of water, and diazotized with one equivalent of sodium nitrite at 5°, maintaining an excess of nitrate for a half-hour, as shown by the starch-potassium iodide test. One-hundredth mole of R-salt, plus 5% excess, is dissolved in 50 cc. of water to which have been added two equivalents of sodium carbonate, and the mixture is cooled to 5°. The diazo solution is added to the alkaline solution of R-salt at this temperature, and the whole stirred half an hour. In some cases the dye separates immediately, while in others it remains in solution. At the end of this time a small sample is salted out and spotted on paper, the clear ring being tested with R-salt solution to detect the presence of any diazo body; none should be present, as shown by the absence of color on this ring. The solution should also be alkaline to Brilliant Yellow paper, adjustments being made in cases where it does not answer these requirements. After the coupling is complete the solution is heated to 45° and enough salt is added in small amounts to obtain a clear, or slightly colored, ring when spotted on paper. The dye is filtered out from the warm solution and dried at 80°.

These dyes belong to the class of acid colors, dyeing animal fiber from a weak acid bath, the application being made in the following way. As the strength of the several dyes varies considerably due to the amount of salt present, in order to obtain dyeings of approximately the same strength for comparison, it is necessary to make standard solutions of 500 cc. of 0.1%, of each. These are spotted on paper and the weak and strong ones noted, corrections being made in the volume of solution used for dyeing. For a 2% dyeing on a 10 g. woolen skein, 200 cc. of this solution is used, and more or less is added according to the strength. The measured volume is diluted to 700 cc., 4% sulfuric acid and 15% Glauber's salt, based on the weight of material dyed, being added. The wool which has been thoroughly wet in warm water, is immersed and the whole is heated slowly to boiling, while the skeins are turned frequently to insure even dyeing. After 30 minutes' boiling the bath is exhausted, and the skeins are removed, washed and dried.

Both in the preparation of the dyes and the application, approximately standard solutions of the various acids, bases and salts were used, so that the desired quantities could be easily measured.

In this same manner, dyes were made from thio-anisidine and thio-ansidine sulfone, the following intermediates being used in addition to R-salt: salicylic acid, Schaeffer's salt, Neville and Winther's acid, L-acid, (1-OH, 5-SO$_3$H) and chromotrope acid. For comparison, the corresponding dyes were prepared from p-toluidine and p-anisidine.

2. From Diamines. See Tables X and XII

One-hundredth g.-mole of the base is dissolved in 100 cc. of hot water containing 0.04 g.-mole of hydrochloric acid, cooled to 5° and diazotized with 0.02 g.-mole of sodium

nitrite, while an excess of nitrite is maintained for one-half hour as shown by the starch-iodide test; 0.022 mole of salicylic acid is dissolved in an equivalent quantity of sodium hydroxide, so that it is just alkaline to Brilliant Yellow paper, and then 0.2 mole of sodium carbonate is added.   This solution is cooled to 5° and the tetrazotized base, which has previously been neutralized to a slight acidity to congo red paper, is added slowly at this temperature.   After three hours it is tested for excess diazo with R-salt solution, by spotting a sample on paper and testing the clear ring.   This should be nega-tive, showing that the first molecule of salicylic acid has coupled; 0.02 moles of sodium hydroxide is added and the temperature brought slowly to 35°, stirring overnight at this temperature.   In the morning the second molecule should be coupled, and the solution should be strongly alkaline to Brilliant Yellow paper.   To test for excess of the second diazo group, a small amount of color is diluted and divided between two test-tubes, and to one several drops of 1% H-acid solution are added.   Both are heated to boiling and should remain the same color.   A change in the one containing H-acid denotes the pres-ence of free diazo group.   The dyes are heated to 50° and salted out.

Dyes containing salicylic acid are commonly known as acid chrome colors, since the color is fixed on the wool with a dichromate mordant.   These colors were dyed as follows.

A standard solution of dye is made as described above, and the quantity measured to give a 2% dyeing; 3% acetic acid and 15% Glauber's salt are added, the skein is im-mersed and boiled for $^1/_2$ hour.   An addition of 3% acetic acid is made and the boiling continued for another half hour.   In case the dye is to be chromed, this is followed by adding 10% dichromate and boiling for another half hour, after which the skeins are removed, washed and dried.

Thio-aniline, thio-aniline sulfone and the diamine from mustard gas, NH_2-$C_6H_4SCH_2CH_2SCH_2CH_2SC_6H_4NH_2$, were tetrazotized and coupled with the other intermediates which were used with the mono-amines described above.

At the same time similar dyes from benzidine itself were prepared for comparison.   The couplings were made in the same way as with salicylic acid described above, except that sodium carbonate was substituted for the hydroxide, the couplings being made in a weaker alkaline solution. In this series also the first molecule of intermediate was coupled at a low temperature and, after testing with R-salt for uncombined tetrazo body, the temperature was elevated to 35° and the suspension stirred overnight.

The dyes obtained were applied to wool in exactly the same way as the acid dyes obtained from mono-amine bases.

Additional dyes were made with these same bases by coupling them with intermediates used to produce direct dyes, using naphthionic, gamma- and H-acids.   The bases were tetrazotized in the usual way, but the couplings were made in the case of the first two intermediates in neutral solutions, neutrality being maintained during the formation of hydro-chloric acid in the course of the coupling; with H-acid the solution was kept alkaline throughout by an excess of carbonate.

These colors are applied to cotton in the following way.

A standard 0.1% solution of the dye is prepared as usual and the required volume for the desired strength is diluted to 250 cc., 15% of sodium chloride, based on the weight of skein used, being added.   The skeins are introduced into the boiling solution and al-lowed to remain there for $^3/_4$ hour and frequently turned.

Colors of the Dyes[35]

1. Mono-amine Bases with R-salt. Dyes from Bases of Tables II, IV, VI and VIII

The first study was of the bases in Table II to determine the effect of changing the radical in $NH_2C_6H_4SR$, R being methyl, ethyl, propyl, *iso*propyl, butyl, *iso*butyl, *iso*-amyl phenyl and benzyl. All of these give red dyes with R-salt, there being no distinguishable difference in color among them except that the —SCH_3 is a bordeaux and the —SC_6H_5 is scarlet. The benzyl group acts exactly like the alkyls higher than the methyl group. The sulfur atom appears here as strongly bathochromic and its influence is so decided that the size or nature of the group beyond it makes little difference; or, what is more probable, the part of the auxochrome group which is in immediate union with the benzene nucleus is the decisive factor. This is shown by a comparison of the isomeric bases containing the groups —$SCH_2C_6H_5$ and —$CH_2SC_6H_5$. The dye from the first is deep red, while that from the second is tangerine, the auxochrome effect of the sulfur being lost by the interposition of the —CH_2— group. The same color is shown by the dye from the base containing —$CH_2SC_5H_{11}$ (*iso*). The oxidation of the —S— in these two to —SO_2— has no effect on the color.

Contrasting the amino sulfones of Tables IV and VIII with the amino sulfides of Tables II and VI we find that the oxidation of —S— to —SO_2— destroys the effect of the —S— completely; in fact the sulfone group is actually hypsochromic, the dyes from $NH_2C_6H_4SO_2R$ being gold while the one from aniline itself is orange. The size and character of the radical carried by the sulfone group have no effect on the color, the dyes from all the bases in Table IV being indistinguishable.

A curious fact appears with the dye from $NH_2C_6H_4SCOC_6H_5$. This contains —S— joined to the nucleus and, according to what was said above, was expected to be deep red like the dye from $NH_2C_6H_4SCH_2C_6H_5$ from which it differs only in the oxidation of the —CH_2—. The dye in question is scarlet but its tinctorial power is so diminished that only a moderate color was obtained by double strength dyeing. Here oxidation, even of a group beyond the sulfur, has lightened the color.

2. Mono-amine Bases with Various Intermediates

As it appears that the alkyl present in the sulfide and sulfones is of little consequence, further comparisons were made between dyes containing the groups —CH_3, —OCH_3, —SCH_3 and —SO_2CH_3; that is, *p*-toluidine, *p*-anisidine, *p*-thio-anisidine and its sulfone were diazotized and coupled with salicylic acid, Schaeffer's salt, Neville and Winther's acid, L-acid,

[35] 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.

R-salt and chromotrope acid. The colors of the dyes obtained are given in the table below.

TABLE XIII

COLORS OF DYES FROM BASES WITH VARIOUS INTERMEDIATES

Acids	—CH₃	Auxochromes —OCH₃	—SCH₃	—SO₂CH₃
Salicylic	Yellow	Yellow	Yellow, darker	Gold
Salicylic, chromed	Yellow	Yellow	Old gold	Old gold
Schaeffer's	Orange	Scarlet	Red	Gold
Neville and Winther's	Scarlet	Scarlet	Red	Orange
L-acid	Red	Red	Bordeaux	Old gold
R-salt	Scarlet	Red	Bordeaux	Gold
Chromotrope	Cardinal	Heliotrope	Violet	Red

We have here the same color relations, the auxochromes being arranged in the order: —SCH₃ > — OCH₃ > — CH₃ > — SO₂CH₃. This is true regardless of the nature of the second constituent of the dye.

3. Diamine Bases with Salicylic Acid, Chromed. See Tables X and XII

The colors obtained are as follows: (1) benzidine, gold; (2) thio-aniline, old gold; (3) and (4) the rings joined by —CH₂S— and —CH₂-SCH₂—, old gold; (5) by —SCH₂S—, old gold but deeper; (6) and (7) by —SCH₂CH₂S— and —SCH₂CH₂SCH₂CH₂S—, gold. The presence of sulfur connected to two rings in thio-aniline darkens the color considerably as compared with benzidine. The introduction of one or two methylene groups with one sulfur atom weakens the coloring property, and the sulfone is still weaker. In the case where two sulfur atoms are separated by CH₂, the color is practically the same as with thio-aniline, the influence of the CH₂ being overcome by the relatively large amount of sulfur adjacent. Where the sulfur atoms are farther apart, being separated by ethylene, the color is much lighter and more greenish, lacking the reddish overcast obtained with thio-aniline and its sulfone. Where the two rings are separated by three sulfur atoms and two ethylene groups, the color is still darker and greener, while the introduction of a sulfone group in the center between the two ethylenes does not change the color at all, showing again that the sulfur atoms connected directly to the rings are the ones that exert the most influence on the color.

The sulfone of thio-aniline gives an old gold, the same as thio-aniline but darker apparently reversing the relationship found above between sulfides and sulfones. The dye from mustard gas sulfone is practically the same as that from mustard gas, which is as would be anticipated since the —SO₂— in the group —SCH₂CH₂SO₂CH₂CH₂S— cannot be expected to show much effect.

For these diamines, alicyclic acid was used because of the importance of Anthracene Yellow C (Cassella)[36] obtained by coupling this inter-

[36] Schultz, "Farbstofftabellen," 1914, p. 294.

mediate with thio-aniline. The couplings were made in the following way, as were also the acid colors described subsequently.

4. Diamine Bases with Various Intermediates

The dyes from thio-aniline, thio-aniline sulfone and the diamine from mustard gas when coupled with various intermediates are contrasted with those from benzidine. The colors are given in the following table.

TABLE XIV

COLORS OF DYES FROM CERTAIN DIAMINES COUPLED WITH VARIOUS INTERMEDIATES

Acids	Benzidine	—S—	—SO₂—	= (SCH₂CH₂)₂S
Salicylic (chromed)	Yellow	Gold	Gold	Yellow
Schaeffer's salt	Maroon	Scarlet	Orange	Scarlet
Neville and Winther's	Heliotrope	Red	Scarlet	Red
L-acid	Claret	Claret	Burnt orange	Red
R-salt	Purple	Claret	Burnt orange	Red
Chromotrope	Purple	Heliotrope	Claret	Heliotrope
Gamma-acid	Violet	Claret	Claret	Red
Chicago acid	Purple	Lilac	Maroon	Violet
H-acid	Blue	Purple	Maroon	Lilac

This series of colors indicates that where the diphenyl rings are separated by sulfur, sulfone and other groups, they no longer possess the properties of benzidine, which gives colors varying from deep reds to blues and violets. The thio-aniline and its sulfone give much lighter colors, differing slightly but practically in the same range of the spectrum as those obtained from the mono-amines coupled with the same acids, though the molecular weight is greater than that of the benzidine dyes and approximately double that of the mono-amine series. The dyes containing three sulfur atoms, with the mustard gas residue between, are also slightly lighter than those from thio-aniline.

In this series the sulfur divides the molecules, so that the colors obtained appear as if each half were acting as a unit, while with benzidine the effect of each group is felt in the opposite ring.

The three diamine bases having —SCH₂S—, —SCH₂CH₂S— and —SCH₂CH₂CH₂S— between the rings were coupled with gamma-acid. The dyes from the first two were red and practically identical, but the last gave a maroon.

The conclusion drawn above, that these diamine bases do not possess the properties of benzidine, is borne out by the fact that they do not form direct cotton dyes. Benzidine, coupled with gamma-acid or H-acid, forms colors which dye cotton direct from a salt bath. Those obtained from the three sulfide bases used in the previous series, when coupled with intermediates suitable for producing direct colors, are found to be lacking in this property. The benzidine dyes exhaust the bath completely, while the others do so only in part; some color, however, remains in the fibre. The

dyes from the trisulfide bases from mustard gas show some tendency towards being direct, as the colors do not wash out in cold water. The monosulfides are poorer, and in the case of the sulfones practically all of the color washes out in cold water. On the other hand, all of them are removed in boiling water.

Table XV gives the colors of these dyes on cotton. Here also the color effect produced by the sulfide and sulfone groups is the same as with the acid dyes described above.

TABLE XV

COLORS OF DYES FROM DIAMINE BASES COUPLED WITH SEVERAL INTERMEDIATES AND DYED OVER COTTON

Intermediates	Benzidine	—S—	—SO₂—	=(SCH₂CH₂)₂S
Naphthionic acid	Red	Burnt orange	Burnt orange	Gold
Gamma-acid	Violet	Claret	Claret	Maroon
H-acid	Blue	Blue	Lilac	Violet

Summary

A series of bases, p-NH₂C₆H₄SR, has been made and these have been diazotized and coupled with R-salt to find the effect of changes in the radical R on the color. Dyes have been made from p-toluidine, p-anisidine, p-thioanisidine and its sulfone by diazotizing and coupling with a number of intermediates. It has been found that —SCH₃ > —OCH₃ > —CH₃ > —SO₂CH₃ act as auxochromes.

Diamine bases of the type p,p'-NH₂C₆H₄-X-C₆H₄NH₂ have been made in which X is —S—, —SO₂—, —SCH₂—, —SCH₂S—, —SCH₂CH₂S—, —SCH₂CH₂SCH₂CH₂S—, etc., and these were tetrazotized and coupled with various intermediates to find the effect of the group between the two rings on the color of the dyes. These bases do not resemble benzidine in giving fast cotton dyes.
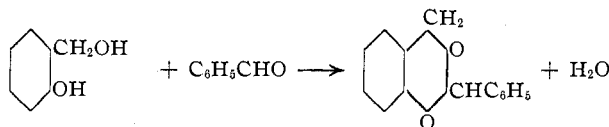
BALTIMORE, MARYLAND

ARYL 1,3-BENZO-DIOXANES (ARYL METHYLENE-SALIGENINS)

BY ROGER ADAMS, A. W. SLOAN AND B. S. TAYLOR

In a contribution from this Laboratory on the structure of disalicyl aldehyde,[1] it was shown that saligenin condensed readily with benzaldehyde to yield 2-phenyl-1,3-benzo-dioxane according to the following equation.

$$\text{(structure: benzene ring with CH}_2\text{OH and OH)} + C_6H_5CHO \longrightarrow \text{(benzo-dioxane structure: } CH_2, O, CHC_6H_5, O) + H_2O$$

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[1] Adams, Fogler and Kreger, THIS JOURNAL, 44, 1126 (1922).