compound was obtained as deep red needles. The corresponding sulfur compound is light brown. The seleno-ether does not melt up to 300°.

Anal. Calcd.: Se, 18.19. Found: 18.49, 18.22.

Summary

The following new compounds have been prepared: 2,2-bis(seleno-ethyl)propane, $(CH_3)_2C(SeC_2H_5)_2$, 2,2-bis(seleno-ethyl)butane, $CH_3(C_2H_5)$-$C(SeC_2H_5)_2$, 3,3-bis(seleno-ethyl)pentane, $(C_2H_5)_2C(SeC_2H_5)_2$, ethyl seleninic acid hydronitrate, $C_2H_5SeO_2H{\cdot}HNO_3$, ethyl selenium tribromide, $C_2H_5SeBr_3$, bis(β-ethyl-selenomercapto-ethyl)sulfide, $(C_2H_5SeCH_2CH_2)_2S$, bis(β-ethyl-selenomercapto-ethyl)sulfoxide, $(C_2H_5SeCH_2CH_2)_2SO$, bis(β-ethyl-selenomercapto-ethyl)sulfone, $(C_2H_5SeCH_2CH_2)_2SO_2$, anthraquinone 1-butylsulfone-5-ethyl selenide, 1,5-$C_2H_5Se{\cdot}C_{14}H_6O_2{\cdot}SO_2C_4H_9$.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF JOHNS HOPKINS UNIVERSITY]

THE INFLUENCE OF SULFUR ON THE COLOR OF AZO DYES. FURTHER INVESTIGATION

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In previous papers from this Laboratory,[2] the influence of sulfur in the *para* and *ortho* positions has been studied, and the position of the sulfur has been found to have marked influence. This suggested the investigation of the effect of sulfur in the *meta* position. In all three series, the four groups $—CH_3$, $—OCH_3$, $—SCH_3$ and $—SO_2CH_3$ have been contrasted. The first line of attack was to couple diazotized bases with *o*-cresol, guaiacol and *o*-methylmercaptophenol assuming that the coupling would take place *para* to the hydroxyl and hence *meta* to the other substituent, so that dyes would be obtained with the desired groups in the *meta* position. Diazotized sulfanilic acid did not couple satisfactorily with these phenols.[3] Naphthionic and gamma acids were diazotized and coupled with them and dyes were obtained, but the couplings did not appear to be complete and difficulties were encountered in proving the structure of the products. The bases *m*-$CH_3SC_6H_4NH_2$ and *m*-CH_3SO_2-$C_6H_4NH_2$, isomeric with those previously employed, have been prepared. These have been diazotized and coupled with R-salt, an intermediate that has been found to give satisfactory contrasts in the *ortho* and *para* series. For comparison, analogous dyes have been made from

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[1] From the Doctor's Dissertation of G. D. Palmer, 1924.

[2] Waldron and Reid, THIS JOURNAL, **45,** 2399 (1923). Foster and Reid, *ibid.*, **46,** 1923 (1924).

[3] Zincke and Müller found difficulties in coupling with a similar compound. *Ber.*, **46,** 780 (1913).

m-toluidine and *m*-anisole. Additional bases *m*-$RC_6H_4NH_2$ and *m*-$RSO_2C_6H_4NH_2$, in which **R** is ethyl, butyl or benzyl, have been prepared and converted into dyes in order to study the effect of the group joined to the sulfur. A dye has been made from the base *m,m'*-$NH_2C_6H_4S.SC_6H_4NH_2$ since the —S.S— group may be present in some, at least, of the sulfur dyes.

Results

The results are similar to those previously reported: sulfur in the group —SR has a marked bathochromic effect which is lost entirely on oxidation to the sulfone, —SO_2R. In fact, the sulfone group is actually hypsochromic. The order of the groups —CH_3, —OCH_3 and —SCH_3 proves to be the same in the *meta* series as in the *para*, but the *meta* dyes resemble the *ortho* in being less intense and distinctive than the *para* dyes.

In the *para* series, the effect of the sulfur is so intense that the alkyl in the —SR makes little difference, but in the *ortho* and *meta* series, where the influence of the sulfur is less pronounced, the differences due to the alkyl groups are more apparent, and there seems to be a sort of periodicity as the molecular weight of the alkyl group increases. In all these series, the dye in which the sulfur carries a methyl group is the furthest toward the red and the deepest in color.

In the case of the sulfone dyes, matters are reversed, the heavier groups seeming to counteract the hypsochromic action of the —SO_2— group, so that the color becomes redder and stronger as we go from methyl to ethyl and to butyl, but when we pass to benzyl a weak buff is obtained.

The effects of the alkyl groups in sulfide and sulfone dyes are shown in the colors as recorded in Table II.

The various amines have been diazotized and coupled with R-salt and 2% dyeings made on woolen skeins. The colors,[4] as judged by the eye, are given in Table I along with those of the *ortho* and *para* series.

TABLE I

COLORS OF DYES CONTAINING THE VARIOUS AUXOCHROME GROUPS

Group	Ortho	Meta	Para
—CH_3	Deep salmon	Yellowish-scarlet	Scarlet
—OCH_3	Carmine	Bordeaux	Red
—SCH_3	Yellowish-red	Scarlet	Bordeaux
—SO_2CH_3	Orange	Yellowish-orange	Gold

In their bathochromic power the groups arrange themselves as follows:

Ortho series	—OCH_3 > —SCH_3 > —CH_3 > —SO_2CH_3
Meta series	—SCH_3 > —OCH_3 > —CH_3 > —SO_2CH_3
Para series	—SCH_3 > —OCH_3 > —CH_3 > —SO_2CH_3

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[4] Thanks to Dr. R. E. Rose, the designations of the colors are from the Technical Laboratory of E. I. du Pont de Nemours and Co.

TABLE II

COLORS OF SULFIDE AND SULFONE DYES OF THE META SERIES CONTAINING VARIOUS ALKYL GROUPS

Group	Sulfide series	Sulfone series
$—CH_3$	Scarlet	Dull yellowish-orange
$—C_2H_5$	Yellowish-scarlet	Salmon
$—C_4H_9$	Yellowish-scarlet	Bright reddish-orange
$—CH_2C_6H_5$	Reddish-buff	Dull buff

The diazotized diamino-disulfide, $NH_2C_6H_4S.SC_6H_4NH_2$, coupled with R-salt, gave a light pink on wool. This dye was fairly well absorbed by cotton, but the bath was not exhausted.

Experimental Part

1. Alkyl Ethers of *m*-Acetyl-aminothiophenol, *m*-$CH_3CONHC_6H_4SR$.—As the halogen in *m*-chloronitrobenzene is not reactive, the method used for *o*- and *p*-nitrothiophenols was not available, and a roundabout method had to be employed. Following the method of Zincke and Müller,[5] the sodium salt of metanilic acid[6] was acetylated and converted to the sulfonic chloride, *m*-$CH_3CONHC_6H_4SO_2Cl$. It was found preferable to use three parts of ice instead of ten, and the operation was completed in two hours. During the slow addition of the sulfone chloride to the reduction mixture, the temperature should be brought up to 30°, but not above 45°, except toward the end of the reaction when it may go to 60°. Refluxing, after the final addition of acid, aids the hydrolysis of the acetyl group and cuts down the yield. As the free *m*-acetyl-aminothiophenol is difficult to handle, being oxidized by the air, it is better to convert it to the disulfide which is readily isolated and can be obtained in 70% yield.

The sodium salt of *m*-acetyl-aminothiophenol, $CH_3CONHC_6H_4SNa$, was prepared according to the method of Zincke and Müller, except that a more concentrated alcoholic solution was used. It was not isolated, its solution being used directly for making the alkyl derivatives by the addition of dimethyl sulfate, ethyl iodide, butyl bromide or benzyl chloride. Enough alcohol was added to effect the solution of the added halide. The reactions took place readily and seemed to be complete in about 30 minutes, after which the bulk of the alcohol was evaporated and water added. The alkyl derivatives separated as oils, which were dissolved in ether or benzene. These solutions were dried over calcium chloride and the solvents evaporated. The methyl and benzyl thio-ethers solidified, while the ethyl and butyl remained as oils. The methyl derivative was recrystallized from water and the benzyl from chloroform and petro-

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[5] Zincke and Müller, *Ber.*, **46**, 775 (1913).

[6] We are indebted to E. I. du Pont de Nemours and Co. for the metanilic acid and for assistance in various ways.

leum ether. Both were fine white needles. These acetylaminothioethers are slightly soluble in hot water, moderately soluble in benzene and very soluble in alcohol. None of them could be distilled without decomposition, even at 3 mm. pressure. Details are given in Table III. The methyl derivative had been previously prepared by Zincke and Müller, who gave the melting point as 75°.

TABLE III

PREPARATION AND PROPERTIES OF *m*-ACETYLAMINO-THIOPHENOL ALKYL ETHERS, *m*-$CH_3CONHC_6H_4SR$

Alkyl	Disulfide, G.	Halide, G.	Yield G.	Yield %	M. p., °C.	d_{25}^{25}
Methyl........	40	26	16	49	75	....
Ethyl..........	40	28	17.5	50	oil	1.0360
n-Butyl........	80	49	51	64	oil	1.0101
Benzyl.........	60	36	36	50	74.1	....

2. **Alkyl Ethers of *m*-Aminothiophenol, *m*-$NH_2C_6H_4SR$.**—The hydrochlorides of these were readily prepared by adding concd. hydrochloric acid to the alcoholic solutions of the acetyl derivatives described above, and refluxing for a short time. The solutions were concentrated until the hydrochlorides separated on cooling. These were recrystallized from dil. hydrochloric acid and dried in a vacuum desiccator. The ethyl and benzyl compounds were further recrystallized from alcohol and ether. The methyl compound had been previously prepared by Zincke and Müller. Details are given in Table IV.

TABLE IV

HYDROCHLORIDES OF *m*-AMINO-THIOPHENOL ALKYL ETHERS, *m*-$NH_2C_6H_4SR.HCl$, PREPARATION, YIELDS, ANALYSES AND PROPERTIES

Alkyl	Acetyl deriv. taken, g.	Yield G.	Yield %	Chlorine, % Calcd.	Chlorine, % Found	Properties
Methyl......	6	4	69	...	...	White powder
Ethyl........	20	16	82	18.70	18.80	Glistening plate
n-Butyl......	20	17	87	16.29	16.47	Fibrous plates
Benzyl.......	15	14	95	14.08	13.94	Glistening plate

3. ***m,m'*-Diamino-diphenyl-disulfide, $(H_2NC_6H_4S)_2$.**—An alcoholic solution of the corresponding diacetyl derivative to which concd. hydrochloric acid had been added was refluxed until hydrolysis was complete. The diamine is readily diazotized and coupled in the usual way.

4. ***m*-Acetylaminophenyl Alkyl Sulfones, *m*-$CH_3CONHC_6H_4SO_2R$.**—These were readily obtained by the method of Zincke and Müller[5] by warming a glacial acetic acid solution of the corresponding sulfides, with the addition of an excess of 30% hydrogen peroxide. The reaction is smooth and gives excellent yields with no sulfoxide.[7] The benzyl derivative could be precipitated as a solid by diluting the acetic acid solution.

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[7] Hinsberg, *Ber.*, **43**, 289 (1910).

The others were obtained by evaporating the acetic acid on the steam-bath. The solid sulfones were recrystallized from chloroform (in which they are very soluble) and petroleum ether. They are white needles, insoluble in petroleum ether, but soluble in alcohol. The preparation and properties are assembled in Table V. The methyl sulfone was prepared by Zincke and Müller.

TABLE V

m-ACETYLAMINOPHENYL ALKYL SULFONES, $m\text{-}CH_3CONHC_6H_4SO_2R$

Alkyl	Sulfide taken, g.	Yield G.	%	M. p.	d^{25}_{25}
Methyl	7	7	85	137	....
Ethyl	10	10	86	96	....
n-Butyl	20	19	83	..	1.3727
Benzyl	9	9.5	94	134.2	....

5. *m*-Aminophenyl Alkyl Sulfone Hydrochlorides, $m\text{-}NH_2C_6H_4SO_2R.HCl$.—These were prepared by the method used by Zincke and Müller for the methyl compound by refluxing the acetyl derivatives in alcoholic solutions with the addition of concd. hydrochloric acid. When the solutions were evaporated nearly to dryness, the hydrochlorides of the sulfones separated as yellowish solids which were recrystallized from alcohol and ether, the crystals washed with ether and dried in a vacuum desiccator. They were all shiny, white plates, very soluble in alcohol, but only slightly so in ether.

TABLE VI

m-AMINO-PHENOL ALKYL SULFONE HYDROCHLORIDES, $m\text{-}NH_2C_6H_4SO_2R.HCl$

Alkyl	Taken, g.	Yield G.	%	Chlorine, % Calcd.	Found
Methyl	7	4	59	...	...
Ethyl	10	5	51	15.99	15.59
n-Butyl	18	10	57	14.20	14.05
Benzyl	9	8.5	96	12.49	12.36

Summary

The influence of sulfur and of the sulfone group on the color of azo dyes has been further studied by preparing the *meta* series of dyes. The bases $m\text{-}NH_2C_6H_4SR$ and $m\text{-}NH_2C_6H_4SO_2R$, in which R is methyl, ethyl, *n*-butyl and benzyl, have been prepared, diazotized and coupled with R-salt and the colors compared. The —S— is strongly bathochromic and the $—SO_2—$ hypsochromic, both effects being most pronounced when the alkyl is methyl. For comparison, dyes containing methyl and methoxyl have been made. The groups arrange themselves in the order $—SO_2CH_3 < —CH_3 < —OCH_3 < —SCH_3$ in the *meta* series as in the *para*, but the bathochromic effect of sulfur is not as distinct or as intense in the *meta* as in the *para* position.

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