51. Preparation of Diazo Phenyl Sulfides. Kinetics and Mechanism of the Diazo Coupling Reaction of *p*-Nitrobenzenediazo Phenyl Sulfide with *β*-Naphthol under Various Conditions

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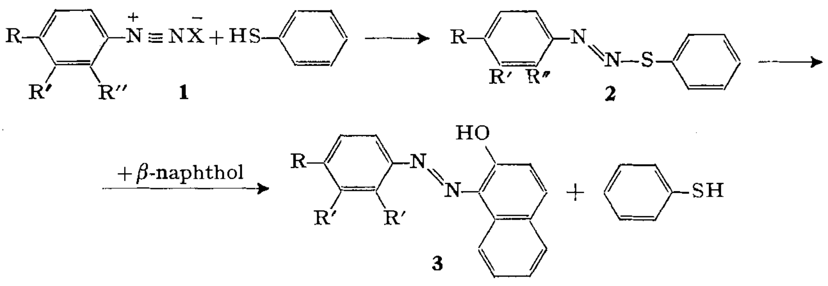
(8.X.73)

Summary. Aryldiazophenyl sulfides prepared from diazotised arylamines and thiophenol at controlled pH, are coupled with *β*-naphthol yielding the corresponding azo dye.

A kinetic study of the diazo coupling reaction of *p*-nitrobenzenediazo phenyl sulfide with *β*-naphthol under various conditions revealed that the reaction is of first order kinetics with respect to the diazo phenyl sulfide, and that the rate of coupling measured colorimetrically is influenced by the hydrogen ion concentration and by the ionising power of the medium.

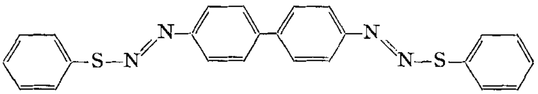
Diazotised arylamines (**1**) reacted with freshly distilled thiophenol in ethanol at controlled faintly acid pH yield nearly quantitatively the corresponding aryldiazophenyl sulfides (**2**). Coupling of these diazo thioethers (**2**) with *β*-naphthol in ethanolic solution gave quantitatively the corresponding azo dyes (**3**).



a) $R = R' = H; R'' = NO_2$
b) $R = R'' = H; R' = NO_2$
c) $R = NO_2; R' = R'' = H$
d) $R = R'' = NO_2; R' = H$
e) $R = Br; R' = R'' = H$
f) $R = Cl; R' = R'' = H$
g) $R = COOH; R' = R'' = H$
h) $R = SO_3Na; R' = R'' = H$

Hantzsch et al. [1] prepared compounds **2c, e, f** and **h** in poor yields by reacting the corresponding diazonium salts (**1**) with sodium thiophenate in alkaline solution. They stated that the ethers obtained did not combine with naphthols either in alkaline, alcoholic or in dilute acid media, whilst by concentrated acids they were split into their components. For comparison we prepared the diazo phenyl sulfides (**2**) from alkaline solutions following the method of *Hantzsch et al.* [1]; the products obtained were identical with our compounds (no depression in the mixed melting point; production of the same azo dyes by coupling with *β*-naphthol). The UV. spectra of compound **2c** obtained by both methods are identical with $\lambda_{max} = 350$ nm.

Biphenyl-4,4'-bis-diazo phenyl sulfide (**4**) was also prepared by the reaction of bis-diazotised benzidine with two equivalents of thiophenol in ethanol at pH 5–6; coupling of **4** with β-naphthol in 95% ethanol gave rise to biphenyl-4,4'-bis-[⟨azo-1⟩-naphth-2-ol].



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The kinetics of the diazo coupling reaction of *p*-nitrobenzenediazo phenyl sulfide (**2c**) with β-naphthol, to give *p*-nitrophenylazo-2-naphthol (*Para Red*, **3c**) were studied in acetone solution under various conditions. The effect of acetic acid, methanol, water and of alkali on the rate of coupling was examined. The rate of coupling measured colorimetrically was found to be influenced by the hydrogen ion concentration and by the ionising power of the solvent.

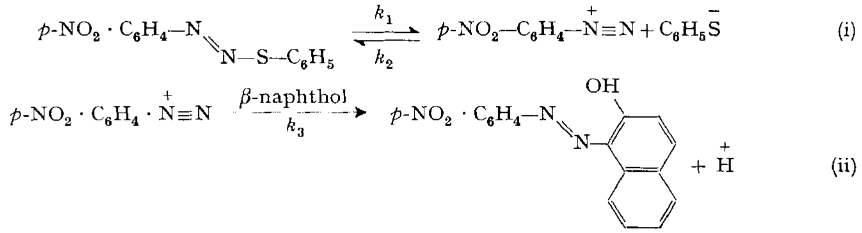
The rate of formation of *Para Red* was assumed to be proportional to the concentration of the diazo phenyl sulfide reacted. The concentration of the former at any time was estimated colorimetrically and the final extent of the reaction was determined by allowing the reaction solutions to stand until the concentration of *Para Red* became constant. The presence of acetic acid, methanol or water was required for coupling, no reaction being observed in dry acetone. Plots of $-\log(a-x)$ against time, where a is the initial concentration of the diazo thioether (**2c**) and x is that reacted at time t, were found to be linear indicating that the reaction is always of the first order with respect to the diazo phenyl sulfide (see Tables 2, 3 and 5).

Friswell & *Green* [2] showed that the change of diazoaminobenzene (**5**) into aminoazobenzene (**6**) consisted in a splitting of the molecule by the acid present into benzenediazonium ion and aniline and that these fragments recombine to form *p*-aminoazobenzene (**6**).

$$\underset{\mathbf{5}}{C_6H_5N{=}N{-}NH{-}C_6H_5} \rightarrow C_6H_5N{\equiv}N^+ + H_2N{-}C_6H_5 \rightarrow \underset{\mathbf{6}}{C_6H_5{=}N{-}C_6H_4{-}NH_2(p)}$$

This mechanism was supported by *Rosenhauer* & *Unger* [3] as well as by *Kidd* [4].

Since diazoamino compounds (**5**, N-azo compounds) are the nitrogen analogues of diazo phenyl sulfide (**2**, S-azo compounds), and since the two series of compounds (**2** and **5**) have the ability to couple with naphthols, one may expect some similarity between the mechanism by which diazonium ions are produced from these compounds and we suggest the following reaction scheme[1]:



$$C_6H_5\overset{-}{S} + \overset{+}{H} \rightleftharpoons C_6H_5SH \qquad \text{(iii)}$$

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[1] We emphasize that (i)–(iii) is only a scheme and not a complete reaction mechanism.

Since all experiments were performed with a considerable excess of β-naphthol, we may assume that the back reaction (k_2) in (i) can be neglected.

Evidence supporting the above mechanism may be obtained from the following results:

a) The reaction rate increases with increasing acetic acid or methanol concentrations. The first order rate constants (k) were found to be proportional to the first power of acetic acid concentration and to the square of methanol concentration (Table 2). This observation is similar to *Goldschmidt*'s finding [5]. He found that the rate of the rearrangement of diazoamino compounds in acidic medium was most nearly proportional to the first power of the acid concentration using strong acids, but with weaker acids it was closer to a second order dependence. From this he concluded that the reaction was ionic at some stage and that the catalyst was the anilinium ion.

b) No simple relation exists between the observed first order rate constant and the concentration of water. The rate of the reaction is approximately a linear function of the square of the water concentration for the two lowest concentrations of water used (4.2–8.4 M). However, in highly dilute solutions (12.6–16.8 M of water), the rate is dependent on the water concentration to a higher power (Table 3).

c) The variation in the rate of the reaction in acetone/water mixtures with respect to the dielectric constant of the medium was studied using the following equation [6]:

$$\ln k = \ln k_0 - A/D\,R\,T$$

where, k_0 is the reaction rate constant in a medium of infinite dielectric constant, A being a constant, D the dielectric constant, R is the gas constant, and T is the absolute temperature. Plot of log k against $1/D$ was linear (Table 4). The values of D were interpolated from the results of *Äkerlof* [7]. The dependence of k upon D clearly demonstrates that the diazo coupling reaction of *p*-nitrobenzenediazo phenyl sulfide (**2c**) with β-naphthol is strongly influenced by the dielectric constant of the medium (see Table 4). The measured first-order rate constant (k) therefore corresponds to a constant containing the dielectric effect and the real influence of the concentration of water. Determination of the reaction order in relation to water would however be possible, if measurable rates could be obtained in a range of about 2 M water.

From these, it seems reasonable that the production of diazonium ions from the diazothio phenyl sulfides is influenced by acids and that the rate of the reaction increases as the ionising power of the solvent is increased.

d) In alkaline medium the diazo coupling reaction was slowed down. The decrease in rate was proportional to the concentration of sodium hydroxide (Table 5).

e) The effect of acetic acid in acetone/methanol was studied. For a constant concentration of methanol the rate is proportional to the first power of acetic acid concentration.

The IR. spectra of the diazo phenyl sulfides (**2**) showed the two characteristic bands at 1406 ± 14 cm^{-1} and at 1577 ± 8 cm^{-1} which were assigned by *Le Fevre et al.* [8] to the –N=N– link.

Experimental part

Starting Materials. – The arylamines used in this investigation, namely *o*-nitroaniline, *m*-nitroaniline, *p*-nitroaniline, 2,4-dinitroaniline, *p*-bromoaniline, *p*-chloroaniline, *p*-aminobenzoic acid, sulphanilic acid, and benzidine were purified by standard techniques [9] [10].

β-Naphthol: pure *Eastman Kodak Co. Methanol R. P.* (*VEB Laborchemie*, Apolda). *Acetic acid* for analysis (*Fein Chemie K. H. Kallies KG, d* = 1.05). *Acetone* for analysis (*Merck*) dried with magnesium sulphate [9]. *Thiophenol* provided by *Prolabo Co. Deionised water* (used in the kinetic studies) was obtained by using Elgastat deioniser (*Elga Products Ltd., Lane End, Bucks*).

Preparation of Aryldiazo phenyl sulfides. – Exemplified by the preparation of *p*-nitrobenzenediazo phenyl sulfide. The cold solution of *p*-nitrobenzenediazonium chloride prepared from recrystallised *p*-nitroaniline (6.9 g; 0.05 mol) and buffered at pH 5–6 by addition of sodium acetate solution (25%), was added slowly to a cold ethanolic solution of freshly distilled thiophenol (5.5 g; 0.05 mol) in ethanol (100 ml) within 20 min with constant stirring. Stirring was then continued for further 30 min while the temperature was kept below 5° during all the procedure. Crushed ice (50 g) was then added to the mixture and the precipitated *p*-nitrobenzenediazo phenyl sulfide was filtered off and recrystallised from absolute ethanol with m.p. and mixed m.p. with an authentic sample [1] 96° (yield 11.0 g; *ca.* 85%).

The following diazo phenyl sulfides were similary prepared (see Table 1) and gave correct analytical results.

Table 1. *Aryldiazo Phenyl Sulfides prepared from Diazonium Chlorides and Thiophenol following General Procedure*

Aryldiazo phenyl sulfides Name	Formula	Diazonium Chloride	pH	Yield *ca.* %	M.p. (°)	Analytical results or reference
o-Nitrobenzenediazo phenyl sulfide	$C_{12}H_9N_3O_3S$ (259.30)	*o*-nitrobenzenediazonium chloride	4.5	88	red oil	Calc. N 16.2 S 12.4% Found N 16.0 S 13.0%
m-Nitrobenzenediazo phenyl sulfide	$C_{12}H_9N_3O_3S$ (259.30)	*m*-nitrobenzenediazonium chloride	5.6	89	48	Calc. C 55.6 H 3.5 ,, N 16.2 S 12.4% Found C 55.5 H 3.5 ,, N 16.2 S 12.4%
p-Bromobenzenediazo phenyl sulfide	$C_{12}H_9BrN_2S$ (293.20)	*p*-bromobenzenediazonium chloride	6.7	90	44	[1]
p-Chlorobenzenediazo phenyl sulfide	$C_{12}H_9ClN_2S$ (248.74)	*p*-chlorobenzenediazonium chloride	5.6	60	60	[1]

2,4-Dinitrobenzenediazo phenyl sulfide: Sodium nitrite (6.9 g; 0.1 mol) was slowly added with stirring to concentrated sulphuric acid (150 ml) and the mixture was heated to 70°. The clear liquid thus obtained was cooled in an icebath, and 2,4-dinitroaniline (16.7 g; 0.1 mol) was added with stirring for 2 hours. After adding crushed ice (*ca.* 500 g) to the pasty mass, the mixture was brought by a saturated solution of sodium acetate to pH 4–5, and then filtered. This solution was added slowly with stirring to a cold solution of thiophenol (11.0 g; 0.1 mol) in ethanol (200 ml). Stirring was continued for one hour. The separated diazo phenyl sulfide was filtered off, and crystallised from ethanol; bright orange-yellow crystals, m.p. 108° (yield: *ca.* 90%).

$C_{12}H_8N_4O_4S$ Calc. C 47.4 H 2.6 N 18.4 S 10.5%
(304.30) Found ,, 47.4 ,, 2.6 ,, 18.4 ,, 10.6%

p-Sulphobenzenediazo phenyl sulfide (sodium salt): A mixture of sulphanilic acid (9.0 g; 0.05 mol) and anhydrous sodium carbonate (2.5 g) in water (50 ml) was warmed gently until a clear solution was obtained. To this solution, cooled to about 15°, an aqueous solution of sodium nitrite (4 g in 20 ml water) was added. The mixture was poured slowly into a mixture of concentrated hydrochloric acid (11.0 ml) and ice (50 g). The whole was then added to a solution of thiophenol (5.5 g; 0.05 mol) in ethanol (100 ml) with stirring. The resulting solution was adjusted to pH 4–5 by the addition of a saturated solution of sodium carbonate with further stirring for one hour. The sodium salt of the diazo phenyl sulfide was obtained by salting out (using sodium chloride). It separated from 80% ethanol as fine yellow plates.

$C_{12}H_9N_2NaO_3S_2$	Calc.	C 45.6	H 2.9	N 8.9	S 20.3%
(316.34)	Found	,, 45.6	,, 2.8	,, 8.9	,, 20.2%

p-Carboxybenzenediazo phenyl sulfide was similarly prepared from *p*-carboxybenzenediazonium chloride (obtained from *p*-aminobenzoic acid, 6.9 g; 0.05 mol) buffered at pH 5 (by addition of a saturated solution of sodium carbonate) and thiophenol (5.5 g; 0.05 mol) in 95% ethanol (100 ml). It crystallised from ethanol as yellow plates m.p. 101° (yield: *ca.* 90%).

$C_{13}H_{10}N_2O_2S$	Calc.	C 60.5	H 3.9	N 10.9	S 12.4%
(258.31)	Found	,, 60.8	,, 4.3	,, 10.6	,, 12.4%

Biphenyl-4,4'-bis-diazo phenyl sulfide. A solution of benzidine (9.5 g; 0.05 mol) in hot dilute hydrochloric acid (10 ml concentrated hydrochloric, and 150 ml water) was cooled in ice-bath to 5°; concentrated hydrochloric acid (15 ml) was then added with stirring. The solution was bisdiazotised with aqueous sodium nitrite (7.0 g; 0.1 mol dissolved in 20 ml water). Stirring was continued until a clear solution was obtained which gave a faint blue colour with iodide-starch paper. The solution was adjusted to pH 5–6 by sodium acetate solution (25%), and was then added slowly with stirring to a solution of thiophenol (11.0 g; 0.1 mol) in ethanol (200 ml). After stirring for 4 h while keeping the temperature below 5° the diazo phenyl sulfide was filtered off and crystallised from abs. ethanol; yellow plates, m.p. 68° (yield: *ca.* 90%).

$C_{24}H_{18}N_4S_2$	Calc.	C 67.6	H 4.2	N 13.1	S 15.0%
(426.58)	Found	,, 68.1	,, 4.0	,, 12.9	,, 15.0%

Diazo coupling of Aryldiazo phenyl sulfides. Diazo coupling of *p*-nitrophenyl-, *o*-nitrophenyl-, *m*-nitrophenyl-, 2,4-dinitrophenyl-, *p*-bromophenyl-, *p*-chlorophenyl-, *p*-carboxyphenyl-, *p*-sulphophenyl- (sodium salt), and biphenyl 4,4'-bis-diazo phenyl sulfide (0.004 mol) with β-naphthol in 95% ethanol gave in quantitative yield the corresponding azo-dyes2), namely *p*-nitrophenylazo-, 250° [11]3); *o*-nitrophenylazo-, 209° [12]3); *m*-nitrophenylazo-, 194° [13]3); 2,4-dinitrophenylazo-, 302° [14]3); *p*-bromophenylazo-, 172° [15]3); *p*-chlorophenylazo-, 160° [16]3); *p*-carboxyphenylazo-, 301° [17]3); (Orange II) [9] and biphenyl-4,4'-bis-[<azo-1>-naphth-2-ol], sample 275° [18]3).

Kinetic Measurements. The progress of the diazo coupling reaction was followed colorimetrically using a *Uvispek* photoelectric spectrophotometer H 700.

The reaction flask was thermostated by means of a water-bath maintained at 25°. Solutions of β-naphthol in dry acetone, and the required solvents, were placed in the reaction flask and kept for 30 min to come to temperature. The diazo phenyl sulfide solutions were prepared fresh each day. A 0.0073 M stock solution of the diazo phenyl sulfide was prepared fresh each day by dissolving 0.1891 g in 100 ml of dry acetone. 1.00 ml of it when diluted to 200 ml in the reaction mixtures gives a 3.65×10^{-5} M solution. Measurements were started as soon as the diazo phenyl sulfide solutions had been added. Samples of the reaction solutions were withdrawn from time to time and the optical density at the wavelength of maximum absorption for *Para Red* (490 nm) was measured as quickly as possible.

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2) The results here contravene those reported by *Hantzsch* [1], who stated that the diazo thioethers seemed not to form dyes with naphthols in aqueous alcoholic solutions. It seems to the authors therefore, that although, *Hantzsch* in the diazo coupling reaction of diazo phenyl sulfides with naphthols, aimed principally at reactions in alcoholic medium, he probably used alkali to dissolve the naphthol. It has now been shown (see Table 5) that alkali prevents or retards the diazo coupling ability of the diazo phenyl sulfide under investigation (**2c**).

3) M.p. and mixed m.p. with an authentic sample.

Results. The following concentrations and conditions remain constant throughout, unless otherwise stated: Conc. of diazo phenyl sulfide = 3.65×10^{-5} M; conc. of β-naphthol = 3.6×10^{-3} M; total volume, 200 ml, temperature, 25°; light path, 1 cm, solvent, acetone.

Table 2. *Effect of acetic acid and of methanol.* k = measured first-order rate constant

CH_3COOH M	$10^5 k$ s^{-1}	$10^5 k_1$ ($k_1 = k/[CH_3COOH]$) l/mol · s
0.4	2.62	6.6
0.8	5.76	7.2
1.2	8.60	7.2
2.0	14.40	7.2
CH_3OH M	$10^5 k$ s^{-1}	$10^6 k_2$ ($k_2 = k/[CH_3OH]^2$) $l^2/mol^2 \cdot s$
6	1.40	0.39
12	5.76	0.40
18	13.30	0.42
24	24.20	0.42

Table 3. *Effect of Water.* Concentration of phenyl sulfide = 4.9×10^{-5} M

$[H_2O]$ M	$10^4 k$ s^{-1}	$10^6 k_2$ $l^2/mol^2 \cdot s$
4.2	0.111	0.63
8.4	0.472	0.67
12.6	1.534	0.96
16.8	3.940	1.40

k = measured first-order rate constant
$k_2 = k/[H_2O]^2$

Table 4. *Variation of the rate of the coupling reaction with dielectric constant in aceton/water*

water wt %	D	$100/D$	$10^5 k$ s^{-1}	$5 + \log k$
7.5	22.5	4.44	1.11	0.045
15.0	27.0	3.70	7.72	0.674
22.5	31.5	3.18	15.34	1.185
30.0	35.7	2.80	39.40	1.600

Table 5. *Effect of Sodium hydroxide.* Conc. of methanol = 12 M

[NaOH] M	$10^5 k_1$ s^{-1}	$10^5 k'$ s^{-1}	$10^5 k'$ l/mol · s	
0.000	5.86	–	–	
0.025	4.15	1.71	68.4	($k' = k_0 - k$)
0.050	2.42	3.44	68.8	
0.075	0.70	5.16	68.8	($k_1 = k'/[NaOH]$)

k_0 = measured first-order rate constant for zero concentration of sodium hydroxide = 5.86×10^{-5} s^{-1}.

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52. 5-(1-Alkenyl)-1,3,4-oxadiazol-2(3*H*)-one

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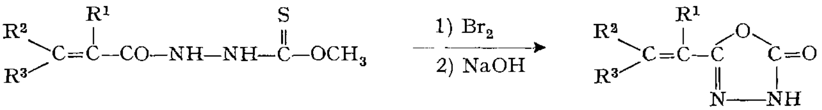
(29. I. 74)

Summary. 3-(2-alkenoyl)-thiocarbazic acid O-methyl esters **1** are desulfurated by bromine and the unknown intermediates are transformed by alkali to 5-(1-alkenyl)-1,3,4-oxadiazol-2(3*H*)-ones (**2**). This type of oxadiazolone substitution is not realizable by the common ring closure of hydrazides with phosgene due to pyrazolidinone ring closure of unsaturated acids with hydrazine.

Beim kürzlich beschriebenen Versuch [1], Brom an die Doppelbindung von 3-(3,3-Dimethylacryloyl)-thiocarbazinsäure-O-methylester (**1d**) anzulagern und mit Alkali einen schwefelhaltigen Ring zu schliessen, entstand über ein nicht identifiziertes Zwischenprodukt eine brom- und schwefelfreie Verbindung $C_6H_8N_2O_2$. Diese



1 **2**

1 und 2	R^1	R^2	R^3
a	H	H	H
b	CH_3	H	H
c	H	H	CH_3
d	H	CH_3	CH_3