Metal Complex Forming Azo Dyes. VII[1])

o'-Hydroxylation of o-hydroxy-azo Dyes Devoid of Water Solubilising Groups

By M. Kamel and S. A. Amin

Summary

Investigations were carried out to o'-hydroxylate the monohydroxy azo types (I) and (II) respectively in different solvents, under varied conditions. A new continuous procedure for o'-hydroxylation is described.

The influence of introduction of o'-hydroxyl group and annullation in compounds (I—IV) on the wave length at maximum absorptions is also described.

Pfitzner et al.[2]) reported that o'-hydroxylation of monohydroxy azo dyes using percompounds in presence of cupric ions gives their corresponding o,o'-dihydroxy azo dyes. Although, this method was extensively used in patent literature, for the oxidation of water soluble azo dyes containing sulphonic acid groups, very few work[3]) was published on its application to water insoluble o-hydroxy azo compounds.

Yoshida et al.[4]) introduced a modification of the method which involved carrying out the o'-hydroxylation of the 1:1 copper complex of the mono-hydroxy azo compound in glacial acetic acid.

Previous investigations from our laboratories described the results of o'-hydroxylation of 9-hydroxy-10-arylazo-phenanthrenes[5a,b]), 1-hydroxy-2-arylazo-naphthalenes[5c]), acenaphthenequione-mono-phenyl-hydrazones[5d]), 6-hydroxy-5-arylazo-chrysenes[6]), and 5-hydroxy-6-arylazo-chrysenes[6]).

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[1]) Part VI: M. Kamel and S. A. Amin, Liebigs Ann. Chem. (in the press).

[2]) H. Pfitzner and H. Baumann (B.A.S.F.), Angew. Chem. **70**, 232 (1958).

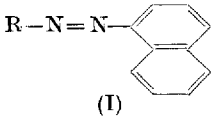
[3]) H. Pfitzner (B.A.S.F.), F.P. 1137 D/22 a, 2. (1950).

[4]) Z. Yoshida, K. Kazama, and R. Oda (Univ. Kyoto), Kogyo Kagaku Zasshi **62**, 1399—1402 (1959); Chem. Abstr. **57**, 13922 (1962).

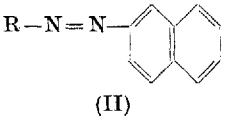
[5]) M. Kamel and S. A. Amin, Indian J. Chem. **2**, a) 60 (1964), b) 62 (1964), c) 232 (1964), d) 282 (1964).

[6]) M. Kamel and S. A. Amin, Liebigs Ann. Chem. (in the press).

We are now reporting on some modifications for o'-hydroxylation of mono-hydroxy azo types (I a—c) and (II a—c) devoid of water solubilising groups in different solvents. Furthermore, the effect of introduction of o'-hydroxyl group and annullation in compounds (I—IV) on the wave lengths at maximum absorption is also studied.



(I)



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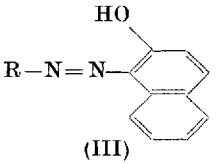

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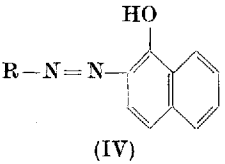


(IV)

R = a) 2-Hydroxy-naphthalene
b) 9-Hydroxy-phenanthrene
c) 6-Hydroxy-chrysene

The application of YOSHIDA's modified procedure revealed that this method cannot be considered of general applicability. Generally, the yields were either too poor or the o'-hydroxylation did not proceed at all (cf. Table 1).

This failure may be attributed to the very low solubility of the copper complexes of the mono-hydroxy azo compounds in acetic acid.

In view of these discouraging results, o'-hydroxylation experiments were attempted in other solvents, e.g. alcohol, isopropyl alcohol, acetone, dimethylformamide, ethylene glycol, and ethylene glycol-mono-methyl-ether. It was found that satisfactory results were obtained only when ethylene glycol or ethylene glycol-mono-methylether were used. However, the results in some cases, e.g. (I c) and (II c) are also unsatisfactory.

The results of the o'-hydroxylation of the above mentioned compounds using the three different solvents (acetic acid, ethylene glycol, and ethylene glycol-mono-methylether) are summarized in Table 1.

Separation of the mono-hydroxy azo from their corresponding o,o'-dihydroxy azo compounds, and determination of the percentage of o,o'-dihydroxy azo compounds in the mixtures (if any) were carried out using thin layer chromatographic analysis[7]).

The data in Table 1 indicate that:

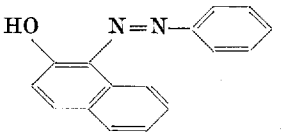
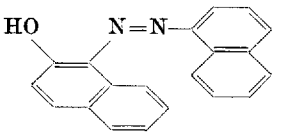
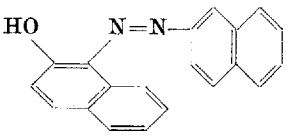
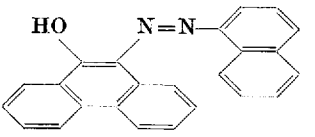
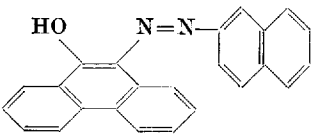
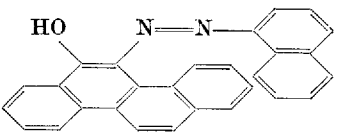
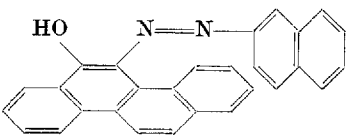
a) When using method A, the o'-hydroxylation proceeds in case of 2-hydroxy-1-phenylazo-naphthalene, (I a), (II a), and (I b). The yields

[7]) E. STAHL, „Dünnschichtchromatographie, Ein Laboratoriumshandbuch", Springer-Verlag, 5 (1962).

follow the order, 2-hydroxy-1-phenylazo-naphthalene > (II a) > (I b) > (I a). Compounds (II b), (I c), and (II c) are not o'-hydroxylated under these conditions.

b) When method B is applied, the compounds are o'-hydroxylated with varying degrees. Compound (II a) and 2-hydroxy-1-phenylazo-naphthalene give yields of 100% and 87.30% respectively. As in case of method A, compounds (I b), (I c), and (II c) remain unchanged.

Table 1
% of o,o'-dihydroxy-azo compounds

Formula	Mono-hydroxyazo-compound	Method A	Method B	Method C
		68.62	87.30	9.10
(I a)		4.76	16.66	100
(II a)		54.02	100	86.44
(I b)		8.75	0.0	22.07
(II b)		0.0	20.00	27.86
(I c)		0.0	0.0	4.79
(II c)		0.0	0.0	20.00

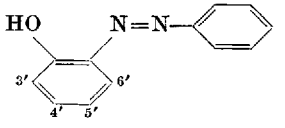
c) When o'-hydroxylation is carried in ethylene glycol-mono-methyl-ether (method C), all compounds are o'-hydroxylated. The order of o'-hydroxylation is as follows: (I a) > (II a) > (II b) > (I b) > (II c) > 2-hydroxy-1-phenylazo-naphthalene > (I c).

d) The yields of o'-hydroxylation of one and the same compound are different in different solvents. Failure to o'-hydroxylate the above mentioned compounds is probably due to the insolubility of the copper complexes of the mono-hydroxy azo compounds.

To overcome the difficulties caused by the insolubility of the copper complexes of the o-hydroxy azo compounds, a new continuous procedure for the o'-hydroxylation was elaborated (cf. experimental part).

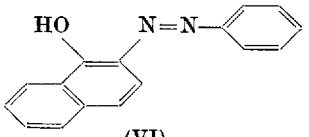
The application of this continuous procedure to oxidise compounds (I b, c) and (II b, c) gave quantitative yields of the corresponding o,o'-dihydroxy azo compounds.

The influence of annullation and substitution on the wave length at maximum absorptions in case of o-hydroxy azo compounds was very little investigated. WEISS-BERG and WIZINGER[8]) showed that transition from o-hydroxy-phenylazo-benzene (V) in positions 3' : 4' and 5' : 6', to give 1-hydroxy-2-phenylazo-naphthalene (VI) and 2-hydroxy-1-phenylazo-naphthalene (VII), results in an increase in the wave length at maximum absorptions of 112 mμ and 91 mμ respectively.



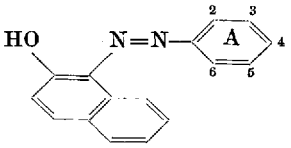
(V)

(λ max. 385 mμ)



(VI)

(λ max. 497 mμ)



(VII)

(λ max. 476 mμ)

In the present communication is reported the effect of annullation of the benzene ring (A) of compounds (VII), (VIII), and (IX), in positions 2:3 to give compounds (I a—c), and in positions 3:4 to give (II a—c).

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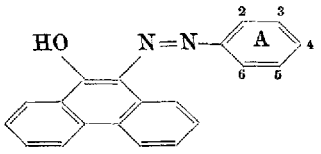
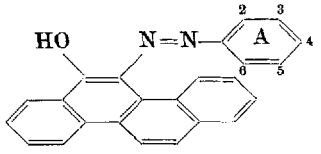
[8]) E. WEISS-BERG and R. WIZINGER, Helv. chim. Acta **40**, 1056 (1957).



(VIII)

(λ max. 483 mμ)

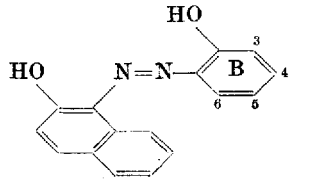


(IX)

(λ max. 512 mμ)

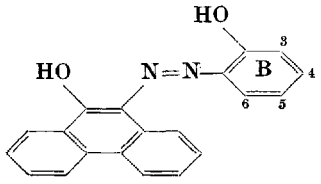
Moreover, the same effect has also been studied when another benzene ring is annullated to the o-hydroxy-phenyl moiety (B) of compounds (X), (XI), and (XII) in positions 5:6 to give compounds (III a—c), and in positions 3:4 to give (IV a—c).

The λ maximum values of the different annullated compounds are given in Table 2. It should be noted that the solutions of these compounds obey BEER's lambert law.



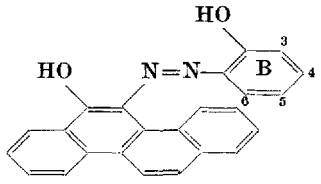
(X)

(λ max. 492 mμ)



(XI)

(λ max. 489 mμ)



(XII)

(λ max. 522 mμ)

The data in Table 2 show that:

a) All types of annullation cause an increase in λ maximum values.

b) Annullation of (VII), (VIII), and (IX) in positions 2:3 results in higher bathochromic shifts than their annullation in positions 3:4. Similarly, annullation of (X), (XI), and (XII) in positions 5:6 causes higher bathochromic shifts than annullation in positions 3:4.

c) Introduction of a hydroxyl group in position 1 of the naphthalene ring results always in higher bathochromic shifts than when it is introduced in position 2.

d) Bathochromic shifts caused by annullation in positions 2:3 in compounds (I a—c) are always greater than the corresponding shifts when (X), (XI), and (XII) are annullated in positions 5:6. On the other hand, annul-

Table 2

Compound	R	Max. values	HO N=N–R	HO N=N–R	HO N=N–R
	A	$\lambda_{max.}$ $\varepsilon_{max.}$	476 (1.60×10^4)	483 (0.67×10^4)	512 (2.75×10^4)
I		$\lambda_{max.}$ $\varepsilon_{max.}$ bathochromic shifts	512 (0.39×10^4) (36)	512 (2.30×10^4) (29)	527 (0.62×10^4) (15)
II		$\lambda_{max.}$ $\varepsilon_{max.}$ bathochromic shifts	492 (3.29×10^4) (16)	500 (0.16×10^4) (17)	520 (2.64×10^4) (8)
	HO B	$\lambda_{max.}$ $\varepsilon_{max.}$	492 (2.67×10^4)	498 (2.64×10^4)	522 (3.88×10^4)
III	HO	$\lambda_{max.}$ $\varepsilon_{max.}$ bathochromic shifts	517 (1.69×10^4) (25)	515 (1.20×10^4) (17)	535 (0.63×10^4) (13)
IV	HO	$\lambda_{max.}$ $\varepsilon_{max.}$ bathochromic shifts	515 (0.08×10^4) (23)	513 (1.07×10^4) (15)	535 (0.19×10^4) (13)

lation of (VII), (VIII), and (IX) in positions 3:4 results in lower bathochromic shifts than the corresponding shifts when (X), (XI), and (XII) annullated in the same positions.

Experimental Part

9-Hydroxy-10-(1'- or 2'-naphthylazo)-phenanthrenes (I b) and (II b)

To a solution of phenanthraquinone (2.08 g., 0.01 mole) in glacial acetic acid (100 ml.), a suspention of 1- or 2-naphthylhydrazine hydrochloride[9]) (1.94 g., 0.01 mole) in 25 ml. water was added in one portion. The mixture was then refluxed for about one hour, giving a red dyestuff, which was filtered quickly from the hot solution, and crystallised from the proper solvent.

[9]) E. FISCHER, Liebigs Ann. Chem. **232**, 237, 242 (1886).

Table 3

Compound	Crystallisation	Colour M. P.	Yield (%)	Col. in Conc. H_2SO_4	Mol. form. Mol. Wt.		Analysis C	H	N
9-Hydroxy-10-(1′-naphthylazo)-phenanthrene (I b)	dil. acetic acid	bright-red 219°	54	blue	$C_{24}H_{16}N_2O$ (348)	calcd.	82.7	4.6	8.0
						found	82.5	4.6	8.3
9-Hydroxy-10-(2′-naphthylazo)-phenanthrene (II b)	dil. acetic acid	red 184°	73	violet	$C_{24}H_{16}N_2O$ (348)	calcd.	82.7	4.6	8.0
						found	82.7	4.8	8.3
6-Hydroxy-5-(1′-naphthylazo)-chrysene (I c)	chloroform	red-violet 222°	81	blue-violet	$C_{28}H_{18}N_2O$ (398)	calcd.	84.5	4.6	7.0
						found	84.4	4.5	6.9
6-Hydroxy-5-(2′-naphthylazo)-chrysene (II c)	chloroform	violet 178°	86	blue-violet	$C_{28}H_{18}N_2O$ (398)	calcd.	84.5	4.6	7.0
						found	84.1	4.5	6.8
2-Hydroxy-1-(2′-hydroxy-1′-naphthylazo)-naphthalene (III a)	acetic acid	red 246°[10][11]	100	violet	$C_{20}H_{14}N_2O_2$ (314)	calcd.	76.5	4.5	8.9
						found	76.3	4.4	8.8
2-Hydroxy-1-(1′-hydroxy-2′-naphthylazo)-naphthalene (IV a)	acetic acid	red above 360°	100	blue	$C_{20}H_{14}N_2O_2$ (314)	calcd.	76.5	4.5	8.9
						found	76.1	4.3	8.6
9-Hydroxy-10-(2′-hydroxy-1′-naphthylazo)-phenanthrene (III b)	acetic acid	bright-red above 360°	100	blue	$C_{24}H_{16}N_2O_2$ (364)	calcd.	79.2	4.4	7.7
						found	78.8	4.2	7.4
9-Hydroxy-10-(1′-hydroxy-2′-naphthylazo)-phenanthrene (IV b)	acetic acid	dark-red, greenish metallic lustre 125°	100	blue	$C_{24}H_{16}N_2O_2$ (364)	calcd.	79.2	4.4	7.7
						found	79.1	4.6	7.3
6-Hydroxy-5-(2′-hydroxy-1′-naphthylazo)-chrysene (III c)	acetic acid	red-violet 172°	100	brown	$C_{28}H_{18}N_2O_2$ (414)	calcd.	81.2	4.4	6.8
						found	80.9	4.2	6.5
6-Hydroxy-5-(1′-hydroxy-2′-naphthylazo)-chrysene (IV c)	acetic acid	dark-red 122° (dec.)	100	brown	$C_{28}H_{18}N_2O_2$ (414)	calcd.	81.2	4.4	6.8
						found	81.0	4.2	6.6

[10]) P. Pelz (to Agfa), U.S. P. 2950273 (1960); Chem. Abstr. **55**, 2116 (1961).

[11]) J. M. Tedder and B. Webster, J. chem. Soc. (London) **1960**, 4417.

6-Hydroxy-5-(1'- or 2'-naphthylazo)-chrysenes (I c) and (II c)

1- or 2-Naphthylamine (1.43 g., 0.01 mole) was diazotised and the brownish diazonium salt was poured, dropwise, onto a cooled solution of 6-hydroxy chrysene (2.44 g., 0.01 mole) in pyridine (100 ml.). The red-violet precipitate, thus formed, was filtered, washed well with water, and crystallised from the proper solvent.

Different produceres of o'-hydroxylation

Method A:

The o-hydroxy azo dye (0.01 mole) was converted into the 1:1 copper complex in acetic acid (ca. 500 ml.), and added to 4—6 moles of hydrogen peroxide (in 100 ml. acetic acid), at 30° in 5 hours with stirring. Agitation was continued for an additional 2.5 hours, and the mixture was concentrated, under vacuum, to half its volume. By cooling, to room temperature, and addition of distilled water (ca. 100 ml.), the copper complex was obtained. It was decomposed by boiling, for 20 minutes, with conc. hydrochloric acid.

Method B:

To a solution of o-hydroxy azo compound (0.01 mole) in ethylene glycol (1000 ml.), copper acetate solution (1.81 g., 0.01 mole/30 ml. water) was added. To the stirred mixture, hydrogen peroxide (10 ml., 30%) was added in portions during 30 minutes, taking care that the temperature did not rise above 80—90°. The completion of the reaction needed an additional period of 3 hours at the same temperature. The mixture was then cooled, at room temperature and the copper complex precipitated by addition of distilled water (ca. 200 ml.). It was then decomposed by boiling with conc. hydrochloric acid for 20 minutes.

Method C:

As in case of method B, except ethylene glycol-mono-methyl-ether (350 ml./0.01 mole o-hydroxy azo compound) was used.

Continuous o'-hydroxylation

A two necked flask fitted with a soxhlet apparatus and a separating funnel was used. The copper complex of the mono-hydroxy azo dyestuff, prepared from (0.01 mole dye) was placed in the thimble of the soxhlet apparatus, and the solvent (ethylene glycol-monomethylether) in the soxhlet flask. Hydrogen peroxide (12 ml., 30%) was added very slowly from the separating funnel, and the extraction was continued for about 7 days. The mixture was then distilled off under vacuum, and water (ca. 100 ml.) was then added to the concentrated solution, to give dark precipitate of the copper complex of the o,o'-dihydroxy azo compound. It was decomposed by boiling with conc. hydrochloric acid for 30 minutes. This process gives a quantitative yield of the o,o'-dihydroxy azo compound.

Cairo (UAR), National Research Centre.

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