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Studies on the Dyes derived from 1,4-Naphthoquinone

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1,4-Naphthoquinone dialkyl ether and monoalkyl ether were obtained from 1,4-naphthoquinone in a single step by the combined reduction and alkylation reaction. The former were derived to azoic dyes by nitration following reduction, and the latter to disperse monoazo dyes by coupling with aromatic amines and to Algol Brilliant Green BK and its homologue by condensing with α -chloride of isatin derivatives. 2,3-Dichloro-1,4-naphthoquinone obtained by chlorination of 1,4-naphthoquinone, were derived to vat dyes, in which derivatives of Helindon Yellow R by condensing with aromatic amines, Helindon Yellow G and its homologue by condensing with 6-hydroxyphenazine derivatives, Indanthrene Yellow 6GD and its homologue by condensing with naphthosultam-phenazine, and brasanquinone derivatives by condensing with hydroxy-compound of Naphthol AS type were included. 1,4-Addition reaction of primary amines to 1,4-naphthoquinone were of use for the preparation of Helindon Red CR and its homologue being used as a vat dye and a disperse dye. 1,4-Naphthoquinone-monoimine derivatives were prepared from 5-nitro-2,3-disubstituted-1,4-naphthoquinone. 1-Phenylazo-2,4-dihydroxynaphthalene derivatives were prepared by the reaction of phenylhydrazine to 2-hydroxy-1,4-naphthoquinone derivatives.

1. Introduction

It has been shown that 1,4-naphthoquinone, benzoic acid, maleic anhydride and 9,10-dihydroxynaphthacenequinone were formed as by-products in the manufacture of phthalic anhydride by vapour-phase catalytic air oxydation of naphthalene. Besides these, triphthaloylbenzene, which has not been detected up to the present, was isolated and identified by the authors.¹⁾

Maleic anhydride has been collected in the form of maleic acid or fumaric acid, or its sodium-salt, and derived to succinic acid and bis-alkyl sodium sulfosuccinate (wetting agent, e. g. Aerosol OT), etc.

The formation of 1,4-naphthoquinone makes up considerable amounts and cannot be evitable through the manufacturing process of phthalic anhydride. Then, the utilization of naphthoquinone are important on phthalic industry.

2-Methyl-1,4-naphthoquinone, antihemorrhagic activity of which is three times more effective than natural vitamine K₁, can be prepared from 1,4-naphthoquinone.²⁾

2,3-Dichloro-1,4-naphthoquinone is outstanding as a agricultural fungicide.³⁾

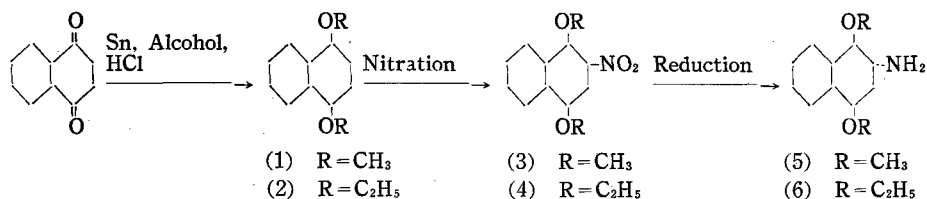
In the present work, the dyes from 1,4-naphthoquinone were investigated with respect to azoic, vat and disperse dyes. The details for the most part had been reported in the Journal of the Society of Organic Synthetic Chemistry in Japan and the present report is giving a comprehensive one on the results.

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2. Azoic Dyes

Among the compounds derived from 1,4-naphthoquinone, only two kinds of azoic dyes have been reported. One is 6-hydroxynaphthophenazine (17),⁴⁾ another is benzo-carbazolequinone derivative in all probability, which is obtained by condensing 2,3-dichloro-1,4-naphthoquinone with aromatic amino-hydroxy compound,⁵⁾ and the both are a azoic coupling component.

2-1 2-Amino-1,4-dialkoxynaphthalene (a diazo component)⁶⁾



1,4-Dimethoxynaphthalene (1) has been prepared by dissolving 1,4-naphthoquinone in an aqueous solution of sodium hydroxyde and methylation under nitrogen-atomsphere by means of dimethylsulphate in the yield of 60% of the theory.²⁾ In the present experiment, a mixture of 1,4-naphthoquinone, methyl or ethyl alcohol and tin powder or stannous chloride was stirred on a steam bath, and saturated with dry HCl gas to give 1,4-dimethoxy- (1) or 1,4-diethoxynaphthalene (2) in a single step. There was obtained 85.2% yield of pure (1) (m. p. 85—6°C) and 77.4% yield of pure (2) (m. p. 89—90°C) without recrystallization.

Nitration of 1,4-dialkoxynaphthalene has not been reported up to the present. On this reaction, the concentration of nitric acid was more effective, and the quantity of the acid and the reaction temperature were less. Thus, 1,4-dialkoxynaphthalene was dissolved in benzene or chlorobenzene, and 2-2.5 times theoretical amount of 20% nitric acid was dropped into the solution at 20—5°C to give the nitro-compound. Oxidation of the nitro-compound by potassium permanganate gave phthalic acid. When NO₂ group was introduced at 5- or 6-position in 1,4-dialkoxynaphthalene, then the oxidation product should be 3- or 4-nitrophthalic acid. Therefore, it was confirmed that the nitration product was 2-nitro-1,4-dialkoxynaphthalene.

Reduction of 2-nitro-1,4-dialkoxynaphthalene was carried out smoothly in an auto-

Table 1. Yield, m. p. and analysis of 2-amino-1,4-dialkoxynaphthalene.

Compd.	Yield %	m.p. °C	N %		Mol. Wt.	
			Calcd.	Found	Calcd.	Found
(3)	60.3	95—6	6.01	6.05	233	231.9
(4)	78.4	78—9	5.36	5.42	261	261.5
(5)	83.0	100—1	5.71*	5.67*	—	—
(6)	90.3	97—8	5.13*	5.15*	—	—

* Stared figure = N % of acetylamino-derivative.

clave by means of catalytic hydrogenation with Raney-Ni at 50–60°C.

2-Amino-1,4-dialkoxynaphthalene could be diazotized by the usual method, and the diazo-solution was dark green. Diazotized amino-dialkoxynaphthalene was combined with Naphthol AS, AS-OL and AS-SW on cotton, and the dyeing results were listed in Table 2.

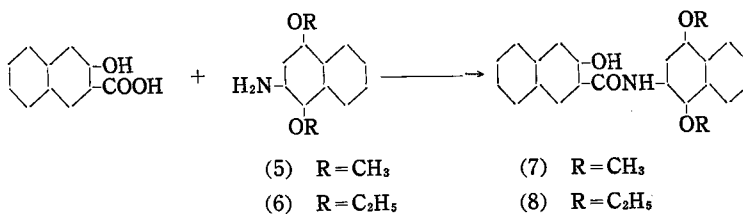
Table 2. Colour shade and fastness for azoic combination of 2-amino-1,4-dialkoxynaphthalene with Naphthol AS, AS-OL and AS-SW on cotton.

Diazo-component	Coupling-component (Naphthol)	Colour Shade	λ_d $m\mu$	Fastness		
				Light	Washing	Rubbing
(5)	AS	Dark Violet	620.0	6	5	3
(6)	AS	Dark Violet	–493.2	6	5	3
(5)	AS-OL	Dark Brownish Violet	–493.5	6	5	3
(6)	AS-OL	Dark Brownish Violet	633.1	5–6	5	3
(5)	AS-SW	Purplish Black	613.5	>6	5	3
(6)	AS-SW	Purplish Black	589.2	6	5	3

Concentration of coupler solution = 10g/l. Liquor ratio = 20 : 1.

2-2 1,4-Dialkoxy-2-naphthylamides of β -hydroxynaphthoic acid

(a coupling component)⁶⁾



According to the usual method, 2-amino-1,4-dialkoxynaphthalene could be condensed with β -hydroxynaphthoic acid (BON acid) in a high yield.

Table 3. Yield, m. p. and analysis of 1,4-dialkoxy-2-naphthylamide of BON acid.

Compd.	Yield %	m. p. °C	N %	
			Calcd.	Found
(7)	80.0	208 — 9	3.75	3.74
(8)	79.9	170 — 1	3.49	3.56

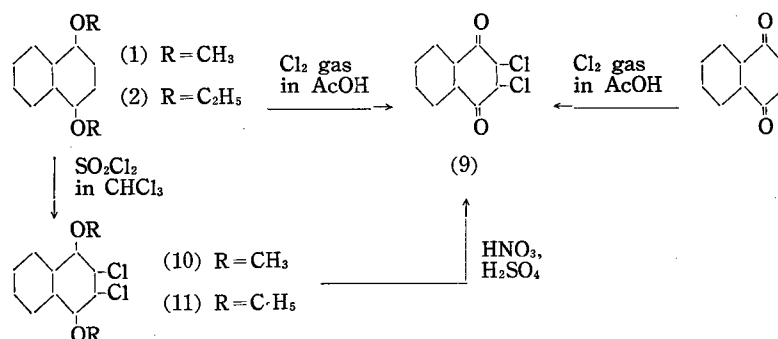
When the coupler (7) and (8) were developed with Scarlet GG on cotton, brown dyeings were obtained, and the colour shades were more brownish than Naphthol AS-BG, the corresponding one in benzene series.

Table 4. Colour shade and fastness for azoic combination of Scarlet GG and Scarlet G with Naphthol AS-BG, 2,5-diethoxyanilide of BON acid, 1,4-dimethoxy and 1,4-diethoxy-2-naphthylamide of BON acid.

Diazo-component	Coupling-component (Naphthol)	Colour Shade	λ_d $m\mu$	Fastness		
				Light	Washing	Rubbing
Scarlet GG	AS-BG	Dark Reddish Orange	598.8	>6	5	5
	-OEt	Yellowish Red	604.3	>6	5	5
	(7)	Reddish Brown	594.6	>6	5	3
	(8)	Dark Reddish Orange	591.7	>6	5	3
Scarlet G	AS-BG	Red	616.8	5-6	5	3
	-OEt	Yellowish Red	613.0	5-6	5	3
	(7)	Red	608.8	>6	5	3
	(8)	Red	615.0	6	5	3

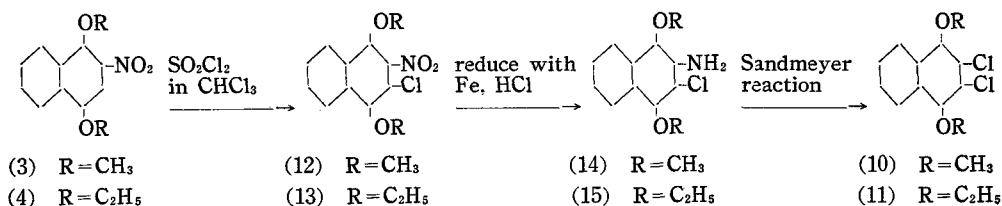
Concentration of coupler solution = 10g/l., Liquor ratio = 20 : 1,
-OEt = 2,5-Diethoxyanilide of BON acid.

2-3 2-Amino-3-chloro-1,4-dialkoxy-naphthalene (a diazo component)⁷⁾



The chlorination of 1,4-dialkoxy-naphthalenes in acetic acid with chlorine gas gave 2,3-dichloro-1,4-naphthoquinone (9) in a high yield beyond expectation. However, dichloro-derivatives of 1,4-dialkoxy-naphthalene were obtained by chlorinating in chloroform with the theoretical amount of suluryl chloride at low temperature.

When the dichlorinated products were treated with a mixed acid, the nitrocompounds could not be produced, but the products derived in the high yield, were proved to be identical with 2,3-dichloro-1,4-naphthoquinone (9) obtained by chlorinating 1,4-naphthoquinone. From this evidence, it was confirmed that the chlorinated products of 1,4-dialkoxy-naphthalene were 2,3-dichloro-derivatives.



2-Nitro-1,4-dialkoxynaphthalene obtained in section 2-1, was also chlorinated in chloroform with sulfuryl chloride and reduced to amino-derivative with iron powder and hydrochloric acid. Thus obtained aminoderivatives were converted into 2,3-dichloro-1,4-dialkoxynaphthalenes by Sandmeyer reaction, hence the structures of (12)–(15) were assigned to monochloro-derivatives of 2-nitro- and 2-amino-1,4-dialkoxynaphthalene.

Table 5. Yield, m. p. and analysis of 2,3-dichloro-, 2-nitro-3-chloro-, and 2-amino-3-chloro-1,4-dialkoxynaphthalene.

Compd.	Yield %	m.p. °C	N %		Cl %	
			Calcd.	Found	Calcd.	Found
(10)	77.9	107–8	—	—	27.64	27.48
(11)	82.5	103–4	—	—	24.92	24.51
(12)	80.0	121–2	—	—	13.27	13.16
(13)	80.4	97–8	—	—	12.01	11.80
(14)	70.1	101–2	5.90	5.94	—	—
(15)	66.3	73–4	5.27	5.28	—	—

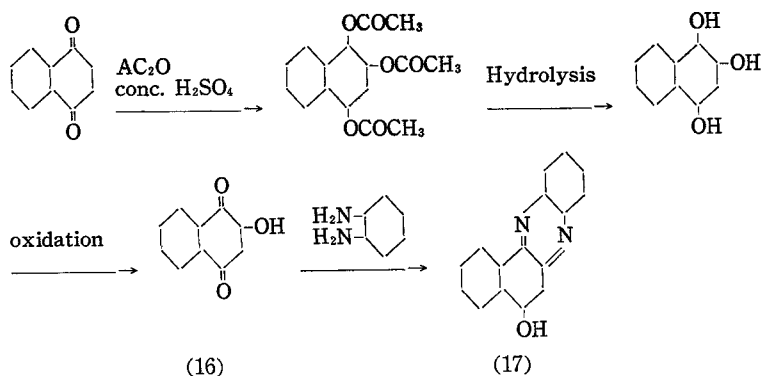
2-Amino-3-chloro-1,4-dialkoxynaphthalene could be diazotized by the usual method, and the diazo solution was pale yellow. Diazotized amino-chloro-dialkoxy-naphthalene was combined with Naphthol AS, AS-BG, 2,5-diethoxyanilide of BON acid, 1,4-dimethoxy-(7) and 1,4-diethoxy-2-naphthylamide of BON acid (8), and the dyeing results were listed in Table 6.

Table 6. Colour shade and fastness for azoic combination of 2-amino-3-chloro-1,4-dialkoxy-naphthalene with the azoic coupling components of Naphthol AS type.

Dizo-component	Coupling-component (Naphthol)	Colour Shade	λ_d $m\mu$	Fastness		
				Light	Washing	Rubbing
(14)	AS	Red	618.1	3–4	5	3
	AS-BG	Red	629.0	4	4	3
	-OEt	Red	620.0	4	4	3
	(7)	Dark Red	608.8	6	5	3
	(8)	Deep Purplish Red	643.0	3–4	4	3
(15)	AS	Deep Purplish Red	657.5	3	4	3
	AS-BG	Red	617.5	3–4	4	3
	-OEt	Deep Purplish Red	631.3	3	4	3
	(7)	Dark Red	608.5	5–6	5	3
	(8)	Deep Purplish Red	650.0	4	4	3

Concentration of coupler solution = 10g/l., Liquor ratio = 20 : 1,
-OEt = 2,5-Diethoxyanilide of BON acid.

2-4 6-Hydroxynaphthophenazine (a coupling component)⁸⁾



6-Hydroxynaphthophenazine (17) has been synthesized by condensing 2-hydroxy-1,4-naphthoquinone (16) with *o*-phenylenediamine in an acidic aqueous medium containing sodium acetate,⁹⁾ but the details has not been manifested. Our experiment gave the yield of 92.8 % of the theory and the melting point was higher than 290°C.

There have been four methods for the preparation of 2-hydroxy-1,4-naphthoquinone; that is, acidic or alkaline hydrolysis of 2-anilino-1,4-naphthoquinone obtained by 1,4-addition of aniline to 1,4-naphthoquinone,¹⁰⁾ alkaline treatment of 1,4-diketo-2,3-tetrahydronaphthyleneoxyde obtainable by the oxydation of 1,4-naphthoquinone with bleaching powder,¹¹⁾ or hydrogenperoxyde,¹²⁾ direct oxydation of 1,4-naphthoquinone with air-oxygen in caustic alkaline aqueous medium,¹³⁾ and oxydation of 1,2,4-trioxynaphthalene which was prepared by hydrolysis of 1,2,4-triacetoxynaphthalene obtainable from 1,4-naphthoquinone by Thiele-reaction.¹⁴⁾ From our experimental results for above four methods, it was shown that the last one gave the highest yield (about 60% of the theory based on 1,4-naphthoquinone).

6-Hydroxynaphthophenazine is soluble in caustic alkali and couples with diazo compound. Thus, 6-hydroxynaphthophenazine was developed with several azoic diazo components and the results were listed in Table 7. The ratio of substantivity of 6-hydroxynaphthophenazine to that of Naphthol AS was 3:4.

Table 7. Colour shade and fastness for azoic combination of 6-hydroxynaphthophenazine with azoic diazo components.

Azoic Base (Salt)	Colour Shade	λ_d $m\mu$	Fastness		
			Light	Washing	Rubbing
Blue BB	Dark Red	493.4	5-6	3-4	5
Variamine Blue B	Dark Brownish Purple	498.5	5-6	4-5	5
Red B	Orange	593.7	3	4	4
Bordeaux GP	Yellowish Red	607.5	3-4	4-5	4
Scarlet GG	Reddish Yellow	582.3	3	4-5	4
Brown RR	Dark Reddish Orange	604.0	4-5	3	4
Green BB	Dark Purple	502.0	5-6	5	4
Yellow GC	Yellowish Orange	585.0	3	4	4

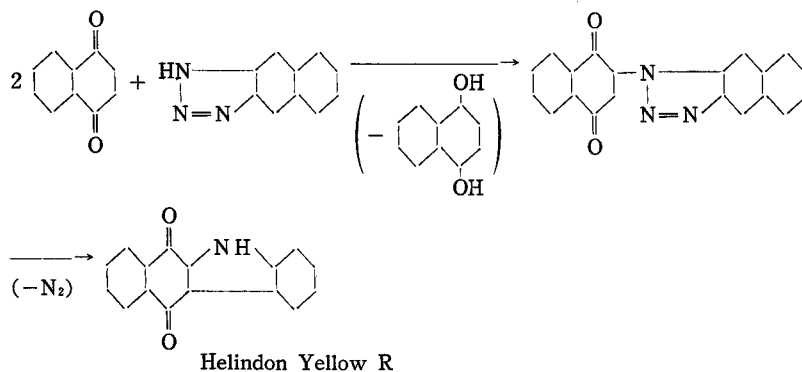
Concentration of coupler solution = 5g/l. Liquor ratio = 20 : 1.

3. Vat Dyes

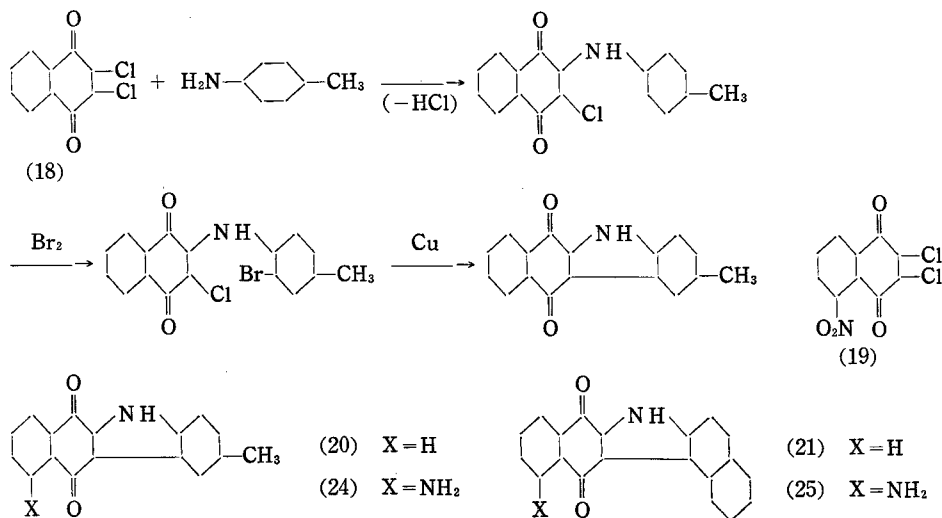
The number of vat dyes derived from 1,4-naphthoquinone, reported upto the present, has been reached to a considerable amount. However, many of them have been found in the patent literature and the details have not been shown. Among these, next five dyes can be found in Colour Index (second edition); that is, Algol Brilliant Green BK (CI 73840), Helindon Yellow R (CI 56070), Helindon Yellow G (CI 56075), Helindon Red CR (CI 56050, CI Vat Red 33) and Indanthrene Yellow 6GD (CI 56080, CI Vat Yellow 27).

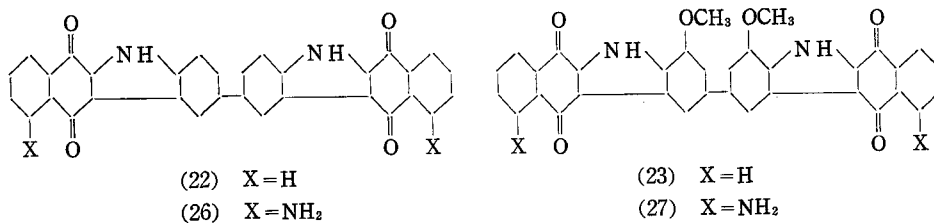
In the present work, these dyes and the derivatives, additionally brasanquinone derivatives were synthesized for the test of dyeing and photosensitized tendering effect.

3-1 Carbazolquinone derivatives¹⁶⁾



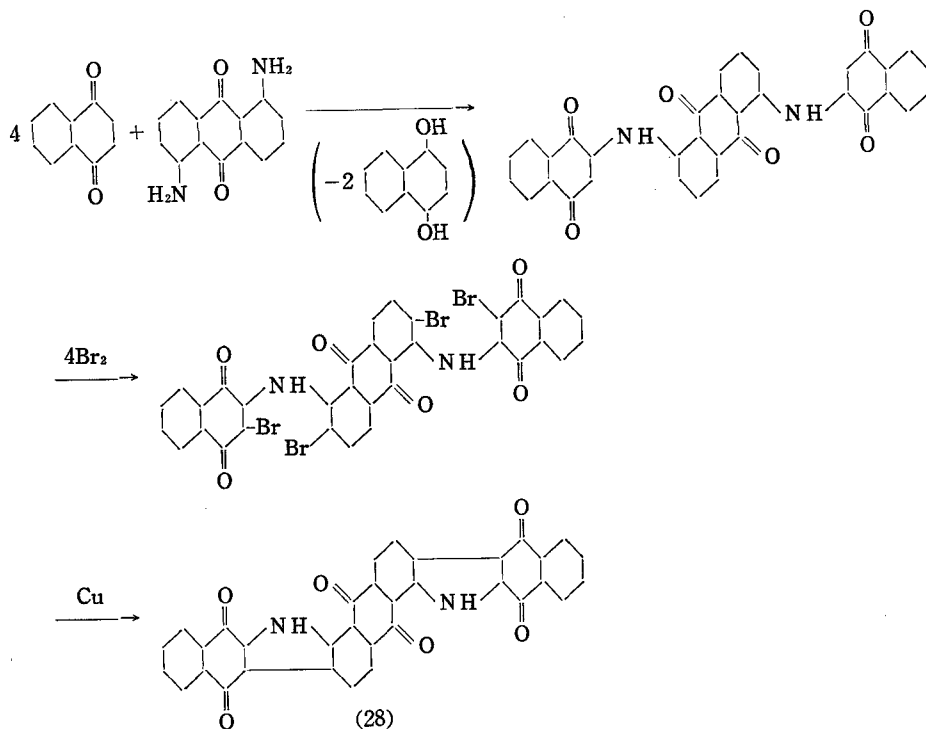
Helindon Yellow R (2,3-benzocarbazol-1,4-quinone) has been synthesized by 1,4-addition of 1,2,3-benzotriazole to 1,4-naphthoquinone and cyclization by heating.¹⁷⁾ However, since 1,2,3-benzotriazole has been prepared from 1,2-diaminobenzene, and then the preparation of the derivatives is difficult.





In the present work, vat dyes containing carbazole ring were prepared by condensing of 2,3-dichloro- (18) and 5-nitro-2,3-dichloro-1,4-naphthoquinone (19) with aromatic primary amines by dehydrochlorination, substitution of the ortho position of imino group with bromine, followed by dehalogenation and cyclization with the use of copper powder.¹⁸⁾ The use of activated copper was shown to be more successful by our experiment. The aromatic primary amines used for the formation of carbazole ring were *p*-toluidine, β -naphthylamine, benzidine, *o*-dianisidine and 1,5-diaminoanthraquinone.

As the condensation of 1,5-diaminoanthraquinone with dichloro-naphthoquinone (18) was difficult, compound (28) was prepared by 1,4-addition of 1,4-naphthoquinone to diamino-anthraquinone (in the yield of 91.0%), bromination (in the yield of 72.4%), and then cyclization with activated copper (in the yield of 90.0%).



It is difficult to determine the position of dehydrochlorination of nitro-dichloro-naphthoquinone (19) with amines, but 5-nitro-2-amino-3-chloro-1,4-naphthoquinone has been assigned to the condensation product of (19) with ammonia without offering substantial evidence.¹⁹⁾ In this report, we assigned the formula of (24)–(27) to the

condensation products of nitro-dichloro-naphthoquinone (19) with the used aromatic amines, in conformity to the above mentioned foundation. The reaction condition, yield, etc. were listed in Table 8—10.

Table 8. Dehydrochlorination of 2,3-dichloro-(18) and 5-nitro-2,3-dichloro-1,4-naphthoquinone-(19) with aromatic amines.

Reagent mol	Solvent (AcOH) cc	React. Temp. °C	React. Time hr	Yield %	Mark of Product
(18) 0.05, <i>p</i> -Toluidine 0.052	70	reflux	1	80.2	(20'')
(18) 0.02, β -Naphthylamine 0.021	45	"	1	80.7	(21'')
(18) 0.025, Benzidine 0.031	55	"	2	80.8	(22'')
(18) 0.05, <i>o</i> -Dianisidine 0.027	100	"	2	67.9	(23'')
(19) 0.02, <i>p</i> -Toluidine 0.022	60	"	2	78.8	(24'')
(19) 0.02, β -Naphthylamine 0.022	60	"	3	78.2	(25'')
(19) 0.015, Benzidine 0.008	40	"	3	85.5	(26'')
(19) 0.02, <i>o</i> -Dianisidine 0.011	50	"	4	76.9	(27'')

Table 9. Bromination of the products in Table 8.

Reagent mol	Solvent (AcOH) cc	React. Temp. °C	React. Time hr	Yield %	Mark of Product
(20'') 0.025, Bromine 0.055	120	room	1	78.7	(20')
(21'') 0.01, " 0.022	50	40—50	4	72.7	(21')
(22'') 0.01, " 0.044	80	room	3	81.6	(22')
(23'') 0.01, " 0.044	80	room	3	70.3	(23')
(24'') 0.01, " 0.022	60	40—50	1	76.2	(24')
(25'') 0.01, " 0.022	40	room	3	76.6	(25')
(26'') 0.01, " 0.044	40	room	4	73.3	(26')
(27'') 0.01, " 0.044	50	room	3	80.2	(27')

Table 10. Cyclization of the products in Table 9.

Reagent g	Solvent (Nitrobenzene) g	React. Temp. °C	React. Time hr	Yield %	Mark of Product	N %	
						Calcd.	Found
(20') 5.0, Cu 3.0	14.0	reflux	1	60.7	(20)	5.36	5.35
(21') 3.0, " 3.0	10.0	"	1	41.7	(21)	4.71	4.62
(22') 3.0, " 3.0	22.0+ Quinoline 4.5	"	2	49.8	(22)	5.89	5.76
(23') 3.5, " 5.0	20.0+ Quinoline 3.0	"	1	40.5	(23)	5.11	5.06
(24') 2.0, " 2.0	10.0	"	4	76.5	(24)	10.15	10.10
(25') 3.0, " 3.0	12.0	"	3	38.9	(25)	8.97	8.86
(26') 3.0, " 3.5	12.0	"	4	52.1	(26)	10.73	10.68
(27') 3.0, " 3.5	12.0	"	5	55.3	(27)	9.62	9.52

The compounds (20)—(28) were reduced by sodium hydrosulfite in a caustic

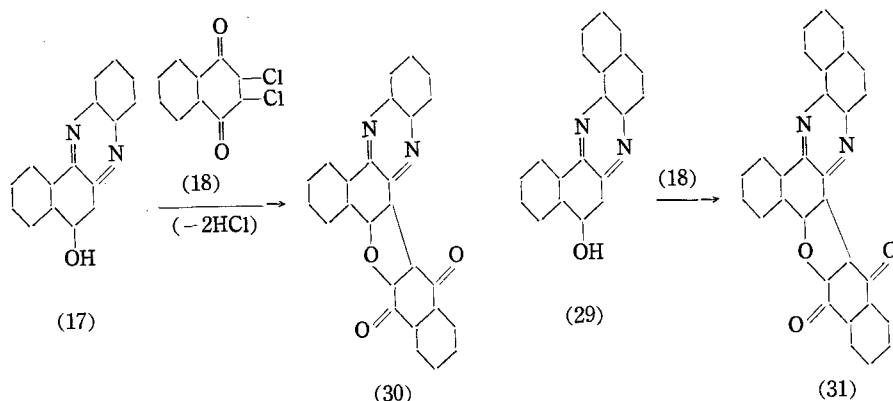
alkaline solution without difficulty, and reoxidized by air. The results of dyeing on cotton were listed in Table 11.

Table 11. Results of dyeing with vat dyes containing carbazole-ring.

Dye	Colour Shade	λ_d <i>m\mu</i>	Dyeings from the Residual Liquor	Fastness		
				Light	Washing	Rubbing
(20)	Yellowish Red	580.0	same	6-7	4-5	4
(21)	Dull Reddish Orange	591.2	faint slightly	6-7	4-5	5
(22)	Red Brown	595.0	faint	3-4	4	5
(23)	Dark Brownish Purple	-493.3	faint	3-4	4	5
(24)	Pale Pink	603.8	same	6-7	4	5
(25)	Greyish Red	601.8	same	6-7	4	5
(26)	Pale Red	610.0	same	4-5	4	5
(27)	Dull Purple	-500.0	same	4-5	4	5
(28)	Greyish Red	605.8	faint slightly	6-7	4	5

Dye=5% on the weight of cotton, Liquor ratio=20:1.

3-2 Derivatives from naphthophenazine, naphthosultamphenazine and brasanquinone²⁰⁾



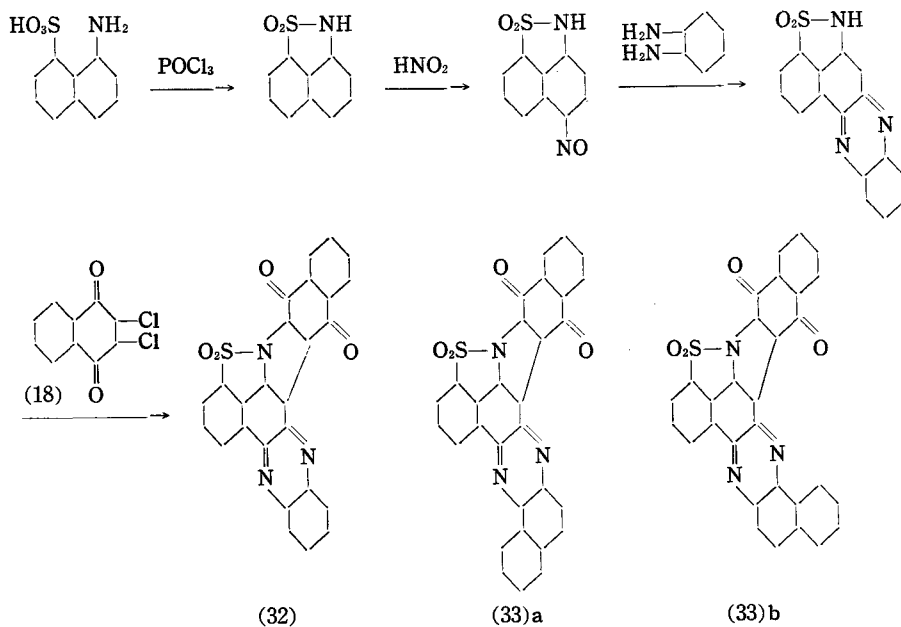
Helindon Yellow G

6-Hydroxynaphthophenazine (17) obtainable by the condensation of 2-hydroxy-1,4-naphthoquinone (16) with *o*-phenylenediamine, has been known to react with dichloro-naphthoquinone (18) by an acid-binding agent to give Helindon Yellow G.²¹⁾

Table 12. Preparation of Helindon Yellow G and its derivatives.

Dye	Reagent mol	Solvent (Nitrobenzene) cc	React. Temp. °C	React. Time hr	Yield %	N %	
						Calcd.	Found
(30)	(17) 0.005, (18) 0.005, CH ₃ COONa 0.013	60	140-50	2	82.8	7.00	6.95
(31)	(29) 0.005, (18) 0.005, CH ₃ COONa 0.013	60	180-200	3	88.9	6.22	6.19

2-Hydroxy-1,4-naphthoquinone was also condensed with 1,2-naphthylenediamine in the yield of 91.2 %, and the product was reacted with dichloro-naphthoquinone in the same manner. The formula of (29) was assigned to the condensation product of hydroxy-naphthoquinone with naphthylenediamine, according to the report²²⁾ in which the formation of 1,2-benzo-6-hydroxyphenazine has been confirmed on the condensation product of 2-hydroxy-1,4-benzoquinone with 1,2-naphthylenediamine.

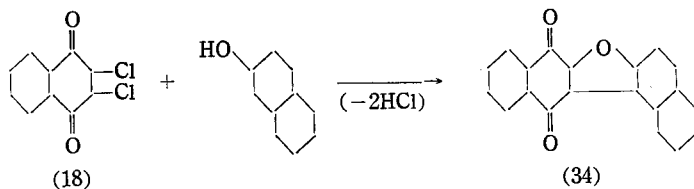


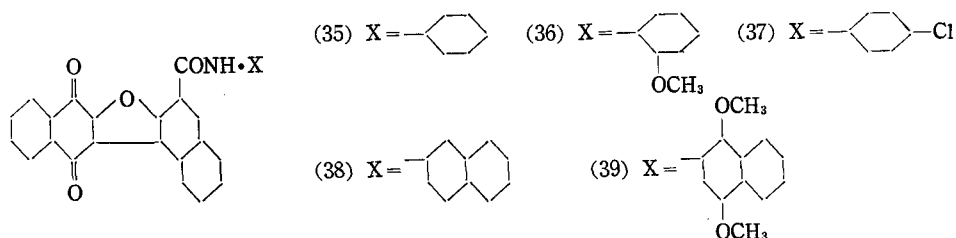
Indanthrene Yellow 6GD has been prepared by the condensation of dichloronaphthoquinone (18) with naphthosultamphenazine derived from naphthosultam, and PB report²³⁾ has given full details for its preparation. In the present work, compound (33) was also prepared by the use of 1,2-naphthylenediamine in the same manner. Two kinds of formula, a- or b-type, could be assumed for compound (33), but there is no means at the present time, by which the chemical constitution was confirmed.

Table 13. Yield and analysis of Indanthrene Yellow 6GD and its homologue.

Dye	Yield %	N %	
		Calcd.	Found
(32)	22.0	9.11	9.03
(33)	24.5	8.22	8.15

Yield = Theoretical yield based on starting Peri-acid.





Dichloro-naphthoquinone (18) can be condensed with aromatic hydroxy-compounds by the aid of acid-binding agent. For example, the use of β -naphthol has given 4,5-benzobrasanquinone (34), but the product had no affinity for a fiber.²⁴⁾ However, it has been shown in Patent²⁵⁾ that the brasanquinone derivatives had affinity for a cotton, when aromatic hydroxy-compound of Naphthol AS type were used. In the present work, Naphthol AS, AS-E, AS-SW and the product (7) from 2-amino-1,4-dimethoxy-naphthalene already mentioned in section 2-2, were condensed with dichloronaphthoquinone by the aid of anhydrous sodium acetate or pyridine.

Table 14. Condensation of hydroxycompound with dichloronaphthoquinone.

Dye	Reagent mol	Solvent (EtOH) cc	React. Temp. °C	React. Time hr	Yield %	N %	
						Calcd.	Found
(35)	Naphthol AS 0.01, (18) 0.01, Pyridine 0.06	90	reflux	2	61.6	3.36	3.33
(36)	Naphthol AS-OL 0.01, (18) 0.01, CH ₃ COONa 0.04	50	"	2	76.0	3.13	3.09
(37)	Naphthol AS-E 0.01, (18) 0.01, CH ₃ COONa 0.04	50	"	2	46.0	3.10	3.12
(38)	Naphthol AS-SW 0.01, (18) 0.01, Pyridine 0.06	60	"	2	83.0	3.00	3.06
(39)	(7) 0.01, (18) 0.01, CH ₃ COONa 0.04	60	"	2	94.0	2.13	2.14

The results of dyeing on cotton were listed in Table 15.

Table 15. Results of vat dyeing with the derivatives of naphthophenazine, naphtho-sultamphenazine and brasanquinone.

Dye	Colour Shade	λ_d $m\mu$	Dyeings from the Residual Liquor	Fastness		
				Light	Washing	Rubbing
(30)	Yellow	577.2	same	4-5	5	5
(31)	Yellowish Orange	587.7	faint slightly	4-5	5	5
(32)	Yellow	577.9	same	4-5	5	5
(33)	Dark Orange	590.8	same	5-6	5	5
(35)	Reddish Yellow	581.0	same	6	5	5
(36)	Light Reddish Yellow	581.3	same	6	5	5
(37)	Yellow	579.2	same	6	5	5
(38)	Light Reddish Yellow	581.1	faint slightly	6	5	5
(39)	Dull Orange	585.0	faint slightly	6	5	5

Dye = 5% on the weight of cotton, Liquor ratio = 20 : 1.

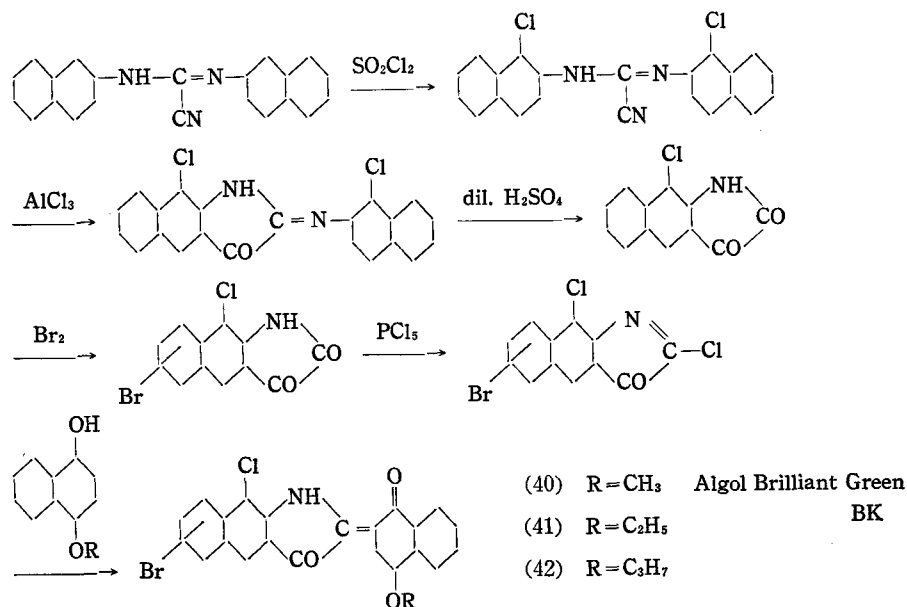
Indanthrene Yellow 6GD is said to be a "nontender",²⁶⁾ an important factor in the field of yellow and orange vat dyes, on the other hand is also said to be actively tendering dye.²⁷⁾ The prepared nine vat dyes were tested for photosensitized tendering activity, and it was shown that the tendering effect was less in naphthosultumphenazine derivatives containing no furan ring and was more prominent in brasanquinone containing furan ring.

Table 16. Photosensitized tendering effect of the vat dyes prepared in this section.

Dye	(30)	(31)	(32)	(33)	(35)	(36)	(37)	(38)	(39)
Tendering %	2.6	3.6	2.4	2.3	5.9	5.7	8.3	7.9	8.2

Tendering % = Mean loss % of tensile strength of dyeings after light exposure.

3-3 Algol Brilliant Green BK and its homologue



Algol Brilliant Green BK has been prepared by condensing α -chloride of α -bromo-1-chloro-2,3-naphthoisatin with 1,4-naphthohydroquinone monomethyl ether, and the details of the preparation has been given in PB report.²⁸⁾ In the present work, Algol Brilliant Green BK and its homologue were prepared by the use of 1,4-naphthohydroquinone monomethyl ether, monoethyl ether and monopropyl ether, derived from 1,4-naphthoquinone respectively.

1,4-naphthohydroquinone mono-alkyl ether has been prepared by heating naphthohydroquinone in 3% alcoholic hydrochloric acid,²⁹⁾ or by treating 1,4-naphthoquinone in alcohol with stannous chloride and phosphorous oxychloride.³⁰⁾

It was already described in section 2-1 that combined reduction and alkylation reaction takes place very smoothly, giving high yields of naphthohydroquinone di-alkyl ether by heating a mixture of 1,4-naphthoquinone, stannous chloride and the corres-

ponding concentrated alcoholic hydrochloric acid. However, naphthohydroquinone monoalkyl ether was also obtained in a single step, when a moderate concentration of alcoholic hydrochloric acid is adopted.

Table 17. Preparation of 1,4-naphthohydroquinone monoalkyl ether.

Ether	Reagent mol			React. Temp. °C	React. Time hr	Yield %	m. p. °C
	N.Q.	SnCl ₂ ·2H ₂ O	5% Alc·HCl				
Methyl	0.05	0.062	0.137	reflux	2	60.9	129—30
Ethyl	0.05	0.062	0.137	"	2	57.6	100— 1
Propyl	0.05	0.062	0.137	"	2	46.5	106— 7

N. Q.=1,4-Naphthoquinone, Mole of 5% alcoholic hydrochloric acid is based on HCl.

Algol Brilliant Green BK and its homologue (40)—(42) were vattable with sodium hydrosulfite in a caustic alkaline solution, but the vattability and dyeability were decreased in the order of (40) to (42). Then, the dye (40)—(42) were solubilized by ICI pyridine-metal method for dyeing, and the results of dyeing with the solubilized dye were listed in Table 19.

Table 18. Yield and analysis of Algol Brilliant Green BK and its homologue.

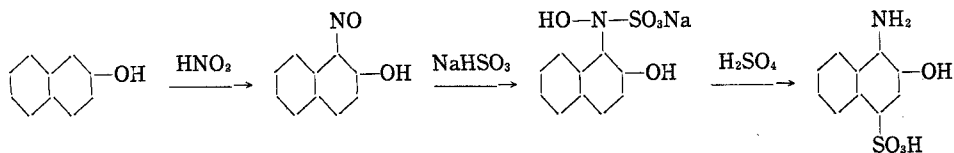
Dye	Yield %	Cl+Br %	
		Calcd.	Found
(40)	73.0	24.49	24.67
(41)	70.9	24.02	23.86
(42)	73.0	23.29	23.20

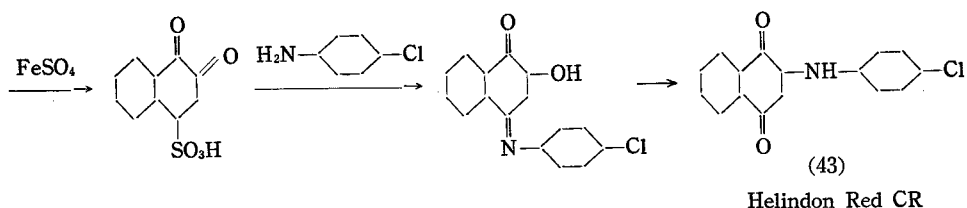
Table 19. Results of dyeing with leuco ester of Algol Brilliant Green BK and its homologue.

Dye	Colour Shade	λ_d <i>mμ</i>	Dyeings from the Residual Liquor	Fastness		
				Light	Washing	Rubbing
On Cotton						
(40)	Deep Bluish Green	498.6	faint slightly	4	5	5
(41)	Bluish Green	497.9	"	4	5	5
(42)	Bluish Green	495.6	"	4	5	5
On Wool						
(40)	Dark Green	498.6	faint	6—7	5	3
(41)	Dark Green	495.8	faint	6—7	5	3
(42)	Deep Greenish Blue	491.3	faint extremely	6—7	5	3

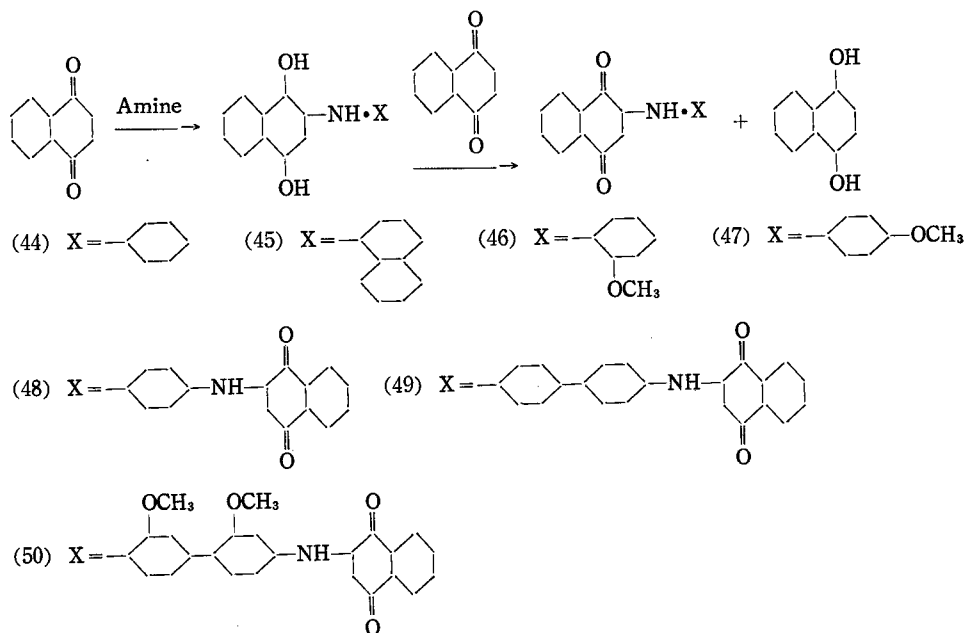
Dye=3% on the weight of cotton or wool, Liquor ratio=20:1.

3-4 2-Arylamino-1,4-naphthoquinone





Helindon Red CR, vat dye for wool, is 2-(4'-chloroanilino)-1,4-naphthoquinone (43). The details of its preparation from β -naphthol has been given in PB report,³¹⁾ and the reaction steps are illustrated as above schema. However, in the present work, Helindon Red CR and its derivatives were prepared by 1,4-addition reaction of aromatic primary amines to 1,4-naphthoquinone for the purpose of utilization of 1,4-naphthoquinone.



In 1,4-addition reaction, normally an excess of 1,4-naphthoquinone is used to oxidize the initially-formed substituted naphthohydroquinone to the corresponding 1,4-naphthoquinone, and then, the products result in 2-arylamino-1,4-naphthoquinone plus naphthohydroquinone. There has been some reports,³²⁾ in which oxidation of substituted naphthohydroquinone was carried out by the use of such carrier as CuCl , CeCl_3 , or $(\text{CH}_3\text{COO})_2\text{Cu}$ and oxygen. It was shown in our experiment that naphthohydroquinone could be recovered with great difficulty and in a little yield. Then, the latter method using a oxygen carrier was more advantageous than the former for industrial practice. Products (43)–(50) were prepared respectively by blowing air into a mixture of naphthoquinone, $(\text{CH}_3\text{COO})_2\text{Cu}\cdot 2\text{H}_2\text{O}$ and such amines as *p*-chloroaniline, aniline, α -naphthylamine, *o*- and *p*-anisidine, *p*-phenylenediamine, benzidine, and dianisidine in boiling methonal.

Table 20. Yield, m. p. and analysis of 2-arylamino-1,4-naphthoquinone.

Dye	Yield		m. p. °C	N %	
	%			Calcd.	Found
(43)	73.6	(43.0)	264—5	4.94	4.78
(44)	52.7		190—1	5.62	5.54
(45)	—	(20.1)	>300	4.68	4.66
(46)	75.3	(17.2)	149—50	5.02	5.03
(47)	94.0		156—7	5.02	4.97
(48)	83.0		>300	6.67	6.49
(49)	74.1	(74.1)	251—2	5.64	5.48
(50)	81.7	(82.0)	275—6	5.04	4.84

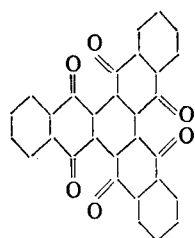
Figure put in bracket is the yield without oxygen-carrier.

Table 21. Results of vat dyeing with 2-arylamino-1,4-naphthoquinone.

	Dye	Colour shade	λ_d <i>m</i> μ	Dyeings from the Residual Liquor	Fastness		
					Light	Washing	Rubbing
On Wool	(43)	Dark Red	616.7	faint	6	3—4	3—4
	(44)	Red	612.0	faint	5—6	3—4	3—4
	(45)	Brown	587.0	faint slightly	5—6	4	5
	(46)	Dull Red	613.5	same	4	3—4	4
	(47)	Dull Red	608.2	same	4	3—4	4
	(48)	Purplish Black	—492.9	faint	6	4	4
	(49)	Brown Purple	—501.9	faint	5—6	4	4
	(50)	Dark Purple	—503.6	faint	5—6	4	4
On Silk	(43)	Dull Red	621.0	faint slightly	5—6	3—4	3—4
	(44)	Dull Red	608.2	faint slightly	5—6	3—4	3—4
	(45)	Brown	587.7	same	5	4	5
	(46)	Dull Red	620.0	same	5	3	4
	(47)	Dull Red	621.7	same	5	3—4	4
	(48)	Dark Brown	—496.1	faint	5	4	4
	(49)	Brown Purple	—499.2	faint slightly	5	4	4
	(50)	Dark Purple	—546.5	faint slightly	5	4	4

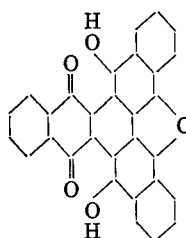
Dye=5% on the weight of wool and silk, Liquor ratio=20:1.

3-5 Triphthaloylbenzene derivatives



Triphthaloylbenzene

Zn in conc. H₂SO₄

Anhydroquinhydrone of
triphthaloylbenzene

Triphthaloylbenzene has been found in the crude phthalic anhydride produced by the vapour phase catalytic oxydation of naphthalene by the authors¹⁾ and prepared also from 1,4-naphthoquinone by its intermolecular condensation in aqueous medium or aqueous phenol.⁴²⁾ It was vatable in an alkaline solution of hydrosulfite, but had no affinity for a cotton. However, anhydroquinhydron, the reduction product of triphthaloylbenzene, had considerable affinity for a cotton and gave brilliant greenish yellow dyeings. It had excellent light fastness (>7), but poor one to chlorine (2) because of the ready conversion into original triphthaloylbenzene by oxidation.

There are two hydroxyl groups in anhydroquinhydron of triphthaloylbenzene which are sensible to an oxidant, the substituted product of the hydroxyl groups by methoxyl groups could not be reduced with an alkaline hydrosulfite solution.

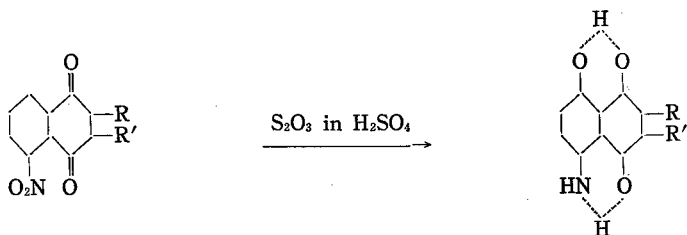
H. E. Fierz-David *et al.*⁴³⁾ has obtained nonuniform derivatives of triphthaloylbenzene by its chlorination and bromination, and tri-sulfonate of anhydroquinhydron by its sulfonation with 20 % oleum.

It was found that the experimental results, checked by the authors, were same as those obtained by Fierz-David *et al.*, though the experimental conditions were modified, and the nitration products of triphthaloylbenzene with mixed acid or kalium nitrate in conc. sulfuric acid were also not quite uniform. Anhydroquinhydron was sulfonated more easily than the original triphthaloylbenzene. For example, triphthaloylbenzene could not be affected by conc. sulfuric acid even at 150°C, but anhydroquinhydron was readily sulfonated at 90°C and the product was a nonuniform hexa-sulfonate.

4. Disperse Dye

Numerous disperse dyes of naphthoquinone or naphthoquinone-imine type have been suggested as cellulose acetate dye. However, many of these dyes have been derived from naphthazarine, then the starting materials have been 1,5-dinitronaphthalene and not 1,4-naphthoquinone. For the preparation of 2,3-dihalogeno-1,4-dihydroxy-5,8-naphthoquinone-monoimine from 5-nitro-2,3-dichloro-1,4-naphthoquinone, Sandoz Co.³³⁾ have gotten an American Patent recently.

4-1 Derivatives from 1,4-naphthoquinone-monoimine³⁴⁾



(19) R = R' = Cl

(51) R = R' = Br

(52) R = NH₂, R' = Cl

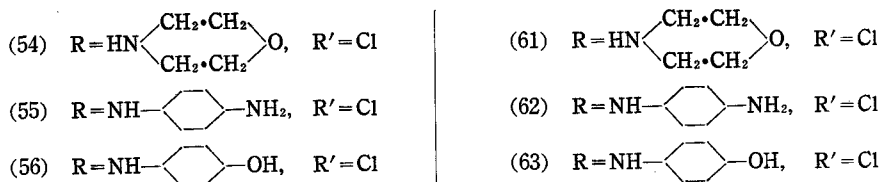
(53) R = NH·CH₂·CH₂OH, R' = Cl

(57) R = R' = Cl

(58) R = R' = Br

(59) R = NH₂, R' = Cl

(60) R = NH·CH₂·CH₂OH, R' = Cl



It was patented that nitro-dichloro-naphthoquinone (19) is reduced to 2,3-dichloro-1,4-dihydroxy-5,8-naphthoquinone-monoimine (57) by sulfur sesquioxide in concentrated sulfuric acid medium, following the rearrangement of oxygen atom in nitro group.³⁹⁾ In the present work, compound (19) and (51)—(56) were synthesized for the preparation of known dye (57), (58) and its homologue (59)—(63), and the structure in above schema were assigned to these compounds, in conformity to the foundation mentioned in section 3-1.

Among the starting materials, compound (19) and (52) are already known. Nitro-dibromo-naphthoquinone (51) were prepared from the known 2,3-dibromo-1,4-naphthoquinone by the same method as the preparation of nitro-dichloro-naphthoquinone (19) (yield 53.0 % m. p. 209—10°C).

Table 22. Condensation 5-nitro-2,3-dichloro-1,4-naphthoquinone with amines.

Compd.	Reagent mol	Solvent (MeOH) cc	React. Temp. °C	React. Time hr	m. p. °C	Yield %	N %	
							Calcd.	Found
(53)	Monoethanolamine 0.044, (19) 0.02	50	room	3	206—7*	48.9	9.45	9.37
(54)	Morpholine 0.044 (19) 0.02	50	"	1.5	106—1	86.8	8.24	8.20
(55)	<i>p</i> -Phenylenediamine 0.022, (19) 0.02	50	reflux	4	>280	91.2	12.23	12.14
(56)	<i>p</i> -Aminophenol 0.022, (19) 0.02	50	"	4	239—9*	69.7	8.13	8.02

* Stared one melted with decomposition.

Naphthoquinone-monoimine dyes were prepared by the modified method, that is a mixture of 0.01 mole of starting material with 0.7 g of sulfur in about 14 % oleum was

Table 23. Yield, analysis and absorption maximum of naphthoquinone-monoimine dye.

Dye	Yield %	N %		Absorption Maximum		
		Calcd.	Found	λ_{max}	$m\mu$	$\epsilon_{max} \times 10^{-4}$
(57)	77.6	5.43	5.14	575		0.84
(58)	77.8	4.04	4.00	580		1.00
(59)	37.6	11.74	11.14	510		0.82
(60)	35.4	9.91	9.61	460		0.66
(61)	35.6	9.08	8.91	520		0.62
(62)	63.7	12.67	12.46	520		0.70
(63)	33.4	8.47	8.19	620		0.67

Concentration in absorption spectrometry = 5×10^{-4} mol/l in 95 % ethanol.

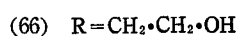
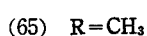
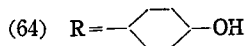
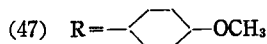
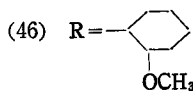
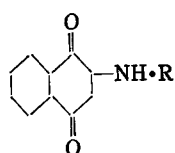
stirred at 35—45°C for four hours. The all products were not melted at 280°C.

Table 24. Results of dyeing with naphthoquinone-monoimine dye.

	Dye	Colour Shade	Dye-ability	Brightness	Fastness		
					Light	Washing	Rubbing
On Acetate	(57)	Bluish Red	3	4	4	2—3	3
	(58)	Blue Purple	2	3	4	2—3	4
	(59)	Dull Red	2	2	1	2—3	4
	(60)	Reddish Orange	3	5	1	2	4
	(61)	Greyish Purple	2	2	1	2—3	4
	(62)	Dull purple	3	2	3	3	4
	(63)	Grey	2	2	1	4	5
On Vinyon	(57)	Dull Blue Purple	2	4	5	3	3
	(58)	Light Blue Purple	2	2	5	3	4
	(59)	Greyish Red Purple	2	2	3	3	4
	(60)	Dull Reddish Orange	3	3	3	2—3	3
	(61)	Greyish Purple	2	2	3	3	4
	(62)	Purple Grey	2	2	4	3	5
	(63)	Greenish Grey	3	3	3	4	5
On 6 Nylon	(57)	Dark Blue Purple	4	4	3—4	2—3	3
	(58)	Light Blue Purple	3	3	4	2—3	4
	(59)	Light Red Purple	3	3	1	2—3	4
	(60)	Dull Reddish Orange	4	5	1	2	4
	(61)	Greyish Purple	3	3	1	2—3	4
	(62)	Dark Purple	3	3	3	3	5
	(63)	Greyish Olive	4	3	1	4	5
On Terylene	(57)	Blue Purple	3	4	6	4—5	5
	(58)	Light Blue Purple	2	3	5	5	5
	(59)	Greyish Red Purple	2	2	4—5	4—5	4
	(60)	Pale Pink	3	3	4—5	4	4
	(61)	Grey	2	3	5	4	4
	(62)	Purplish Grey	2	2	5	4	5
	(63)	Grey	2	2	5	4	5

Dye=2% on the weight of fiber, Liquor ratio=20:1, Dyeing on Terylene were carried out at 100°C without carrier.

4-2 2-Alkylamino- and 2-arylamino-1,4-naphthoquinone



It was found that *o*- and *p*-anisidino-1,4-naphthoquinone mentioned in section 3-4 could dye a acetate fiber by the usual method. Then, compound (64)—(66) were also prepared by the same method as the one in section 3-4 for using as a disperse dye.

Table 25. Yield, m. p., analysis and absorption maximum of 2-allyl- and 2-arylamino-1,4-naphthoquinone.

Dye	Yield %	m. p. °C	N %		Absorption Maximum		
			Calcd.	Found	λ_{max}	$m\mu$	$\epsilon_{max} \times 10^{-4}$
(46)	—	—	—	—	482		0.55
(47)	—	—	—	—	460		0.45
(64)	52.8	248	5.28	5.16	500		0.43
(65)	70.7	232	7.49	7.42	452		0.33
(66)	53.4	154	6.45	6.37	443		0.36

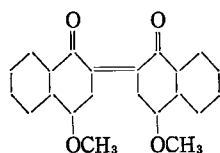
Concentration in absorption spectrometry = 5×10^{-4} mol/l in 95 % ethanol.

Table 26. Results of dyeing 2-allyl- and 2-arylamino-1,4-naphthoquinone.

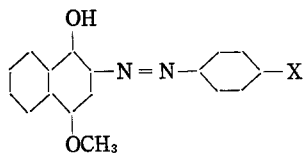
	Dye	Colour Shade	Dye-ability	Brightness	Fastness		
					Light	Washing	Rubbing
Acetate	(46)	Yellowish Red	4	4	3	3-4	5
	(47)	Yellowish Red	4	3	3	3-4	5
	(64)	Red Brown	4	3	2-3	2	4
	(65)	Yellow Orange	4	4	<1	1-2	4-5
	(66)	Yellow Orange	4	4	<1	1	5
Vinylon	(46)	Dull Red	2	2	3-4	3	3-4
	(47)	Dull Red	2	2	4	2-3	3-4
	(64)	Dull Red	2	2	4	2-3	4-5
	(65)	Dull Orange	2	3	3-4	1-2	4-5
	(66)	Dull Yellow	2	3	3	1	5
6 Nylon	(46)	Purplish Red	4	4	3	2	3-4
	(47)	Purplish Red	3	3	3-4	2	4-5
	(64)	Deep Red Purple	4	3	3-4	2	4-5
	(65)	Light Yellowish Orange	4	3	2-3	1	4-5
	(66)	Light Yellow	4	4	1-2	1	5

Dye=2 % on the weight of fiber, Liquor ratio=20 : 1.

4-3 Derivatives from 1-hydroxy-2-phenylazonaphthalene⁸⁵⁾



Russig Blue



(67) X = H

(68) X = NO₂

(69) X = SO₂NH₂

(70) X = NHAc

1,4-Naphthohydroquinone monomethyl ether prepared in section 3-3 has been coupled with diazo compound.⁸⁶⁾ Thus, compound (67)–(70) were prepared for using as a disperse dye. Since 1,4-naphthohydroquinone monomethyl ether was readily oxidized by air in alkaline solution to give Russig Blue (or Russig Indigo),⁸⁷⁾ the coupling reaction was carried out under hydrogen atmosphere.

Table 27. Yield, m. p., analysis and absorption maximum of 1-hydroxy-2-phenylazonaphthalene derivatives.

Dye	Yield %	m. p. °C	N %		Absorption Maximum		
			Calcd.	Found	λ_{max}	$m\mu$	$\epsilon_{max} \times 10^{-4}$
(67)	90.0	134—5	10.07	9.85	530		1.945
(68)	91.0	241—3	17.38	17.01	515		1.940
(69)	91.0	234—8	11.76	11.47	520		2.105
(70)	91.0	229—31	12.53	12.11	540		2.375

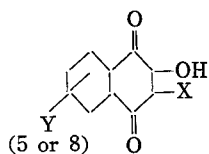
 Concentration in absorption spectrometry = 5×10^{-4} mol/l in 85% ethanol.

Table 28. Results of dyeing with 1-hydroxy-2-phenylazonaphthalene derivatives.

	Dye	Colour Shade	Dye-ability	Brightness	Fastness		
					Light	Washing	Rubbing
Acetate	(67)	Deep Purplish Red	4	4—5	3	3	3
	(68)	Purplish Red	2	2	3	3	3
	(69)	Purplish Red	3	3	3	3	2
	(70)	Deep Red Purple	3	3	2	3	3
Vinylon	(67)	Light Purplish Red	3	3	4	2—3	3
	(68)	Dull Red Purple	1—2	1—2	4—5	2—3	3
	(69)	Dull Red Purple	2	2	3—4	2—3	3
	(70)	Reddish Purple	2	2—3	3—4	2—3	3
6 Nylon	(67)	Deep Red Purple	4	4	4—5	3	2
	(68)	Dark Red Purple	3	3	4—5	3	3
	(69)	Purplish Red	3—4	3—4	4—5	3	2
	(70)	Deep Red Purple	3—4	3—4	4—5	3	3

Dye = 2% on the weight of fiber, Liquor ratio = 20 : 1.

4-4 Derivatives from 1-phenylazo-2,4-dihydroxynaphthalene

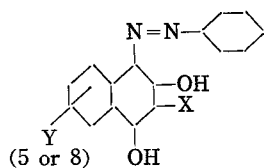


(71) X = Y = H

 (72) X = NO₂, Y = H

(73) X = Cl, Y = H

 (74) X = Y = NO₂

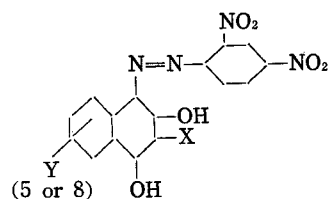
 (75) X = Cl, Y = NO₂


(76) X = Y = H

 (77) X = NO₂, Y = H

(78) X = Cl, Y = H

 (79) X = Y = NO₂

 (80) X = Cl, Y = NO₂


(81) X = Y = H

 (82) X = NO₂, Y = H

(83) X = Cl, Y = H

 (84) X = Y = NO₂

 (85) X = Cl, Y = NO₂

1,4-Naphthoquinone does not react with phenylhydrazine to give the hydrazone, but reacts to give 1-phenylazo-4-hydroxynaphthalene.³⁸⁾ Fierz-David *et al.*³⁹⁾ has prepared Orange I by coupling phenylhydrazine-*p*-sulfonic acid with 1,4-naphthoquinone. In the present work, monoazo compound (76)—(85) were prepared by the use of phenylhydrazine or 2,4-dinitrophenylhydrazine and the intermediate (71)—(75) obtained from 1,4-naphthoquinone.

2-Hydroxy-1,4-naphthoquinone (71) was already mentioned in section 2-4. 2-Hydroxy-3-nitro-1,4-naphthoquinone (72) has been prepared by the action of sodium nitrite in aqueous methanol,⁴⁰⁾ and 2-hydroxy-3-chloro-1,4-naphthoquinone (73) by the action of caustic alkali solution⁴¹⁾ to dichloro-naphthoquinone. Intermediates (74) and (75) were prepared by the same method as the preparation of (72) and (73) from 5-nitro-2,3-dichloro-1,4-naphthoquinone.

Table 29. Yield, m. p. and analysis of 2,3-di- and 2,3,5-trisubstituted-1,4-naphthoquinone.

Compd.	Yield %	m. p. °C	N %		Compd.	Yield %	m. p. °C	N %	
			Calcd.	Found				Calcd.	Found
(72)	77.8	160—1	—	—	(73)	91.1	216—8	—	—
(74)	45.5	>250	10.60	10.28	(75)	92.1	200—3	5.52	5.36

Table 30. Preparation of monoazo dye from 1,4-naphthoquinone.

Dye	Reagent mol	Solvent cc	React. Temp. °C	React. Time hr	Yield %	m. p. °C	N %	
							Calcd.	Found
(76)	(71) 0.02, PH 0.03	MeOH 50 + H ₂ O 48	room	3	96.2	236	10.60	10.49
(77)	(72) 0.02, PH 0.03	MeOH 55 + H ₂ O 48	"	3	70.9	193—4	13.59	13.36
(78)	(73) 0.02, PH 0.03	MeOH 65	"	3	68.3	211	9.38	9.21
(79)	(74) 0.02, PH 0.03	MeOH 70 + H ₂ O 48	"	3	21.3	271—2	15.82	15.58
(80)	(75) 0.02, PH 0.03	MeOH 55 + H ₂ O 40	"	3	96.2	118—9	12.20	11.99
(81)	(71) 0.005, NPH 0.005	EtOH 30	80	4	98.4	220—4	15.82	15.67
(82)	(72) 0.005, NPH 0.005	EtOH 30	"	4	72.5	234—5	17.54	17.23
(83)	(73) 0.005, NPH 0.005	EtOH 25	"	4	85.4	268	14.41	14.16
(84)	(74) 0.005, NPH 0.005	EtOH 30	"	4	50.2	260	18.92	18.71
(85)	(75) 0.005, NPH 0.005	EtOH 20	"	4	43.1	230	16.15	16.19

PH = Phenylhydrazine, NPH = 2·4-Dinitrophenylhydrazine.

Dye (81)—(85) were carried out by the use of two drops of conc. H₂SO₄ as a catalyst.

Table 31. Absorption maximum of monoazo dye from 1,4-naphthoquinone.

Dye	λ_{max}	$m\mu$	$\epsilon_{max} \times 10^{-4}$	Dye	λ_{max}	$m\mu$	$\epsilon_{max} \times 10^{-4}$
(76)	437		2.51	(81)	456		2.45
(77)	434		3.35	(82)	442		2.67
(78)	451		3.10	(83)	444		3.15
(79)	440		1.74	(84)	450		3.24
(80)	448		1.84	(85)	450		2.45

Concentration in absorption spectrometry = 5×10^{-4} mol/l in 95 % ethanol for (76)–(80), 10^{-5} mol/l in 95 % ethanol for (81)–(85).

Table 32. Results of dyeing with monoazo dye from 1,4-naphthoquinone.

	Dye	Colour Shade	Dye-ability	Bright-ness	Fastness		
					Light	Washing	Rubbing
On Acetate	(76)	Yellow Orange	4	4	<1	1	3–4
	(77)	Reddish Yellow	3–4	3	<1	1	3–4
	(78)	Reddish Yellow	3–4	4	<1	1	4–5
	(79)	Yellow Brown	3–4	3	<1	2	5
	(80)	Light Brown	3–4	4	<1	1–2	4–5
	(81)	Light Brown	3–4	3	1–2	3	3–4
	(82)	Yellow Orange	3	3	1	1–2	3
	(83)	Pale Reddish Orange	2	3	1	2	4
	(84)	Reddish Yellow	3	3	1	3	5
	(85)	Reddish Orange	3	3	1	2	4
On Vinylon	(76)	Reddish Yellow	3–4	4	3	2	4
	(77)	Reddish Yellow	3–4	4	<1	1	3–4
	(78)	Yellow Orange	4	4	4	1	4–5
	(79)	Yellow Brown	3–4	3	3	2	5
	(80)	Yellowish Orange	3	4	2	1–2	4–5
	(81)	Pale Brown	3	3	3–4	3–4	4
	(82)	Reddish Yellow	3	4	1	2	4–5
	(83)	Pale Reddish Orange	2	3	3	2–3	4–5
	(84)	Reddish Yellow	3	4	3	2–3	5
	(85)	Reddish Orange	3	3	2	2	4
On 6 Nylon	(76)	Yellowish Orange	4	4	<1	2	4
	(77)	Reddish Yellow	4	4	<1	1	5
	(78)	Light Yellow Orange	4	4	3	2	5
	(79)	Light Brown	3–4	3	1	2	5
	(80)	Dark Orange	4	4	1	1–2	5
	(81)	Brown	3–4	3	1	4	3
	(82)	Yellowish Orange	4	4	1	2–3	5
	(83)	Red	5	5	1	2–3	5
	(84)	Light Brown	4	4	2	3	4–5
	(85)	Deep Red	4	4	1	2–3	4

Dye = 2 % on the weight of fiber, Liquor ratio = 20 : 1.

Addendum

Dyeings from the Residual Liquor: In order to estimate the dyeability of vat dyes roughly, dyeing from the residual liquor was carried out under the same dyeing conditions as the original ones. In this case, it is true that the more faint the tinctorial degree of the dyeings from the residual liquor compared with that of the original dyeings, the better is the dyeability.

Dyeability and Brightness: For disperse dyes, 2% dyeings with Diacelliton Fast Orange GIF (in Table 24, 26 and 32) or Celiton Scarlet B (in Table 28) on acetate was selected as the standard, and its colour depth and brightness were defined as 4. The rating of dyeability and brightness were estimated at 5, 4, 3, 2 and 1 according to the colour depth and brightness of the sample, comparing with that of the standard.

Light fastness was determined by a progression comparing with *Gakushin* blue scale, using Toyo Rika Co. Fade-O-tester model FA-1.

Washing and Rubbing fastness were determined by the method of JIS K-4002.

Absorption and Reflection spector were measured with a Hitachi Spectrophotometer model EPU-2 at room temperature.

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