Mosby and Silva:

756. Naphthaquinone Chemistry. Part III.¹ New Derivatives of 1,2- and 1,4-Naphthaquinone.

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Various substituted naphthaquinones were prepared, often by nucleophilic displacement reactions on chloro- or sulpho-quinones. The convenient preparation of three quinone diazo-oxides is described.

IN Parts I and II¹ the preparation was described of the quinones either (II) or (III), depending upon the nature of R' in the quinones (Ia) and (Ib). The reaction of either quinone (Ia) or (IVa) with 2-aminopyridine yields exclusively (II), whilst (Ib) gives exclusively (III).



At room temperature, sodium 1,2-naphthaquinone-4-sulphonate (IVb) reacts with 2-aminopyridine in water to give (V), as reported by Carrara and Bonacci² [who, however, give the melting point as 225— 228° (decomp.)]. If, however, the reaction mixture is boiled, product (II) is produced; this is the most convenient, although not the most efficient method of preparing it. Also, it was found that potassium 1,4-naphthaquinone-2-sulphonate yielded the isomeric compound (VI). In this instance, however, cyclization to (III) could not be induced. While quinone (IVb) reacted with 2-aminopyrazine to give a mixture of the cyclic and open homologues of (II) and (V), it did not react with 2-aminopyrimidine under these conditions, and the *para*-isomer (Ic) failed to react with either 2-aminopyrazine or 2-aminopyrimidine. Both quinones (Ic) and (IVb) reacted with 3-aminopyridine, and (IVb) yielded a normal product with 4-aminopyridine, but (Ic) gave a dark blue, high-melting insoluble product which could not be purified for analysis. Both

¹ Part II, Mosby, J. Org. Chem., 1961, 26, 1316.

² Carrara and Bonacci, Chimica e Industria (Milan), 1944, 26, 75.

salts reacted with benzhydrazide, and (IVb) (but not Ic) gave a product with 1,1-dimethylhydrazine, but both were decomposed by treatment with hydrazine. The products of these reactions of (Ic) and (IVb) with various nucleophiles in aqueous solution are listed in Tables 1 and 2.

Various new naphthaquinones are listed in Table 3.

Fries and Ochwat³ reported the reaction of 2,3-dichloronaphthaquinone with sodium acetate in ethanol to yield 2-acetoxy-3-chloronaphthaquinone. Fieser 4 and Brown used this same method to prepare 2-alkoxy-3-chloronaphthaquinones, and we have confirmed that the resulting product is indeed 2-chloro-3-ethoxynaphthaquinone, not the acetoxyderivative. The methoxy-homologue was obtained similarly. Acetylation of 2-chloro-3-hydroxynaphthaquinone afforded the 2-acetoxy-compound.

Oxidation of perchloronaphthalene with fuming nitric acid in a sealed tube was reported ⁵ to yield hexachloronaphthaquinone. However simply refluxing the mixture afforded a 70% yield of the quinone. Hexachloronaphthaquinone and 2,3-dichloronaphthaquinone were used to prepare the series of amino- and azido-naphthaquinones in Tables 3 and 4.



Treatment of 2,3-dichloro-5-nitronaphthaquinone⁶ with ammonia gave a mixture of amines (compounds Nos. 29 and 30, Table 3) with two distinct crystal types. These were separated by hand, and acetylated. It is not clear which product corresponds with which structure, hence the ambiguous entries in the Table.

Oxidation of the known 2,3-diethoxycarbonyl-1,4-dihydroxynaphthalene⁷ with lead

			-		-						
		Vield (9/)			Fo	und		Calculated			
Cpd	. 4-Substituent	pure	М. р.	c	Н	N	6	c	н	N	<u> </u>
1	2-Pyridylamino-	41	$236 \cdot 5 - 237 \cdot 0^{\circ}$	71.9	4.00	11.2	12.6	72.0	4.00	11.2	12.8
2	3-Pyridylamino-	36	242 - 244	71.9	4.01	11.2	12.8	,,	,,	,,	,,
3	4-Pyridylamino-	32	231 - 232	71.9	4.04	11.1	12.8	,,	,,	,,	,,
4	4-(1-Methylpyridinium)- amino benzene sulphonate	42	218219	62·3	4 ∙29	6.77	18.7	62·6	4 ∙26	6.64	18.9
5	$N:C < (CH:CH)_{2} > NMe$	14	278 - 279	72.0	4.90	9.85	$12 \cdot 1$	72.7	4.55	10.6	12.1
6	2-Pyrazinylamino-	20	$254 \cdot 0 - 255 \cdot 5$	67.1	3.60	16.7	12.6	67.0	3.59	16.7	12.8
7	NH•NH•Bz	41	280 - 281	69.7	4 ·44	9.56	16.4	69.9	4.11	9.59	16.4
8	NH•NMe,	21	138.0 - 138.5	66.5	5.62	12.9	14 ·8	66.7	5.55	12.9	14.8
9	4-Azido	25	d. 126	60.2	2.68	21.0	16.1	60· 3	2.51	$21 \cdot 1$	16.1

TABLE 1. 4-Substituted 1,2-naphthaquinones.

¹ Crystallized from dichlorobenzene or nitromethane. Carrara and Bonacci (ref. 2) give m. p. 225-228 (decomp.). ² Crystallized from glycol diacetate. ³ Crystallized from glycol diacetate. ⁴ Obtained by quaternizing (3) with methyl benzenesulphonate. Crystallized from methanol. ⁵ Prepared from (4) by treatment with aqueous sodium hydroxide. Crystallized from nitromethane. ⁶ Crude reaction product was extracted with warm pyridine, diluted with water, and filtered. The filtrate was acidified with acetic acid and the resulting precipitate was crystallized from acetic acid. 7 Crystallized from acetic acid. 8 Crystallized from nitromethane. 9 Chromatographed in ethyl acetate solution upon acid washed alumina. Compound is photosensitive.

- ⁴ Fieser and Brown, J. Amer. Chem. Soc., 1949, 71, 3609.
- Schvemberger and Gordon, J. Gen. Chem., 1932, 2, 921.
- ⁶ Fries, Pense, and Peeters, Ber., 1928, 61, 1395; Ger. Pat. 468,507; Friedländer, 1931, 16, 520.
 ⁷ Schwerin, Ber., 1894, 27, 104; Homeyer and Wallingford, J. Amer. Chem. Soc., 1942, 64, 798.

³ Fries and Ochwat, Ber., 1923, 56, 1291.

tetra-acetate readily gave 2,3-diethoxycarbonylnaphthaquinone. Treatment of this ester with ammonia afforded the cyclic imide (compound 28, Table 3). Condensation of diethyl phthalate with succinonitrile produced, after oxidation, 2,3-dicyanonaphthaquinone (compound 26, Table 3). Attempts to obtain this nitrile by displacement reactions of various metal cyanides upon dichloronaphthaquinone were not successful.

TABLE 2.

N-Substituted 2-amino-1,4-naphthaquinones.

Yield (%)	Found						Calculated				
pure	М. р.	c	н	N	6	c	Н	N	0		
20	$200.5 - 201.5^{\circ}$	71.6	4.24	10.8	12.5	72.0	4 ·00	11.2	12.8		
29	247 (Inst.)	72.0	3.99	11.2	12.9	,,	,,	,,	,,		
27	228—229 d.	69.7	4.33	9.54	16.3	69.7	4.44	9.56	16.4		
rom o-dichl	orobenzene. 11	Crysta	allized	from	glycol	diaceta	te 12	Crysta	allized		
	Yield (%) pure 20 29 27 from <i>o</i> -dichl	Yield (%) pure M. p. 20 200.5-201.5° 29 247 (Inst.) 27 228-229 d. From o-dichlorobenzene. ¹¹	Yield (%) $pure$ M. p. C 20 $200 \cdot 5$ — $201 \cdot 5^{\circ}$ $71 \cdot 6$ 29 247 (Inst.) $72 \cdot 0$ 27 228 — $229 d$. $69 \cdot 7$ From <i>e</i> -dichlorobenzene. ¹¹ Crystz	Yield (%) pure Fo 20 $200.5-201.5^{\circ}$ 71.6 4.24 29 247 (Inst.) 72.0 3.99 27 $228-229$ 69.7 4.33 rom <i>e</i> -dichlorobenzene. ¹¹ Crystallized	Yield (%) Found pure M. p. C H N 20 $200 \cdot 5$ — $201 \cdot 5^{\circ}$ $71 \cdot 6$ $4 \cdot 24$ $10 \cdot 8$ 29 247 (Inst.) $72 \cdot 0$ $3 \cdot 99$ $11 \cdot 2$ 27 228 — 229 $d.$ $69 \cdot 7$ $4 \cdot 33$ $9 \cdot 54$ rom o-dichlorobenzene. ¹¹ Crystallized from 112 112 112	Yield (%) Found pure M. p. C H N O 20 200.5 — 201.5° 71.6 4.24 10.8 12.5 29 247 (Inst.) 72.0 3.99 11.2 12.9 27 228 — 229 d. 69.7 4.33 9.54 16.3 rom e-dichlorobenzene. ¹¹ Crystallized from glycol 10.23 10.23 10.23	Found Yield (%) Found pure M. p. C H N O C 20 200.5 — 201.5° 71.6 4.24 10.8 12.5 72.0 29 247 (Inst.) 72.0 3.99 11.2 12.9 $$ 27 228 — 229 $6.9.7$ 4.33 9.54 16.3 69.7 row odichlorobenzene. ¹¹ Crystallized from glycol diaceta	Yield (%) Found Calcul pure M. p. C H N O C H 20 200.5-201.5° 71.6 4.24 10.8 12.5 72.0 4.00 29 247 (Inst.) 72.0 3.99 11.2 12.9 , , , 27 228-229 d. 69.7 4.33 9.54 16.3 69.7 4.44 rom e-dichlorobenzene. ¹¹ Crystallized from glycol diacetate ¹² 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 12 13 12 12 13 12 12 12 12 12 12 14 14 14 14 14 16 <t< td=""><td>Found Calculated Pure M. p. C H N O C H N 20 200.5—201.5° 71.6 4.24 10.8 12.5 72.0 4.00 11.2 29 247 (Inst.) 72.0 3.99 11.2 12.9 , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , ,</td></t<>	Found Calculated Pure M. p. C H N O C H N 20 200.5 — 201.5° 71.6 4.24 10.8 12.5 72.0 4.00 11.2 29 247 (Inst.) 72.0 3.99 11.2 12.9 , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , , ,		

TABLE 3.

Di- and tri-substituted naphthaquinones.

	Substit	uent at position	1	Yield		Found				Calc.			
Cpd	. 2	3	5	pure	M. p.	\tilde{c}	н	N	6	c	н	N	ò
13	ОМе	Cl	н	89	148—149°	59.2	$2 \cdot 90$	15.8	21.7	59.3	3.14	15.9	21.6
14	OAc	CI	н	54	$142 \cdot 5 - 143 \cdot 5$	57.5	2.41	14.0	$25 \cdot 2$	57.5	2.79	$14 \cdot 2$	25.5
15	ОМе	NH_2	н	50	$142 \cdot 7 - 143 \cdot 2$	64.7	4.47	6.81	$23 \cdot 9$	65 .0	4.44	6.91	23.7
16	OMe	N ₃	н	17	93—94 d.	58.7	3.07	18.8	19.0	57.7	3.06	18.4	21.0
17	NAc ₂	Cl	н	40	160-161	57.3	3.56	4.71	12.4 (Cl)	57.6	3.43	4.80	12.2 (Cl)
18	NH∙Āc	OCH ₃	н	65	183-184	63.7	4.59	5.77		63.7	4.50	5.72	'
19	NH•Ac	N ₃	H	55	d. ~200	$56 \cdot 2$	2.92	21.8	18.8	56.3	3.11	$21 \cdot 9$	18.8
20	NAc ₂	N ₃	н	69	141—142 d.	56.3	3.42	18.7	21.6	56.4	3.32	18.8	21.5
21	NHAc	NHAc	H	77	248·5-251·0 d.	61.7	4.24	10.2	$23 \cdot 6$	61.8	4.40	10.3	23.5
22	NH•NHBz	NHAc	н	40	$209 \cdot 5 - 210 \cdot 5$	64·9	$4 \cdot 20$	$12 \cdot 2$	18.3	65.3	4.30	12.0	18.3
23	NH•NH•Bz	NAc ₂	н	16	195—196 d.	64.5	4.25	10.7		64.5	4.35	10.8	
24	OH	N ₃	н	57	121° d. (Inst.)	$55 \cdot 8$	2.52	19.4	$22 \cdot 3$	$55 \cdot 8$	$2 \cdot 32$	19.5	$22 \cdot 3$
25	OH	CN	н	12	190—193 d.	66.8	3.07		24.5	66.4	2.51		24.5
26	CN	CN	н	4 ∙8	$272 \cdot 0 - 273 \cdot 5$	$69 \cdot 2$	1.81	13.9	15.3	69.3	1.92	13.5	15.4
27	CO ₂ Et	CO ₂ Et	н	85	$53 \cdot 7 - 54 \cdot 7$	63.6	4.52		31.7	63.6	4.64		31.7
28	2 + 3 = CO	NHCO	н	21	$131 \cdot 2 - 132$	63.5	2.45	6.11	28.0	63.5	$2 \cdot 20$	6.17	28.2
29	Cl (or NH ₂)	NH ₂ (or Cl)	NO ₂	10	$266 \cdot 5 - 267 \cdot 2$	47.5	1.92	$11 \cdot 2$	14·2 (Cl)	47.5	1.98	11.1	14·0 (Cl)
30	$\rm NH_2$ (or Cl)	Cl (or NH_2)	NO ₂	14	244.0 - 245.5	47.4	2.02	11.1	14·2 (Cl)	,,	,,	,,	,,
31	Cl (or NHAc)	NHAc (or Cl)	NO_2	9 0	$234 \cdot 5 - 235 \cdot 5$	49.2	$2 \cdot 17$	10.1	12·3 (Cl)	48.9	2.38	9.53	12.0 (Cl)
32	NHAc (or Cl)	Cl (or NHAc)	NO_2	82	$231 \cdot 5 - 232 \cdot 5$	49 ·0	2.75	9.85	12.2	,,	,,	,,	,,
33	NHAc	NHAc	NO_2	34	239240 d.	52.8	3.36	13.0		53.0	3.47	$13 \cdot 2$	
34	N_3	N ₃	NO_2	64	121—122 d.	$42 \cdot 1$	1.03	34.1	$22 \cdot 2$	42.1	1.02	$34 \cdot 4$	$22 \cdot 4$
35	N ₃	N ₃	NH_2		134 d.	46.6	1.63	37.6	12.8	47·1	1.96	38.4	12.6
36	NH ₂	NH ₂	NH_2	11	∼260 d.	58.9	4 ·09	20.0		59.1	4.43	20.7	
37	N ₃	N ₃	NHAc	74	130—131 d.	48.7	2.30	32.5		48.5	2.38	33 ·0	

³⁰ NH₂ NH₂ NH₂ NH₂ 11 \sim 200 d. 589 4.09 20.0 — 59.1 4.43 20.7 — 37 N₃ NH₄ 71 130—131 d. 48.7 2.30 32.5 — 48.5 2.38 33.0 — ¹³ Prepared from (Ia) and sodium acetate in methanol. ¹⁴ Obtained from 2-chloro-3-hydroxynaphthaquinone, acetic anhydride, and pyridine. Crystallized from ethyl acetate, or chromatographed in ethyl acetate on acid-washed alumina. ¹⁵ Obtained by vatting (16) followed by air-oxidation. Chromatographed in benzene on acid-washed alumina, developing with 1: 4 ethyl acetate-benzene. ¹⁶ Prepared from (13) and sodium azide in dimethylformamide. Some 2,3-bisazidonaphthoquinone is also formed. Crystallized from ethyl acetate-cyclohexane. ²⁷ Obtained by heating the amine with excess of acetic anhydride and a drop of sulphuric acid. Recrystallized from methanol. ¹⁸ From the reaction of sodium methoxide on 2-acetamido-3-chloronaphthaquinone. Crystallized from ethyl acetate, ²⁰ From (17) and sodium azide in dimethylformamide. Crystallized from ethyl acetate, ²⁰ Preom (17) and sodium azide in the same way as (22), but from (17). Crystallized from nitromethane. ²⁴ Prepared from (XI) by reaction with sodium azide in dimethylformamide. Crystallized from thyl acetate. ²⁴ Synthesized from ethyl acetate. ²⁴ Synthesized from ethyl acetate. ²⁴ Synthesized from ethyl acetate. ²⁴ Obtained from (XI) by reaction with sodium azide in dimethylformamide. Crystallized from ethyl acetate. ²⁴ Synthesized by the Dieckmann condensation of ethyl phthalate with succinonitrile and oxidation of the quinol with ferric chloride. ²⁴ Obtained by oxidation of the quinol⁷ with lead tetra-acetate in toluene. Crystallized from cyclohexane. ²⁵ From the tratement of (27) with ammonium hydroxide. Chromatographed in ethyl acetate. ²⁶ Synthesized the mixture from nitromethane and separated the two crystal types by hand. ⁴¹ Obtained by acetylating (29). ³⁵ The mixture of (29) and (30) was acetylated and the mixed acetamine-choro-choronaphthaquinone sucenda lumina. ⁴⁵ Obtained by acetyl

TABLE 4.

5,6,7,8-Tetrachloro-1,4-naphthaquinones; products from hexachloronaphthaquinone.

Subst. at position		Yield		Found					Calc.			
Cpd.	2	3	pure	М. р.	ć	H (Cl)	N (Cl)	O`	ć	H (Cl)	N (Cl)	0
38	OEt	Cl	50	156160° d.	38.1	1.56	48.1 (Cl)	12.6	38.4	1.34	47.4 (Cl)	12.8
39	NH,	Cl	80	227.0 - 228.0	35.0	0.76	4.14	9.56	34.7	0.58	4.06	9.28
40	NHĂc	C1	63	235·0-236·2 d.	36.6	0.98	3.68	12.7	$37 \cdot 2$	1.06	3.65	$12 \cdot 4$
41	NAc.	CI	59	187.5 - 189.0	38.9	1.50	3.37	15.0	39.2	1.40	3.26	14.9
42	NH.	NH.	46	264·0 (inst.)	36.8	0.87	8.56	43·8 (Cl)	36.8	1.23	8.59	43·6 (Cl
43	NHÃc	NH,	67	271.0-272.0	38.9	1.94	7.41	37.9 (Cl)	$39 \cdot 2$	1.66	7.61	38·6 (Cl)
44	NHAc	NHÃc	51	d. ~ 290	41 ·0	2.00	6.84	15.8	41 ·0	1.95	6.85	15.6
45	N ₃	N_3	97	$134 \cdot 0 - 136 \cdot 0$	31.5	37·2 (Cl)	$22 \cdot 3$	8.69	31.7	37·5 (Cl)	$22 \cdot 2$	8.46

⁴⁵ N₃ N₃ 97 134⁴0–136⁴⁰ 31⁴⁵ 31⁴⁵ (CI) 22⁴³ 8⁴⁰ 31⁴⁷ 134⁵ (CI) 22⁴² 8⁴⁰ ³⁸ Perchloronaphthaquinone was refluxed with sodium acetate in ethanol. The photosensitive product was crystallized from methylcyclohexane and chromatographed in ethyl acetate solution upon acid-washed alumina. ³⁹ A slurry of perchloronaphthaquinone in boiling ethanol was treated under reflux with ammonia gas. The product was crystallized from chlorobenzene or from nitromethane. ⁴⁰ Treated, at room temperature, a slurry of (39) in a slight excess of acetic anhydride with a drop of sulphuric acid. Crystallized twice from nitromethane. ⁴¹ Obtained as was (40), but the reaction mixture was boiled. Crystallized from either acetic acid or acetic anhydride. ⁴² Obtained by vatting (45), followed by air-oxidation. Crystallized from nitromethane. ⁴³ Treated a solution of (40) in a small volume of nitrobenzene at 100° with ammonia gas. ⁴⁴ Treated (43) with acetic anhydride and a drop of sulphuric acid in nitromethane at the b. p. Recrystallized from nitromethane. ⁴⁵ Obtained from perchloronaphthaquinone and sodium azide in dimethylformamide.

Oxidation of 1,2,3,4,5,6-hexachloro-7-nitronaphthalene (VII) with nitric acid gave the quinone (VIII).



By treating compound (IX) with nitric acid, Kehrmann⁸ obtained a product to which he assigned structure (X). However, Beilstein⁹ suggests structure (XI) as a possible alternative for this substance. We have found that the diazo-oxide (XI) is readily obtained, in nearly quantitative yield, by treating 2-amino-3-chloro-1,4-naphthaquinone with nitrosylsulphuric acid (or sodium nitrite in sulphuric acid). Curiously, a similar treatment of 4-amino-3-bromo-1,2-naphthaquinone gave none of the isomeric quinone diazooxide (XII), and the amine was recovered. However, the perchloro-compound (XIII) was obtained from 2-amino-3,5,6,7,8-pentachloro-1,4-naphthaquinone, and (XIV), previously obtained ¹⁰ by other methods, was easily prepared from 2,5-diamino-3,6-dichlorobenzo-



quinone. When compound (XI) was allowed to react with sodium azide and with sodium cyanide, the corresponding 3-substituted 2-hydroxynaphthaquinones (compounds 24 and 25, Table 3) were obtained.

EXPERIMENTAL

Melting points were taken in Pyrex capillaries using a Hershberg apparatus and Anschütz thermometers.

2,3,5,6-Tetrachloro-7-nitro-1,4-naphthaquinone (VIII).—Hexachloro-2-nitronaphthalene (from the Fundamental Research Co., Berkeley, California; 5.00 g.) and fuming (90%) nitric acid (35 ml.) were stirred and boiled under reflux for 10 min. The resulting solution was cooled and

- ⁸ Kehrmann, Ber., 1888, 21, 1781.
- ⁹ Beilstein, "Handbuch der Organischen Chemie," 4er. Aufl., Springer, Berlin, 1933, Vol. 16, p. 541.
- ¹⁰ Henle, Annalen, 1906, **350**, 335.

diluted with ice and filtered, giving a solid (3.83 g., 93%), m. p. $187.5 - 188.5^{\circ}$, yellow needles (from methylcyclohexane), m. p. $188.0 - 188.9^{\circ}$, overall yield (84%) (Found: C, 35.2; H, 0.4; Cl, 41.6; N, 4.25; O, 18.7. Calc. for C_{10} HCl₄NO₄: C, 35.2; H, 0.3; Cl, 41.6; N, 4.11; O, 18.8%).

1,4-Naphthaquinone 2,3-Diazo-oxide (XI).--2.08 g. of 2-amino-3-chloronaphthaquinone in 20 ml. of 1M-nitrosylsulphuric acid (in sulphuric acid) was stirred at 45° for $\frac{1}{4}$ hr. and then was diluted with water. The solid was filtered off, washed well with water and with methanol, and dried, giving the diazo-oxide in quantitative yield as a bright yellow powder. The compound has no definite m. p., and decomposes vigorously but irregularly when put into the bath above 100°; it may, however, be heated slowly from below 100 to 165° without melting. Attempts to recrystallize the diazo-oxide gave a less pure product (Found C, 60.0; H, 2.2; N, 13.9; O, 24.0. Calc. for $C_{10}H_4N_2O_3$: C, 60.0; H, 2.0; N, 14.0; O, 24.0%.)

Perchloro-1,4-naphthaquinone 2,3-diazo-oxide (XIII). To 15.0 ml. of nitrosylsulphuric acid (1M in sulphuric acid) was added 1.00 g. of 2-aminoperchloronaphthaquinone. The deep red solution was stirred at 30-35° for 5 min. then poured on ice and filtered. The pale orange solid was washed well with water and then with methanol and dried in air, affording a quantitative yield. When put into the m. p. bath below 108°, it was unmelted below 150°, but if put in at 108.5° or higher, it decomposed vigorously. The compound could not be recrystallized satisfactorily (Found: C, 35.2; Cl, 42.0; N, 7.9. Calc. for $C_{10}Cl_4N_2O_3$: C, 35.5; Cl, 42.0; N, 8.3%).

1,4-Bisdiazocyclohexanetetraone (XIV).—A solution of 2.07 g. of 2,5-diamino-3,6-dichlorobenzoquinone in 50 ml. of nitrosylsulphuric acid (1M-solution in sulphuric acid) was warmed to 50° for 1 hr., then was cooled an diluted with ice until turbid and filtered. The solid was washed well with water and dried, giving 1.85 g. (96.4% yield). It explodes at about 85°, and the infrared spectrum shows strong bands at 4.65 μ (diazo-group) and 6.10 μ (carbonyl group).

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