Quinones. Part IV. The Elimination of Substituents from* 1 : 4-*Naphthaquinones.*

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The groups halogen, NHPh, SR, SO_2R, SO_3H, and (in some cases) OH can be removed from positions 2 and 3 of 1 : 4-naphthaquinones by reduction with stannous chloride–hydrochloric acid–acetic acid and subsequent reoxidation with chromic acid. Halogeno-1 : 4-naphthaquinones can be dehalogenated with hydriodic acid.

Many well-known procedures exist for the preparation of substituted 1 : 4-naphthaquinones but very little has been recorded on the elimination of substituents. Methods for achieving this would be of value in synthetic and degradative work. We previously observed that certain groups can be eliminated from *peri*-hydroxy-1 : 4-naphthaquinones by reduction with stannous chloride (*J.*, 1952, 2759) and we now find that more stringent conditions, *viz.*, refluxing with stannous chloride in hydrochloric acid–acetic acid, provide a general method for the elimination of various substituents (in positions 2 and 3) from 1 : 4-naphthaquinones. The unsubstituted quinone can be readily isolated by direct oxidation of the dilute reaction liquor. In this way halogen, NHPh, SR, SO_2R, and SO_3H groups can be removed, and in some cases OH groups, though with difficulty; but the reaction failed with 3-hydroxy-2-methyl- and 6-bromo-2-hydroxy-1 : 4-naphthaquinone. Some examples are tabulated below.

Three previous instances of this type of reaction have been noted : 1 : 4-naphthaquinol was obtained by Zincke (*Ber.*, 1879, **12**, 1641) by reduction of 2-anilino-1 : 4-naphthaquinone with zinc and alcoholic hydrochloric acid and by Graebe (*Annalen*, 1869, **149**, 6) by treatment of 2 : 3-dichloro-1 : 4-naphthaquinone with tin and hydrochloric acid, and Kehrmann (*Ber.*, 1895, **28**, 345) isolated 1 : 2 : 4-trihydroxynaphthalene from the reduction of 2-hydroxy-3-iodo-1 : 4-naphthaquinone with alcoholic acid stannous chloride.

In the case of the *peri*-hydroxy-1 : 4-naphthaquinones it was postulated that the quinol, formed initially by reduction, tautomerised to a diketone from which the substituent was removed by an acid-catalysed elimination. The same mechanism would account for all the eliminations observed in the present work but it is only necessarily called for in the elimination of anilino-, sulphone, and hydroxyl groups. In the other cases the reaction is probably a direct reduction (or hydrolysis) of an *o*-substituted naphthol (or its keto-isomer) for which parallels exist. *o*-Halogenonaphthols have been reduced by various reagents including stannous chloride (Franzen and Stäuble, *J. pr. Chem.*, 1921,

* Part III, *J.*, 1953, 2910.

103, 382; Fries, *Annalen*, 1930, **484**, 293) and naphtholsulphonic acid can be desulphonated by reduction with sodium amalgam under acid conditions (Friedländer and Lucht, *Ber.*, 1893, **26**, 3031) and by hydrolysis with hydrochloric acid (Nietzki, *Ber.*, 1882, **15**, 305; Leman, *Ann. Chim.*, 1938, **9**, 372). We found that α-naphthol was readily obtained from its 4-sulphonic acid by reduction with stannous chloride. The reduction of hydroxynaphthyl sulphides appears to be new although β-keto-sulphides (which are

Elimination of substituents from 1 : 4-*naphthaquinones.*

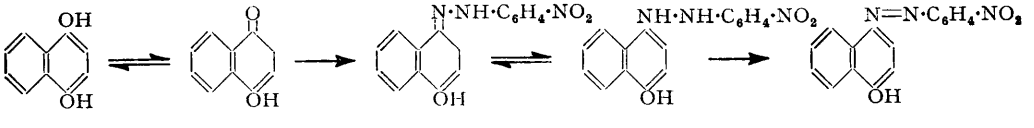
(NQ = 1 : 4-Naphthaquinone.)

Derivative	Product	Yield, %
2-Chloro- *	NQ	66
2-Bromo- *	NQ	52
2 : 3-Dichloro- *	NQ	59
2 : 3-Dibromo-	NQ	50
3-Chloro-2-methyl- *	2-Methyl-NQ	91
3-Chloro-2-ethyl- *	2-Ethyl-NQ	90
3-Bromo-2-ethyl-	2-Ethyl-NQ	90
2 : 6-Dibromo-5-hydroxy- *	5-Hydroxy-NQ	47
2 : 3 : 6-Tribromo-5-hydroxy- *	5-Hydroxy-NQ	43
2-Bromo-6-hydroxy-	6-Hydroxy-NQ	93
3 : 6-Dibromo-2-hydroxy-	6-Bromo-2-hydroxy-NQ	65
2-Hydroxy-	NQ	22
3-Chloro-2-hydroxy-	NQ	20
3-Hydroxy-5-methyl-	5-Methyl-NQ	20
2-Anilino-	NQ	40
2-Anilino-3-chloro-	NQ	32
2-Anilino-6-hydroxy-	6-Hydroxy-NQ	50
3-Anilino-6-chloro-	6-Chloro-NQ	58
2-*p*-Tolylthio-	NQ	70
6-Hydroxy-2(or 3)-*p*-tolylthio-	6-Hydroxy-NQ	83
2-Benzenesulphonyl-	NQ	45
2-Toluene-*p*-sulphonyl-	NQ	60
3-Carboxymethylthio-2-methyl-	2-Methyl-NQ	90
2-Sulphonic acid	NQ	47
2-Methyl-NQ-3-sulphonic acid	2-Methyl-NQ	90

* These compounds were also reduced with hydriodic acid, giving the same products.

analogous) have been reduced; *e.g.*, Wahl (*Ber.*, 1922, **55**, 2454) obtained toluene-ω-thiol by treatment of benzyl phenacyl sulphide with zinc and acetic acid. We found that toluene-*p*-thiol was evolved when 1-*p*-tolylthio-2-naphthol was reduced with stannous chloride although the reduction was much slower than that of 2-*p*-tolylthio-1 : 4-naphthaquinone. Sulphones are normally very stable under reducing conditions but several β-keto-sulphones have been reduced. Thus reduction of benzenesulphonylacetone with sodium amalgam gives benzenesulphinic acid and *iso*propyl alcohol, and with zinc and hydrochloric acid benzenethiol is obtained (Otto and Otto, *J. pr. Chem.*, 1887, **36**, 403). However, neither 1-toluene-*p*-sulphonyl-2-naphthol nor 2-toluene-*p*-sulphonylquinol was affected by treatment with stannous chloride. After vigorous reduction of 1 : 2-naphthaquinone, Japp and Klingemann (*J.*, 1893, **63**, 770) isolated some β-naphthol as well as 1 : 2-dihydroxynaphthalene, but Liebermann and Jacobsen (*Annalen*, 1882, **211**, 58) found, and we have confirmed, that stannous chloride reduction of 1 : 2-naphthaquinone yields 3 : 4 : 3′ : 4′-tetrahydroxy-1 : 1′-dinaphthyl. β-Naphthol was not detected. 1-Anilino-2-naphthol was recovered unchanged after similar treatment.

The tautomerisation of 1 : 4-naphthaquinols (lacking *peri*-hydroxyl groups) has never been observed in solution although it appears to occur in certain of the elimination reactions described above. In an attempt to detect such compounds three naphthaquinols were heated in boiling aqueous alcohol in the presence of *p*-nitrophenylhydrazine. However, bis-*p*-nitrophenylhydrazones were not obtained, the products being hydroxyazo-compounds arising from monoketo-structures probably *via* the following route :



The corresponding reactions of α- and β-naphthol with *p*-nitrophenylhydrazine gave small yields of unexpected products; β-naphthol and *p*-nitrophenylhydrazine yielded 2-*p*-nitrophenylazo-1-naphthol, and the corresponding reaction with α-naphthol gave a trace of the same azo-compound but the principal product, dark red needles, m. p. 292—293°, has not been identified. It is known that the reaction of naphthols with phenylhydrazines in the presence of hydrochloric acid gives rise to benzocarbazoles (Japp and Maitland, *J.*, 1903, **83**, 267) but the compound, m. p. 292—292°, is not the nitrobenzcarbazole which would be expected. These reactions are being examined further.

The first reagent employed for the reduction of halogenonaphthols was hydriodic acid (Franzen and Stäuble, *loc. cit.*). Reduction of halogenated 1 : 4-naphthaquinones in the same way eliminates the halogen atoms. This is a satisfactory method for the dehalogenation of 2-alkyl-3-halogeno-1 : 4-naphthaquinones but in other cases the yields are usually poor (*ca.* 20%) and the two-stage stannous chloride reduction and reoxidation is much superior. Some examples are included in the Table.

Experimental

Reduction by Stannous Chloride of Substituted 1 : 4-*Naphthaquinones.*—The following experiment is typical. A mixture of 2 : 3-dibromo-1 : 4-naphthaquinone (0·5 g.), stannous chloride (2 g.), concentrated hydrochloric acid (5 c.c.), and acetic acid (5 c.c.) was refluxed for 30 min., cooled, diluted with water (15 c.c.), and oxidised by addition of chromium trioxide (1 g.) in water (5 c.c.). After cooling in ice, the precipitate was collected. One crystallisation from light petroleum (b. p. 100—120°) gave yellow needles of 1 : 4-naphthaquinone, m. p. 125°. In the case of anilinonaphthaquinones the quinol was extracted from the diluted reaction mixture with ether, and the extract shaken immediately with chromium trioxide in water. Thiols formed by reduction were removed by boiling in an open vessel before oxidation of the quinol.

Miscellaneous Reductions by Stannous Chloride.—(*a*) A mixture of 1-naphthol-4-sulphonic acid (1 g.), stannous chloride (4 g.), concentrated hydrochloric acid (10 c.c.), and acetic acid (10 c.c.) was refluxed for 30 min., diluted with water, and extracted with ether. The extract was evaporated to dryness to yield plates, m. p. and mixed m. p. with α-naphthol, 96° (40%). (*b*) A mixture of 1-*p*-tolylthio-2-naphthol (0·25 g.), stannous chloride (1 g.), concentrated hydrochloric acid (2·5 c.c.), and acetic acid (5 c.c.) was refluxed for 90 min. The odour of toluene-*p*-thiol was soon apparent. The residue [from ether as in (*a*)] was extracted with boiling light petroleum (b. p. 50—60°), to give β-naphthol in leaflets, m. p. and mixed m. p. 122° (35 mg.), and starting material. (*c*) A mixture of 1-toluene-*p*-sulphonyl-2-naphthol (0·28 g.), stannous chloride (1·5 g.), concentrated hydrochloric acid (4 c.c.), and acetic acid (4 c.c.) was refluxed for 2 hr. Starting material (0·27 g.) separated on cooling. Ether-extraction of the diluted filtrate gave a sticky residue smelling faintly of toluene-*p*-thiol, but no β-naphthol was detected.

Reduction by Hydriodic Acid of Halogenated 1 : 4-*Naphthaquinones.*—The following experiment is typical. A mixture of 3-chloro-2-methyl-1 : 4-naphthaquinone (0·3 g.), hydriodic acid (3 c.c.; s.g. 1·7), and acetic acid (3 c.c.) was refluxed for 10 min., cooled, and diluted with water, and the precipitate collected. One crystallisation from light petroleum (b. p. 50—60°) afforded 2-methyl-1 : 4-naphthaquinone in yellow needles, m. p. 106° (66%). In these reductions the crude material was occasionally pink owing to formation of anthocyanidin (cf. Fieser and Fieser, *J. Amer. Chem. Soc.*, 1941, **63**, 1574; Thomson, *J.*, 1953, 1196) which was easily separated owing to its insolubility in light petroleum.

2-*Chloro*-1 : 4-*naphthaquinol.*—2-Chloro-1 : 4-naphthaquinone (0·6 g.) in ether (15 c.c.) was shaken with sodium dithionite (1 g.) in water (10 c.c.) until the colour no longer faded. The ethereal layer was then dried and evaporated *in vacuo*. The residual *quinol* separated from benzene as small crystals, m. p. 153° (decomp.) (Found : C, 61·7; H, 3·5. $C_{10}H_7O_2Cl$ requires C, 61·7; H, 3·6%). The *diacetate* formed needles, m. p. 137—138°, from alcohol (Found : C, 60·2; H, 4·1. $C_{14}H_{11}O_4Cl$ requires C, 60·3; H, 4·0%).

Reaction of Naphthaquinols with p-*Nitrophenylhydrazine.*—(*a*) Hot solutions of 2-chloronaphthaquinol (0·28 g.) in water (50 c.c.) containing concentrated hydrochloric acid (0·5 c.c.), and *p*-nitrophenylhydrazine (0·42 g.) in alcohol (10 c.c.) were mixed, refluxed under nitrogen for 1 hr., and filtered hot. The precipitate (0·13 g., m. p. 260—265°) separated from *o*-dichlorobenzene in dark red crystals, m. p. 274° (Found : C, 58·4; H, 2·9; N, 12·6. $C_{16}H_{10}O_3N_3Cl$

requires C, 58·6; H, 3·1; N, 12·8%). The 2(or 3)-*chloro*-4-p-*nitrophenylazo*-1-*naphthol* gave a blue colour in concentrated sulphuric acid and in aqueous methanolic sodium hydroxide. (*b*) 2-Chloronaphthaquinone (0·19 g.) and *p*-nitrophenylhydrazine (0·15 g.) were dissolved in warm alcohol (10 c.c.). After addition of 3 drops of concentrated hydrochloric acid the product separated rapidly. Crystallisation from *o*-dichlorobenzene yielded material identical with that obtained in (*a*). Hydroxyazo-compounds were similarly obtained from 1 : 4-naphthaquinol and 2-methyl-1 : 4-naphthaquinol. The product from the former (m. p. 280°) did not depress the m. p. of the compound, m. p. 274°, described above.

Reaction of Naphthols with p-*Nitrophenylhydrazine.*—(*a*) A mixture of β-naphthol (1 g.; " AnalaR "), *p*-nitrophenylhydrazine (1 g.), alcohol (25 c.c.), water (50 c.c.), and concentrated hydrochloric acid (1 c.c.) was refluxed for 12 hr. The orange-brown crystalline precipitate obtained (130 mg.; m. p. 225°) crystallised from toluene in light red needles with a green sheen, m. p. 240° (80 mg.) (Found : C, 65·8; H, 3·75. Calc. for $C_{16}H_{11}O_3N_3$: C, 65·5; H, 3·8%). Admixture with 2-*p*-nitrophenylazo-1-naphthol did not depress the m. p. The acetate formed brick-red micro-needles, m. p. 181—182° (Found : C, 64·3; H, 3·9. Calc. for $C_{18}H_{13}O_4N_3$: C, 64·5; H, 3·9%); mixed m. p. with 1-acetoxy-2-*p*-nitrophenylazonaphthalene, 181—182°. Under the same conditions β-naphthol did not react with phenylhydrazine or 2 : 4-dinitrophenylhydrazine. (*b*) The above reaction was carried out upon α-naphthol (1 g.; " AnalaR "). The product (0·18 g.; dark brown; m. p. *ca.* 240°) was chromatographed in *o*-dichlorobenzene on alumina (" Woelm " Acid). On elution with the same solvent a bluish-red band developed from which a *compound*, m. p. 292—293° (dark red needles with a green sheen, from toluene) (35 mg.), was isolated (Found : C, 63·2; H, 3·54; N, 19·1. $C_{12}H_8O_2N_3$ requires C, 63·7; H, 3·55; N, 18·6. $C_{12}H_9O_2N_3$ requires C, 63·4; H, 4·0; N, 18·5%). The compound gave a dark green colour to concentrated sulphuric acid but no colour was produced with alcoholic sodium hydroxide. A second darker zone on the column yielded the azo-dye obtained in (*a*) (17 mg.); the remaining minor bands were not examined.

6-*Nitro*-1 : 2-*benzocarbazole.*—A solution of 1-tetralone *p*-nitrophenylhydrazone (2 g.) in glacial acetic acid (20 c.c.) saturated with dry hydrogen chloride was heated on the steam-bath for 1 hr. Crystals of 3 : 4-*dihydro*-6-*nitro*-1 : 2-*benzocarbazole* (0·67 g.) separated and were collected after cooling. [Dilution of the mother-liquor afforded starting material (0·93 g.).] Recrystallisation from glacial acetic acid gave orange-brown needles, m. p. 277—278° (decomp.) (Found : C, 72·55; H, 4·6; N, 10·3. $C_{16}H_{12}O_2N_2$ requires C, 72·7; H, 4·6; N, 10·6%), which gave a blue colour in concentrated sulphuric acid. When the dihydrocarbazole (0·45 g.) and chloranil (0·45 g.) were refluxed in dry xylene (50 c.c.) for 4 hr., 6-*nitro*-1 : 2-*benzocarbazole* separated on cooling. After trituration with dilute aqueous sodium hydroxide it crystallised from *o*-dichlorobenzene in light orange-brown plates, m. p. 318—319° (90%) (Found : C, 73·2; H, 3·7; N, 10·4. $C_{16}H_{10}O_2N_2$ requires C, 73·25; H, 3·8; N, 10·7%), which gave a blue colour in concentrated sulphuric acid.

2-*Benzenesulphonyl*-1 : 4-*naphthaquinone.*—A solution of 1 : 4-naphthaquinone (1 g.) in warm methanol (30 c.c.) was added to sodium benzenesulphinate (1·5 g.) in water (10 c.c.) and methanol (20 c.c.) acidified with 2N-hydrochloric acid (10 c.c.). When the colour had faded and crystals of the quinol began to separate, a solution of ferric chloride (10 g.) in water (50 c.c.) containing hydrochloric acid (1 c.c.) was added. The precipitated *quinone* was collected after some hours and crystallised from aqueous acetic acid. It formed yellow plates, m. p. 192° (75%) (Found : C, 64·65; H, 3·2; S, 10·7. $C_{16}H_{10}O_4S$ requires C, 64·4; H, 3·4; S, 10·7%).

1-*Toluene*-p-*sulphonyl*-2-*naphthol.*—1-*p*-Tolylthio-2-naphthol (0·5 g.) in acetic anhydride (1 c.c.) containing a trace of concentrated sulphuric acid was boiled for 2—3 min., and the solution diluted with glacial acetic acid (20 c.c.). The solution was stirred at 50°, and potassium permanganate (0·5 g.) in water (20 c.c.) added slowly. After addition of a little sodium hydrogen sulphite to destroy the colour, the mixture was poured into ice-water. The precipitated sulphone acetate was boiled for 1 hr. in a mixture of alcohol (10 c.c.) and hydrochloric acid (10 c.c.; 2N) from which 1-*toluene*-p-*sulphonyl*-2-*naphthol* separated on cooling. It formed needles, m. p. 133° (from aqueous alcohol) (60%) (Found : C, 68·4; H, 4·5; S, 11·3. $C_{17}H_{14}O_3S$ requires C, 68·4; H, 4·7; S, 10·75%).

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