582. *Quinones. Part III.* Addition Reactions of* 1 : 4-*Naphthaquinones substituted in the* 6-*Position.*

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The addition of aniline, acetic anhydride, toluene-*p*-thiol, and bromine to 6-hydroxy-, 6-acetoxy-, 6-methyl-, 6-chloro-, and 6-acetamido-1 : 4-naphthaquinone has been studied and the majority of the products orientated. The substituent has a marked effect on the course of the reactions, resulting in the predominant formation of one isomer in all cases except the additions of toluene-*p*-thiol. The reactions with aniline and bromine readily gave single products and are of value for synthetic purposes. The direction of addition of aniline and acetic anhydride is in accord with the electronic character of the 6-substituent, but the latter exerts no control over the addition of toluene-*p*-thiol. The reactions with bromine were anomalous.

Addition reactions are a characteristic feature of the chemistry of quinones, and many derivatives can be conveniently obtained in this way, *e.g.*, hydroxyquinones are readily available *via* the addition of amines or acetic anhydride. However, these methods are of less value in unsymmetrical quinones where more than one product may result. This is the case with monobenzo-derivatives of 1 : 4-naphthaquinones and synthetic work in this field would be assisted if more information were available about the course of addition to such compounds. A study of addition reactions with 5-hydroxy- and 5-acetoxy-1 : 4-naphthaquinone revealed some unexpected results (Thomson, *J. Org. Chem.*, 1951, **16**, 1082) but very little is known concerning the addition reactions of 6-substituted 1 : 4-naphthaquinones. Fieser and Brown (*J. Amer. Chem. Soc.*, 1949, **71**, 3615) obtained two products by Thiele acetylation of 6-chloro-1 : 4-naphthaquinone whereas Kegel (*Annalen*, 1888, **247**, 187) by addition of aniline and *p*-toluidine to 6-benzoyl-1 : 4-naphthaquinone obtained only one amino-derivative in each case. It is evident from the latter work that the 6-substituent can have a pronounced effect on the reaction taking place in the quinone ring, and a study of some addition reactions of 6-hydroxy-, 6-acetoxy-, 6-methyl-, 6-chloro-, and 6-acetamido-1 : 4-naphthaquinone has now confirmed this.† The reagents used were aniline (a typical nucleophilic reagent), acetic anhydride (which gives an acid-catalysed electrophilic reaction) and toluene-*p*-thiol (this reagent appears to add to 5-hydroxy- and 5-acetoxy-1 : 4-naphthaquinone by a radical mechanism). The formation of bromoquinones by the addition of bromine and elimination of hydrogen bromide from the dibromides was also investigated. The results are set out in the Table. The products were isolated by conventional methods and mother-liquors, etc., were not exhaustively searched. Thus the isolation of only one isomer does not exclude the formation of another in small amount, but we were mainly concerned with the preparative value of these reactions. From this point of view the reactions with aniline and bromine are of value as single products were readily isolated in a pure state, whereas the reactions with acetic anhydride and toluene-*p*-thiol led to mixtures and separation was frequently tedious, involving appreciable loss.

The results bear out earlier suggestions put forward to account for the influence of benz-substituents in 1 : 4-naphthaquinones (Thomson, *loc. cit.*; Cooke and Segal, *Austral. J. Sci. Res.*, 1950, *A*, **3**, 628). In the addition reactions with aniline and acetic anhydride one isomer predominates, electron-repelling substituents at $C_{(6)}$ directing entering groups to $C_{(2)}$, whereas in 6-chloro-1 : 4-naphthaquinone reaction is mainly at $C_{(3)}$. We consider therefore that Kegel's compounds (*loc. cit.*) are probably 3-arylamino-6-benzoyl-1 : 4-naphthaquinones. In contrast the reactions with toluene-*p*-thiol gave roughly equal amounts of the two isomers in all cases, which again suggests a radical mechanism as substituents at $C_{(6)}$ have little effect on the course of the reaction. The

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† Since this paper was submitted we have seen a publication by Cooke, Dowd, and Segal (*Austral. J. Chem.*, 1953, **6**, 38) who show that addition of dimethylamine to 6-methyl-1 : 4-naphthaquinone yields 2-dimethylamino-6-methyl-1 : 4-naphthaquinone and possibily a small amount of the 3-isomer.

reactions with bromine are anomalous and in several instances we failed to isolate the initial adduct.

Products obtained by addition to 6-*substituted* 1 : 4-*naphthaquinones.*

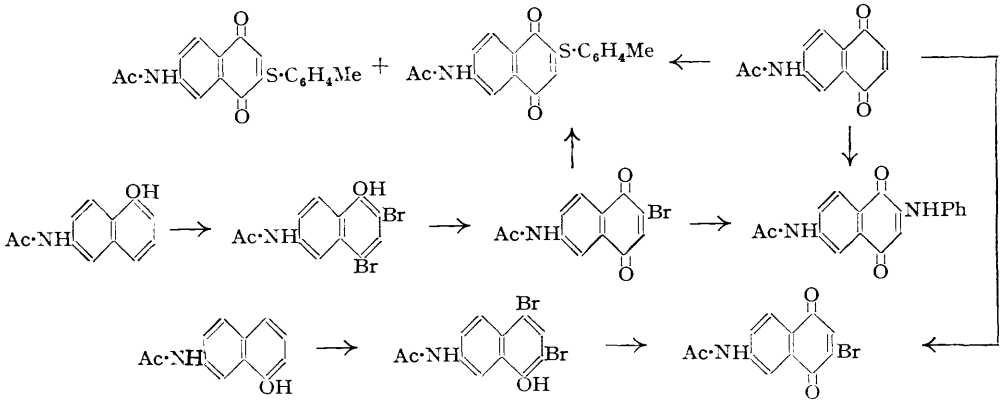
6-Substituent	NH_2Ph [1]	*p*-$C_6H_4Me{\cdot}SH$ [1]	Br [2]	Ac_2O [3]
	Orientation * and yield of compound(s) produced by			
OH	2 (88%)	*x* (37%); *y* (34%)	2 (70%)	—
OAc	2 (83%)	*x* (38%); *y* (31%)	2 (60%)	2 (58%); 3 (8%)
Me	2 (78%)	2 (36%); 3 (30%)	3 (78%)	2 (?62%); 3 (?7%)
Cl	3 (84%)	*x* (36%); *y* (49%)	3 (81%)	2 (36%); 3 (49%)
NHAc	2(89%)	2 (42%; 3 (31%)	3 (67%)	—

* $x = 2$, and $y = 3$, or *vice versa*.

[1] Yields are for the quinones obtained by oxidation of the initial adduct. [2] Yields are for the bromoquinones obtained by elimination of hydrogen bromide from the initial adduct. [3] Yields are for the triacetoxynaphthalenes obtained by complete reaction with acetic anhydride.

Orientation of the Products.—6-*Hydroxy*-1 : 4-*naphthaquinone.* Hydrolysis of the anilino-derivative yielded the known 2 : 6-dihydroxy-1 : 4-naphthaquinone, reductive acetylation of which gave 1 : 2 : 4 : 6-tetra-acetoxynaphthalene identical with the product obtained by Dimroth and Kerkovius (*Annalen*, 1913, **399**, 37) by Thiele acetylation of 6-hydroxy-1 : 2-naphthaquinone. The identity of the bromo-6-hydroxy-1 : 4-naphthaquinone was determined by reaction with aniline which gave 2-anilino-6-hydroxy-1 : 4-naphthaquinone. The toluene-*p*-thio-derivatives could not be orientated either by replacement reactions or by alternative methods of preparation. The acetates of all the above compounds were obtained both by acetylation and by the corresponding addition reactions with 6-acetoxy-1 : 4-naphthaquinone. The products of Thiele acetylation were compared with authentic specimens.

6-*Methyl*-1 : 4-*naphthaquinone.* Hydrolysis of the anilino-derivative gave the known 2-hydroxy-6-methyl-1 : 4-naphthaquinone. The structure of the bromo-derivative was established by reaction with hydrochloric acid to give a chloroquinone which was different from that obtained by treatment of 2-hydroxy-6-methyl-1 : 4-naphthaquinone with thionyl chloride. Two toluene-*p*-thiol addition products were obtained, one of which was also prepared from 3-bromo-6-methyl-1 : 4-naphthaquinone by reaction with toluene-*p*-thiol. Thiele acetylation gave a mixture of acetates which was converted into a mixture of hydroxymethylnaphthaquinones; neither mixture could be separated. Evidence was obtained (see Experimental section) which indicated that the major product was 1 : 2 : 4-triacetoxy-6-methylnaphthalene.



6-*Chloro*-1 : 4-*naphthaquinone.* The structures of the Thiele acetylation products were established by Fieser and Brown (*loc. cit.*). 1 : 3 : 4-Triacetoxy-6-chloronaphthalene was also obtained by hydrolysis of the anilino-derivative followed by reductive acetylation. Reaction of the bromo-compound with hydrochloric acid gave a dichloroquinone identical with that obtained from 6-chloro-3-hydroxy-1 : 4-naphthaquinone with the aid of thionyl

chloride, and different from 2 : 6-dichloro-1 : 4-naphthaquinone (Claus and Müller, *Ber.*, 1885, **18**, 3073). The two 6-chloro-*p*-tolylthio-1 : 4-naphthaquinones were not identified.

6-*Acetamido*-1 : 4-*naphthaquinone*. This quinone was less reactive than the others, and the products were relatively less soluble and of higher melting point. The orientations in this group were based on the 2- and 3-bromo-derivatives. These were obtained by bromination of 6- and 7-acetamido-1-naphthol to dibromo-compounds, which were oxidised to monobromoacetamido-1 : 4-naphthaquinones. One of these was also obtained by bromination of 6-acetamido-1 : 4-naphthaquinone, and the other contained a reactive bromine atom replaceable by aniline. Thus bromination occurred exclusively in the hydroxylated ring of the acetamidonaphthols. One of the toluene-*p*-thiol addition products was also obtained from the 2-bromo-derivative. These reactions are set out in the annexed scheme. Thiele acetylation of 6-acetamido-1 : 4-naphthaquinone was unsuccessful with concentrated sulphuric acid or boron trifluoride–ether complex as catalyst; some reaction took place in the presence of perchloric acid, but was difficult to reproduce. The product obtained, in poor yield, appeared to be a single compound but has not been identified

Experimental

6-*Hydroxy*-1 : 4-*naphthaquinone*.—Recorded preparations (Fischer and Bauer, *J. pr. Chem.*, 1916, **94**, 1; Dimroth and Roos, *Annalen*, 1927, **456**, 185) utilise 1 : 6-dihydroxynaphthalene as starting material. By a similar procedure we coupled 1-amino-7-naphthol with diazotised sulphanilic acid in acid solution, reduced the azo-compound with zinc dust and hydrochloric acid, and subsequently oxidised the diamino-naphthol with ferric chloride. The quinone crystallised from water in orange needles, m. p. 170° (decomp.) (20%). The *acetate* formed pale yellow needles, m. p. 102° (from aqueous methanol) (Found: C, 66·6; H, 4·0. $C_{11}H_8O_4$ requires C, 66·7; H, 3·7%). Fischer and Bauer (*loc. cit.*) prepared this compound but did not describe it.

2-*Anilino*-6-*hydroxy*-1 : 4-*naphthaquinone*.—(*a*) 6-Hydroxy-1 : 4-naphthaquinone (1·5 g.) in alcohol (20 c.c.) was refluxed with aniline (0·8 g.) for 10 min. and allowed to cool overnight. The crystalline product was collected and more was obtained by concentration of the reaction liquor. Recrystallisation from acetic acid afforded the *anilino-quinone* as dark red needles, m. p. 302° (88%). (*b*) A mixture of 2-bromo-6-hydroxy-1 : 4-naphthaquinone (1 g.), aniline (0·4 c.c.), and alcohol (40 c.c.) was boiled for 1 hr. and then diluted with water. On cooling, dark red needles, m. p. 294° (63%), separated. Recrystallisation gave crystals indistinguishable from those described in (*a*) (Found: C, 72·4; H, 4·4; N, 5·0. $C_{16}H_{11}O_3N$ requires C, 72·5; H, 4·2; N, 5·3%). The *acetate* was obtained by cold acetylation in pyridine and by addition of aniline to 6-acetoxy-1 : 4-naphthaquinone according to the above procedure (83%). It crystallised from aqueous acetic acid in light red crystals, m. p. 205° (Found: C, 70·1; H, 4·1; N, 4·7. $C_{18}H_{13}O_4N$ requires C, 70·4; H, 4·2; N, 4·55%).

2 : 6-*Dihydroxy*-1 : 4-*naphthaquinone*.—To a solution of 2-anilino-6-hydroxy-1 : 4-naphthaquinone (1 g.) in concentrated sulphuric acid (10 c.c.), water (10 c.c.) was added cautiously. The mixture was brought to the boil and then poured into water (50 c.c.). The crude dihydroxyquinone which was precipitated was extracted with aqueous sodium acetate (2%) and crystallised from acetic acid as yellow needles which decomposed gradually between 100° and 200° (77%). The diacetate formed yellow plates, m. p. 163° (from alcohol) (this was prepared by Dimroth and Kerkovius, *Annalen*, 1913, **339**, 36, who did not record the m. p.). Reductive acetylation of the diacetate with zinc dust, acetic anhydride, and a drop of pyridine yielded 1 : 2 : 4 : 6-tetra-acetoxynaphthalene in needles, m. p. and mixed m. p. 184°.

6-*Hydroxy*-2- *and* -3-p-*tolylthio*-1 : 4-*naphthaquinone*.—A solution of 6-hydroxy-1 : 4-naphthaquinone (0·5 g.) and toluene-*p*-thiol (0·3 g.) in alcohol (20 c.c.) was kept at room temperature for 30 min. and then oxidised by addition of sodium dichromate (0·5 g.) in water (20 c.c.) containing concentrated sulphuric acid (0·3 c.c.). Fractional crystallisation from acetic acid yielded two *products*: (*a*) less soluble orange-yellow needles, m. p. 247—251° (37%) and (*b*) more soluble orange-yellow crystals, m. p. 208° (34%) [Found: (*a*) 68·6; H, 4·2; S, 10·5; (*b*) C, 68·85; H, 4·2; S, 10·8. $C_{17}H_{12}O_3S$ requires 68·9; H, 4·0; S, 10·8%). These gave *acetates*, (*a*) yellow crystals, m. p. 175° (from acetic acid) and (*b*) small yellow needles, m. p. 155° (from aqueous alcohol) [Found: (*a*) C, 67·5; H, 4·2; S, 9·15; (*b*) C, 67·6; H, 4·3; S, 9·2. $C_{19}H_{14}O_4S$ requires C, 67·45; H, 4·15; S, 9·45%). The two acetates were

also obtained by addition of toluene-*p*-thiol to 6-acetoxy-1 : 4-naphthaquinone by the same procedure and were separated by fractional crystallisation from acetic acid.

2-*Bromo*-6-*hydroxy*-1 : 4-*naphthaquinone*.—A solution of bromine (1·6 g.) in acetic acid (5 c.c.) was added to one of 6-hydroxy-1 : 4-naphthaquinone (1·7 g.) in acetic acid (40 c.c.). After 10 min. the solution was poured on to ice-water (200 c.c.) and set aside for several hours. The *bromohydroxyquinone* slowly separated and was crystallised from acetic acid, forming yellow needles, m. p. 188° (70%) (Found : C, 47·6; H, 2·3; Br, 31·1. $C_{10}H_5O_3Br$ requires C, 47·4; H, 2·0; Br, 31·6%). The *acetate* formed yellow needles, m. p. 120° (Found : C, 48·8; H, 2·6; Br, 26·8. $C_{12}H_7O_4Br$ requires C, 48·8; H, 2·4 : Br, 27·1%). This compound was also obtained by bromination of 6-acetoxy-1 : 4-naphthaquinone by the above procedure (60%); again no dibromide was isolated.

1 : 2 : 4 : 6- *and* 1 : 3 : 4 : 6-*Tetra-acetoxynaphthalenes*.—6-Hydroxy-1 : 4-naphthaquinone (0·5 g.) in acetic anhydride (4 c.c.) was treated with two drops of concentrated sulphuric acid. After 5 days the mixture was diluted with water, and the precipitate obtained was recrystallised from aqueous methyl alcohol. Two fractions were isolated : (*a*) less soluble needles, m. p. 184—185° (58%), and (*b*) more soluble crystals, m. p. 139° (after several crystallisations from light petroleum) (8%) (Found : C, 60·3; H, 4·7. Calc. for $C_{18}H_{16}O_8$: C, 60·0; H, 4·5%). Mixed m. p. determinations with authentic specimens established that (*a*) was 1 : 2 : 4 : 6- and (*b*) 1 : 3 : 4 : 6-tetra-acetoxynaphthalene.

2-*Anilino*-6-*methyl*-1 : 4-*naphthaquinone*.—6-Methyl-1 : 4-naphthaquinone (1 g.) and aniline (0·5 c.c.) were refluxed in ethyl alcohol (20 c.c.) for 1 hr., and the *product* collected next morning. It formed red crystals, m. p. 206° (from aqueous acetic acid) (78%) (Found : C, 77·7; H, 5·2; N, 4·9. $C_{17}H_{13}O_2N$ requires C, 77·6; H, 5·0; N, 4·9%).

2-*Hydroxy*-6-*methyl*-1 : 4-*naphthaquinone*.—A solution of 2-anilino-6-methyl-1 : 4-naphthaquinone (0·5 g.) in concentrated sulphuric acid (4 c.c.) was diluted with water (4 c.c.), boiled for 1 min., and poured into cold water. The hydroxy-quinone was isolated by extracting the precipitate with 2% aqueous sodium acetate, and crystallised from light petroleum (b. p. 100—120°) in yellow needles, m. p. and mixed m. p. with authentic 2-hydroxy-6-methyl-1 : 4-naphthaquinone, 198° (65%).

Thiele Acetylation of 6-*Methyl*-1 : 4-*naphthaquinone*.—To a solution of 6-methyl-1 : 4-naphthaquinone (1 g.) in acetic anhydride (8 c.c.) concentrated sulphuric acid (4 drops) was added. After 6 days the colourless needles (m. p. 141°) which had separated were collected. Dilution of the mother-liquor with water gave a precipitate which, after repeated crystallisation from aqueous acetic acid and then from benzene–light petroleum, afforded needles, m. p 139—141° (total yield 69%). (1 : 2 : 4-Triacetoxy-6-methylnaphthalene has m. p. 158°, 1 : 3 : 4-triacetoxy-6-methylnaphthalene has m. p. 161—162°. A mixture of the two has m. p. *ca.* 140°. A mixture of either with the product of m. p. 141° has an intermediate m. p.) The product of m. p. 141° was rapidly hydrolysed by cold aqueous-alcoholic sodium hydroxide, and acidification of the red solution obtained gave, after crystallisation from benzene–light petroleum, clusters of yellow needles, m. p. 177—178° (Found : C, 70·1; H, 4·25. $C_{11}H_8O_3$ requires C, 70·2; H, 4·25%). (2-Hydroxy-6-methyl-1 : 4-naphthaquinone has m. p. 198—199°, 3-hydroxy-6-methyl-1 : 4-naphthaquinone has m. p. 206°. A mixture of the two has m. p. *ca.* 180°. A mixture of either with the product of m. p. 177—178° has an intermediate m. p.). Attempts to separate the material of m. p. 177—178° into two components by fractional crystallisation, extraction with buffer solutions, chromatography on calcium carbonate, etc., were unsuccessful. However, when the product of m. p. 177—178° (1 g.) was refluxed in alcohol (80 c.c.) with aniline (0·5 c.c.) for 24 hr., 2-anilino-6-methyl-1 : 4-naphthaquinone separated on cooling. This was collected and the process repeated, giving in all a 90% yield of the 2 : 6-isomer, but no 3 : 6-isomer could be isolated. It is therefore concluded that the material m. p. 177—178° is a mixture of 2- and 3-hydroxy-6-methyl-1 : 4-naphthaquinones which is largely the 2 : 6-isomer, and that the Thiele acetylation product of m. p. 141° is a mixture of triacetates in which the 1 : 2 : 4 : 6-isomer predominates.

6-*Methyl*-2- *and* -3-p-*tolylthio*-1 : 4-*naphthaquinone*.—A solution of 6-methyl-1 : 4-naphthaquinone (1 g.) and toluene-*p*-thiol (0·6 g.) in methyl alcohol (40 c.c.) was set aside until it became quite dark and then poured on to ice-water (40 c.c.) containing sodium dichromate (1·2 g.) and concentrated sulphuric acid (0·6 c.c.). The precipitate obtained was crystallised several times from light petroleum (b. p. 100—120°), to give two fractions, (*a*) less soluble yellow needles, m. p. 173° (32%), and (*b*) more soluble yellow crystals, m. p. 148° (36%) [Found : (*a*) C, 73·7; H, 5·0; S, 10·7; (*b*) C, 73·9; H, 5·0; S, 10·9. $C_{18}H_{14}O_2S$ requires C, 74·0; H, 4·7; S, 10·8%). Product (*a*) was shown to be 6-*methyl*-3-p-*tolylthio*-1 : 4-*naphthaquinone* as follows : a solution

of toluene-*p*-thiol (0·9 g.) in a little alcohol was neutralised with aqueous sodium hydroxide, brought to the b. p. and added to a hot solution of 3-bromo-6-methyl-1 : 4-naphthaquinone (1·8 g.) in alcohol (100 c.c.). The product obtained on cooling crystallised from light petroleum in yellow needles, m. p. and mixed m. p. with (*a*) 173° (88%). Product (*b*) is presumably the 2-p-*tolylthio*-isomer.

3-*Bromo*-6-*methyl*-1 : 4-*naphthaquinone*.—A solution of 6-methyl-1 : 4-naphthaquinone (1 g.) and bromine (0·9 g.) in glacial acetic acid (20 c.c.) was kept for 10 min. and then poured into ice-water (100 c.c.). The almost colourless precipitate of dibromide (1·5 g.) was collected and added to glacial acetic acid (16 c.c.) containing sodium acetate (0·8 g.). After 5 min.' boiling, water (20 c.c.) was added and the solution filtered (charcoal). The *bromo-quinone* separated on cooling and recrystallised from methyl alcohol in yellow needles, m. p. 103° (78% from the dibromide) (Found: C, 52·45; H, 2·9; Br, 31·6. $C_{11}H_7O_2Br$ requires C, 52·6; H, 2·8; Br, 31·9%).

3-*Chloro*-6-*methyl*-1 : 4-*naphthaquinone*.—A solution of 3-bromo-6-methyl-1 : 4-naphthaquinone (1 g.) in alcohol (30 c.c.) containing concentrated hydrochloric acid (0·5 c.c.) was refluxed for 12 hr., diluted with water, and allowed to cool. The 3-*chloro-quinone* which separated crystallised from aqueous alcohol in yellow crystals, m. p. 91—92° (64%) (Found: C, 63·7; H, 3·3; Cl, 17·3. $C_{11}H_7O_2Cl$ requires C, 63·9; H, 3·4; Cl, 17·15%).

2-*Chloro*-6-*methyl*-1 : 4-*naphthaquinone*.—A mixture of 2-hydroxy-6-methyl-1 : 4-naphthaquinone (0·3 g.) and thionyl chloride (3 c.c.) was refluxed for 12 hr. and excess of thionyl chloride then allowed to evaporate at room temperature. The residual 2-*chloro-quinone* formed yellow crystals, m. p. 149° (52%), from alcohol (Found: C, 63·8; H, 3·25; Cl, 17·35%).

6-*Chloro*-1 : 4-*naphthaquinone*.—Direct oxidation of the chloroprene–benzoquinone Diels–Alder adduct with potassium dichromate and sulphuric acid was found more satisfactory than the step-wise oxidation procedure of Fieser and Brown (*loc. cit.*). Crystallisation from aqueous methyl alcohol yielded yellow crystals, m. p. 109—110° (Fieser and Brown give m. p. 107°).

3-Anilino-6-chloro-1 : 4-naphthaquinone.—A mixture of 6-chloro-1 : 4-naphthaquinone (1 g.), aniline (0·23 c.c.), and alcohol (40 c.c.) was boiled for 1 hr. After being kept at room temperature for several hours, the *anilinoquinone* was collected and crystallised from acetic acid, forming red needles, m. p. 235—236° (84%) (Found: N, 5·15; Cl, 12·3. $C_{16}H_{10}O_2ClN$ requires N, 4·9; Cl, 12·4%).

6-*Chloro*-2- *and* -3-p-*tolylthio*-1 : 4-*naphthaquinone*.—A solution of 6-chloro-1 : 4-naphthaquinone (1 g.) and toluene-*p*-thiol (0·65 g.) in methyl alcohol (25 c.c.) was kept for 15 min. and then oxidised in the usual manner. The product was separated by fractional crystallisation from ethyl alcohol into (*a*) less soluble yellow crystals, m. p. 170° (from glacial acetic acid) (49%), and (*b*) more soluble yellow crystals, m. p. 130° (from methyl alcohol) (36%) [Found: (*a*) Cl, 11·5; S, 10·15; (*b*) Cl, 11·1; S, 10·4. $C_{17}H_{11}O_2ClS$ requires Cl, 11·3; S, 10·2%].

6-*Chloro*-3-*hydroxy*-1 : 4-*naphthaquinone*.—3-Anilino-6-chloro-1 : 4-naphthaquinone was hydrolysed by boiling 50% (v/v) sulphuric acid for 5 min. Crystallisation from methyl alcohol gave yellow crystals, m. p. 204° (Fieser and Brown, *loc. cit.*, give m. p. 205—207°). Reductive acetylation yielded 1 : 3 : 4-triacetoxy-6-chloronaphthalene, m. p. and mixed m. p. 149—150°.

3-*Bromo*-6-*chloro*-1 : 4-*naphthaquinone*.—6-Chloro-1 : 4-naphthaquinone (1 g.) in glacial acetic acid (28 c.c.) was treated with bromine (0·8 g.). After 10 min. the solution was diluted with water, and the dibromide (97%; m. p. 122—126°) collected. The *bromochloroquinone* was obtained by boiling the dibromide with sodium acetate in glacial acetic acid for a few minutes. It crystallised from alcohol in yellow needles, m. p. 175° (81% from dibromide) (Found: C, 43·95; H, 1·5; Hal, 41·4. $C_{10}H_4O_2BrCl$ requires C, 44·2; H, 1·5; Hal, 42·5%).

3 : 6-*Dichloro*-1 : 4-*naphthaquinone*.—(*a*) A solution of 3-bromo-6-chloro-1 : 4-naphthaquinone (0·5 g.) in alcohol (40 c.c.) containing concentrated hydrochloric acid (2 c.c.) was refluxed for 30 min. and filtered (charcoal). The *dichloro-quinone* separated in yellow plates, m. p. 188—189° (88%). (*b*) 6-Chloro-3-hydroxy-1 : 4-naphthaquinone (0·5 g.) and thionyl chloride (5 c.c.) were heated under reflux overnight. After evaporation of the excess of thionyl chloride, the residue was taken up in ether, extracted with 2% aqueous sodium acetate, and dried, and the solvent was removed. The residue crystallised from alcohol in yellow plates, m. p. 188—189° (Found: C, 52·6; H, 1·8; Cl, 31·0. $C_{10}H_4O_2Cl_2$ requires C, 52·9; H, 1·8; Cl, 31·3%).

1 : 2 : 4- *and* 1 : 3 : 4-*Triacetoxy*-6-*chloronaphthalene*.—The results of Thiele acetylation of 6-chloro-1 : 4-naphthaquinone were substantially the same as recorded by Fieser and Brown (*loc. cit.*). We obtained (*a*) 1 : 2 : 4-triacetoxy-6-chloronaphthalene, m. p. 163—164° (36%), more soluble in methyl alcohol than (*b*) 1 : 3 : 4-triacetoxy-6-chloronaphthalene, m. p. 149—150°

(49%) (Fieser and Brown give m. p. 143—144°. These authors have confused the m. p.s of the two isomers).

6-*Acetamido*-1 : 4-*naphthaquinone*.—This was prepared by the procedure of Fierz-David, Blangey, and Krannichfeldt (*Helv. Chim. Acta*, 1947, **30**, 831) using the mixture of 6- and 7-acetamido-1-naphthols obtained by sulphonation of β-naphthylamine followed by potash fusion and acetylation (yield 70%).

6-*Acetamido*-2-*anilino*-1 : 4-*naphthaquinone*.—(*a*) 6-Acetamido-1 : 4-naphthaquinone (0·5 g.) and aniline (0·25 c.c.) were refluxed in alcohol (50 c.c.) for 10 hr. and then set aside. The *anilinoquinone* separated overnight and recrystallised from alcohol as red needles, m. p. 330° (89%). (*b*) 6-Acetamido-2-bromo-1 : 4-naphthaquinone (0·5 g.) and aniline (0·25 c.c.) were refluxed in alcohol for 10 hr. Red needles, m. p. 328° (76%), separated on cooling, identical with those obtained as above (Found : C, 70·2; H, 4·5; N, 8·8. $C_{18}H_{14}O_3N_2$ requires C, 70·6; H, 4·6; N, 9·15%).

6-*Acetamido*-2- *and* -3-p-*tolylthio*-1 : 4-*naphthaquinone*.—A mixture of 6-acetamido-1 : 4-naphthaquinone (1 g.) and toluene-*p*-thiol (0·3 g.) in methyl alcohol (50 c.c.) was heated to the b. p. and then kept at room temperature for several hours. Small yellow needles, m. p. 244—245° (0·2 g.), separated. Oxidation of the mother-liquor with sodium dichromate and sulphuric acid at room temperature gave a product which was separated into two fractions by crystallisation from glacial acetic acid : (*a*) a *tolylthio*-compound as yellow needles, m. p. 255° (decomp. from 230°) (42%) (from methyl alcohol), less soluble than (*b*) its *isomer*, orange crystals, m. p. 220° (31%) (from aqueous acetic acid). Recrystallisation of the first crop gave (*a*) [Found : (*a*) N, 4·3; S, 9·6; (*b*) N, 3·9; S, 9·3. $C_{19}H_{15}O_3NS$ requires N, 4·15; S, 9·5%]. Product (*a*) was also obtained as follows: toluene-*p*-thiol (0·2 g.) in a little alcohol was neutralised with aqueous sodium hydroxide, and the solution brought to the boil and added to a hot solution of 6-acetamido-2-bromo-1 : 4-naphthaquinone in alcohol (50 c.c.). On cooling, yellow needles, m. p. 252—254°, separated : mixed m. p. with material (*a*), 254—255°.

6-*Acetamido*-3-*bromo*-1 : 4-*naphthaquinone*.—(*a*) 6-Acetamido-1 : 4-naphthaquinone (0·4 g.) and bromine (0·32 g.) were dissolved in glacial acetic acid (50 c.c.). After 15 min. the solution was poured into water (300 c.c.) from which the *bromo-quinone* gradually separated. It crystallised from alcohol in orange crystals, m. p. 237° (67%). (*b*) 7-Acetamido-2 : 4-dibromo-1-naphthol (1 g.) in glacial acetic acid (50 c.c.) was oxidised by the addition of chromium trioxide (1 g.) in water (3 c.c.). After 15 min. the solution was diluted with water, and the precipitate was crystallised from alcohol in orange crystals, m. p. 237° (73%), identical with the above product (Found : N, 4·5; Br, 27·0. $C_{12}H_8O_3NBr$ requires N, 4·7; Br, 27·2%).

6-*Acetamido*-2-*bromo*-1 : 4-*naphthaquinone*.—6-Acetamido-2 : 4-dibromo-1-naphthol was oxidised with chromic acid as before. The *quinone* separated from alcohol in orange crystals, m. p. 241° (82%) (Found : N, 4·4; Br, 27·0. $C_{12}H_8O_3NBr$ requires N, 4·7; Br, 27·2%).

6-*Acetamido*-2 : 4-*dibromo*-1-*naphthol*.—6-Acetamido-1-naphthol (1·6 g.) in glacial acetic acid (20 c.c.) was treated with bromine (3 g.). A precipitate appeared immediately and was collected after 30 min. and crystallised from chlorobenzene, to yield plates, m. p. 205—207° (decomp. from 187°) (86%) (Found : N, 3·85; Br, 44·2. $C_{12}H_9O_2NBr_2$ requires N, 3·9; Br, 44·5%). The *acetate* was obtained in needles, m. p. 225° (from aqueous methanol) (Found : N, 3·3; Br, 39·6. $C_{14}H_{11}O_3NBr_2$ requires N, 3·5; Br, 39·9%).

7-*Acetamido*-2 : 4-*dibromo*-1-*naphthol*.—This *isomer* was prepared by the foregoing procedure from 7-acetamido-1-naphthol. It separated from chlorobenzene in needles, m. p. 212° (decomp. from 200°) (80%) (Found : N, 3·75; Br, 44·3%). The *acetate* crystallised from acetic acid in needles, m. p. 210° (decomp. from 196°) (Found : N, 3·7; Br, 40·2%).

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