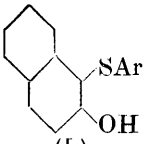
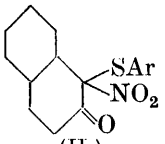
CLVII.—*Thioquinols.*

By LEONARD ARTHUR WARREN and SAMUEL SMILES.

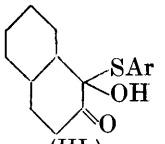
IN previous communications (J., 1930, 959, 1742) it has been shown that the 1-thio- and 1-dithio-derivatives of 2-naphthol are converted into cyclic quinols by oxidation. Since this behaviour has been quoted in connexion with other work (*e.g.*, this vol., p. 916) as showing the tendency of the thio-derivatives in question to assume the ketonic form, it seemed desirable to add to this evidence by a further study of thio-derivatives of 2-naphthol of the general type (I). It is now shown that these substances are converted by dilute nitric acid into quinonitroles (II) of a type similar to that derived from 1-methyl-2-naphthol (Fries and Hübner, *Ber.*, 1906, **39**, 435). Under the action of heat in solvents the thioquinonitroles decompose, yielding complex mixtures; the chief process involved is



(I.)

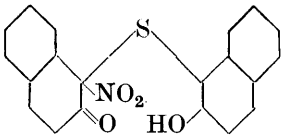


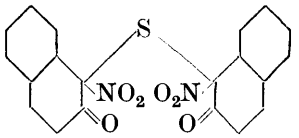
(II.)



(III.)

(IV.)





(V.)

usually that of hydrolysis (compare Fries and Hübner, *loc. cit.*), leading to nitrous acid and the thioquinols (III), but, as might be expected from the instability of the additive compounds of ketones or aldehydes with thiols (Baumann, *Ber.*, 1885, **18**, 262; Bongartz, *Ber.*, 1886, **19**, 1934), these have not been isolated, the disulphides $(Ar{\cdot}S^{-})_2$ resulting from oxidation of the thiols liberated by fission of the thioquinols (III) being obtained instead. Concurrently with hydrolysis, migration of the nitro-group may occur, but the resulting nitro-derivatives of the parent sulphide (I), owing to difficulties of

isolation, have been obtained from only three of the examples studied. Included among the latter are the nitroquinols derived from 2-naphthol 1-sulphide (IV) and its monomethyl ether and monoacetyl derivative (IV, where OH is OMe or ·O·CO·CH_3). Hydrolysis of the acetyl derivative led to the 1-disulphide of 2-acetoxynaphthalene, but (IV) yielded the dehydro-derivative of 2-naphthol 1-disulphide (J., 1930, 1742). A third type of decomposition, observed in presence of alkali, involves the removal of the thioaryl group, leaving 1-nitro-2-naphthol (compare Fries, *Annalen*, 1912, **389**, 315). Further nitration of the thioquinonitroles derived from 2-naphthol 1-sulphide and disulphide leads to the interesting diquinols (V). These substances readily yield 1-nitro-2-naphthol on alkaline hydrolysis.

The formation of dehydro-2-naphthol 1-sulphide has not been observed during the hydrolysis of (IV): evidently, under the conditions, rupture of the thioquinol group (IV, where NO_2 is OH) takes place before dehydration leading to the more stable cyclic quinol can be effected to an appreciable extent.

EXPERIMENTAL.

In most cases the thioquinonitroles described below were prepared by the following method. A solution (10%) of nitric acid (1 mol.) in acetic acid was added to a shaken suspension or a solution of the sulphide (1 mol.) in the same solvent. A yellow solution of the required material was obtained, and when it was suitably agitated the thioquinonitrole separated in the crystalline state. The material was usually purified by addition of alcohol to an ice-cold acetone solution. The products, unless otherwise stated, were yellow crystalline materials; they were unaltered by dilute aqueous sodium carbonate or cold dilute aqueous alkali hydroxide. When heated, they profoundly decomposed with liberation of oxides of nitrogen; the m. p.'s recorded therefore vary somewhat with the rate of heating.

2-*Naphthyl* 1-*Nitro*-2-*keto*-1 : 2-*dihydro*-1-*naphthyl Sulphide* (II, where Ar is 2-$C_{10}H_7$).—The required sulphide (I, where Ar is 2-$C_{10}H_7$) may be obtained from 2-naphthyl disulphoxide and sodium 2-naphthoxide as previously described (J., 1926, 1728), but it was more conveniently prepared as follows. A suspension of 2-naphthyl disulphide (3 g.) in carbon tetrachloride (100 c.c.) was treated with dry chlorine until the disulphide had dissolved. After the excess of halogen had been removed, 2-naphthol (3·5 g.) was added to the solution of the chlorothiol. The solvent was then (12 hours) evaporated, and the residue purified (3·5 g.) from alcohol.

The corresponding *thioquinonitrole* formed plates, m. p. 116° (decomp.) (Found: C, 69·2; N, 4·2. $C_{20}H_{13}O_3NS$ requires C, 69·1; N, 4·0%). When this substance (1 g.) was warmed (80°) with acetic

acid (10 c.c.), it dissolved and oxides of nitrogen were liberated; 2-naphthyl disulphide (m. p. 139°. Found: C, 75·3; H, 4·6. Calc.: C, 75·4; H, 4·4%) separated from the cooled liquid. The remaining solution when treated with phenylhydrazine yielded a mixture of hydrazones. The quinonitrole was also decomposed by warm alcoholic sodium hydroxide, yielding 2-naphthyl disulphide; the sodium salt of 1-nitro-2-naphthol separated from the cooled solution, and after purification the nitro-naphthol had m. p. 102° and was identified in the usual manner.

p-*Tolyl* 1-*nitro*-2-*keto*-1 : 2-*dihydro*-1-*naphthyl sulphide* (II, where Ar is *p*-C_7H_7) formed colourless plates, m. p. 112° (decomp.) (Found: C, 65·8; N, 4·6. $C_{17}H_{13}O_3NS$ requires C, 65·6; N, 4·2%).

o-*Nitrophenyl* 1-*nitro*-2-*keto*-1 : 2-*dihydro*-1-*naphthyl sulphide* (II, where Ar is *o*-$C_6H_4{\cdot}NO_2$), m. p. 105° (decomp.) (Found: C, 56·5; N, 8·3. $C_{16}H_{10}O_5N_2S$ requires C, 56·1; N, 8·2%), decomposed in warm acetic acid. The material which separated from the cooled mixture was purified by conversion into the sodium salt. The o-*nitrophenyl* ?-*nitro*-2-*hydroxy*-1-*naphthyl sulphide* liberated from this formed yellow plates, m. p. 192°, from acetic acid (Found: C, 56·1; H, 3·1; N, 8·5. $C_{16}H_{10}O_5N_2S$ requires C, 56·1; H, 2·9; N, 8·2%). When the nitrole was suspended in boiling aqueous sodium hydroxide (2*N*), it decomposed. The insoluble material was identified as *o*-nitrophenyl disulphide, and from the red solution 1-nitro-2-naphthol (m. p. 102°) was isolated which was identified in the usual manner.

p-*Nitrophenyl* 1-*nitro*-2-*keto*-1 : 2-*dihydro*-1-*naphthyl sulphide* (II, where Ar is *p*-$C_6H_4{\cdot}NO_2$) had m. p. 116° (decomp.) (Found: C, 56·2; N, 8·3. $C_{16}H_{10}O_5N_2S$ requires C, 56·1; N, 8·2%) and was decomposed by warm acetic acid. The solid which separated after water had been added to the mixture was treated with warm aqueous sodium hydroxide (10%). The sparingly soluble sodium salt was purified from hot water (charcoal) and treated with mineral acid. The liberated p-*nitrophenyl* ?-*nitro*-2-*hydroxy*-1-*naphthyl sulphide* separated from acetic acid as a yellow crystalline powder, m. p. 187° (Found: C, 56·3; H, 3·3. $C_{16}H_{10}O_5N_2S$ requires C, 56·1; H, 2·9%).

1-*Nitro*-2′-*hydroxy*-2-*keto*-1 : 2-*dihydrodi*-1-*naphthyl sulphide* (IV) formed prisms, m. p. 116° (decomp.) (Found: C, 66·2; N, 3·9. $C_{20}H_{13}O_4NS$ requires C, 66·1; N, 3·8%). It was rapidly decomposed by warm acetic acid; dehydro-2-naphthol 1-disulphide (J., 1930, 1745) separated from the cooled solution and was identified in the usual manner.

1-*Nitro*-2-*keto*-2′-*methoxy*-1 : 2-*dihydrodi*-1-*naphthyl sulphide* (IV, where OH is OMe) had m. p. 105° (decomp.) (Found: C, 67·1; N, 4·0. $C_{21}H_{15}O_4NS$ requires C, 66·8; N, 3·7%).

1-*Nitro*-2-*keto*-2'-*acetoxy*-1 : 2-*dihydrodi*-1-*naphthyl Sulphide* (IV, where OH is ·O·CO·CH_3).—The *monoacetyl* derivative of 2-naphthol 1-sulphide required for the preparation of this quinonitrole was obtained as follows. A suspension of 2-acetoxynaphthalene 1-disulphide (1 mol.) in carbon tetrachloride was shaken and treated with chlorine until solution was complete. 2-Naphthol (2 mols.) was added after the excess of halogen had been removed; hydrogen chloride was liberated while the required material separated (84% yield). This formed plates, m. p. 164°, from acetic acid (Found: C, 73·3; H, 4·7. $C_{22}H_{16}O_3S$ requires C, 73·3; H, 4·4%). The *quinonitrole* prepared from this by the usual method was colourless and had m. p. 102° (decomp.) (Found: C, 64·8; N, 3·7. $C_{22}H_{15}O_5NS$ requires C, 65·2; N, 3·5%). When a hot acetic acid solution of this substance was cooled, the diacetyl derivative of 2-naphthol 1-disulphide was deposited (70%); this had m. p. 200° and was identical with an authentic sample. Decomposition also occurred when the substance was kept in acetic acid (15°; 5 days). When the solid product was treated with dilute alkali hydroxide, the diacetyl derivative of 2-naphthol disulphide remained undissolved. The red alkaline solution contained nitro-derivatives of naphthol sulphide.

1-*Nitro*-2-*keto*-2'-*hydroxy*-1 : 2-*dihydrodi*-1-*naphthyl disulphide* (IV, where S is $-S{\cdot}S-$).—Application of the usual method to 2-naphthol 1-disulphide gave a mixture of mono- and di-quinonitroles. The *monoquinonitrole* was prepared by shaking the disulphide (1 mol.) with ether and dilute sulphuric acid in presence of sodium nitrite (1 mol.); the disulphide dissolved in the ether, from which the required product separated on further agitation. It crystallised from acetone in needles, m. p. 109° (decomp.) (Found: C, 61·1; N, 3·7. $C_{20}H_{13}O_4NS_2$ requires C, 60·75; N, 3·5%). This quinonitrole dissolved in warm aqueous sodium hydroxide (2*N*); the sodium salt of 1-nitro-2-naphthol separated from the cooled solution. The nitronaphthol had m. p. 102° and was identical with an authentic sample.

Di-1-*nitro*-2-*keto*-1 : 2-*dihydro*-1-*naphthyl sulphide* (V) was obtained from 2-naphthol 1-sulphide by the usual method with nitric acid (2 mols.). It formed clusters of needles, m. p. 121° (decomp.) (Found: C, 59·0; N, 6·9. $C_{20}H_{12}O_6N_2S$ requires C, 58·8; N, 6·8%), which were attacked by warm aqueous sodium hydroxide, yielding a red solution from which a mixture of sodium salts separated. The nitronaphthols liberated from these were fractionated, 1-nitro-2-naphthol being readily obtained; this was identified in the usual manner.

Di-1-*nitro*-2-*keto*-1 : 2-*dihydro*-1-*naphthyl disulphide* (V, where S is $-S{\cdot}S-$), prepared by the usual method as in the foregoing case, had m. p. 124—127° (decomp.) (Found: C, 54·8; N, 6·3. $C_{20}H_{12}O_6N_2S_6$

requires C, 54·5; N, 6·3%). When the solution obtained by boiling this diquinonitrile with sodium hydroxide (2*N*) was cooled, a mixture of sodium salts separated. The naphthols liberated from these were fractionated from alcohol; the more soluble portion was further purified as the sodium salt, which yielded 1-nitro-2-naphthol. This was identified in the usual manner.

Finally the behaviour of 2-naphthol *iso*-sulphide under the conditions leading to these quinonitroles is recorded. When the usual solution of nitric acid (1 mol.) was added to a suspension of the *iso*-sulphide (1 mol.) in the same solvent, the nitrodehydro-2-naphthol 1-sulphide (J., 1914, **105**, 1746) was formed in high yield (95%). Reaction of nitrous acid with the dehydro-sulphide did not yield this nitration product.

KING'S COLLEGE, LONDON. [*Received, March 4th*, 1931.]