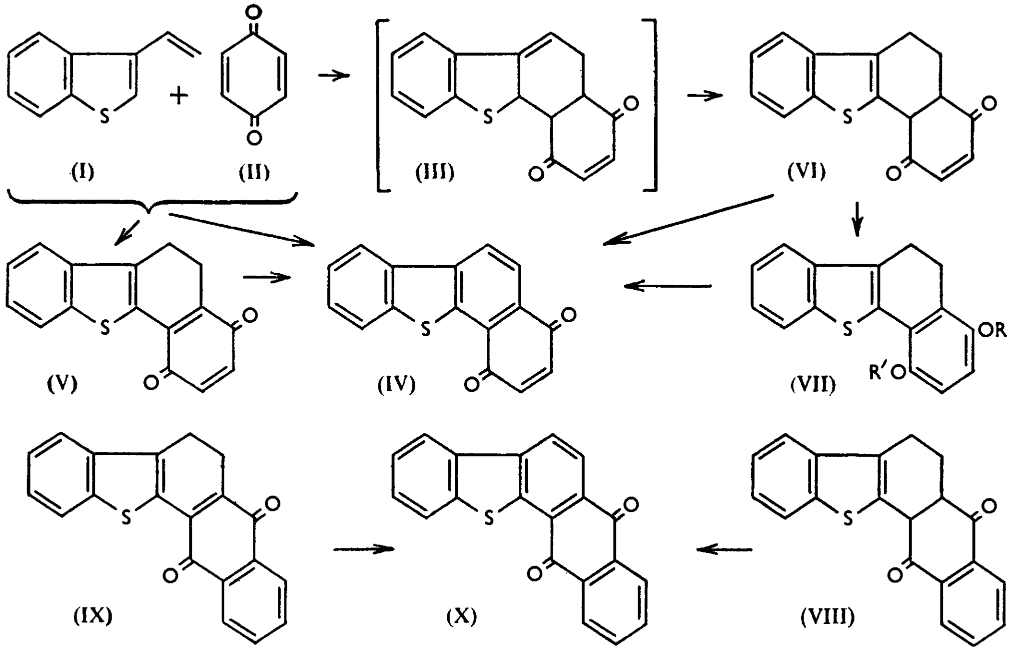
# **992.** *The Synthesis of Condensed Heterocyclic Systems. Part II.*[1] *The Use of 3-Vinylthionaphthen and* 3-cyclo*Hex-1'-enylthionaphthen in the Diene Synthesis.*

By W. DAVIES and Q. N. PORTER.

Polycyclic thiahydrocarbons containing one thiophen and two—four benzene rings are prepared from the adducts of 3-vinylthionaphthen with maleic anhydride, *p*-benzoquinone, and 1 : 4-naphthaquinone respectively. The acetates of 2- and 5-hydroxy-1 : 4-naphthaquinone also react. From the adduct of thionaphthen 1 : 1-dioxide and 3-vinylthionaphthen a pentacyclic compound with two thiophen rings is obtained, while penta- and hexacyclic quinones containing one thiophen ring are formed from 3-*cyclo*hex-1'-enylthionaphthen with *p*-benzoquinone and 1 : 4-naphthaquinone respectively.

THE ready production[2] of a naphthothiafluorene by interaction of thionaphthen 1 : 1-dioxide and 1-vinylnaphthalene suggested that the reverse type of process might be fruitful, namely, the reaction of a sulphur-containing diene with a benzenoid dienophil.



The preliminary work[1] is now amplified, chiefly with respect to reaction of 3-vinylthionaphthen with benzoquinone and with 1 : 4-naphthaquinone and some of its derivatives.

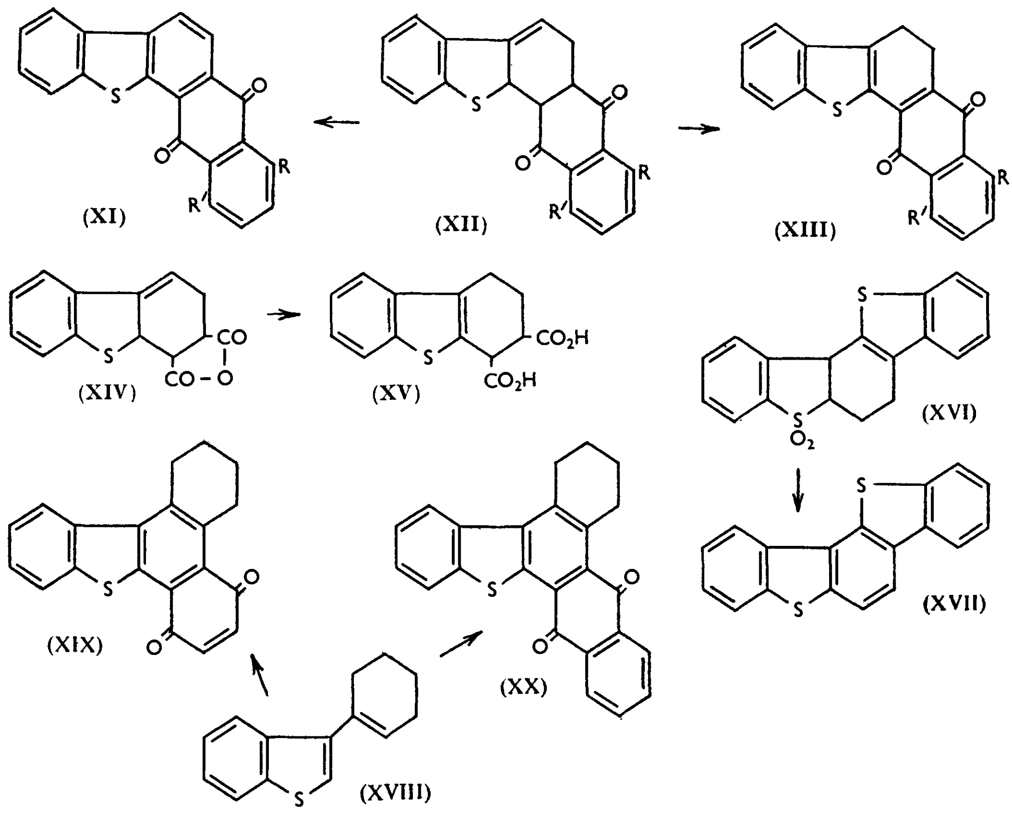
Elucidation of the structure of our partly hydrogenated products has been aided by a relation between degree of conjugation and colour, and by the effect of mineral acid, any resulting rearrangements leading to increased conjugation. Diene syntheses were carried out in acetic acid at 100° unless otherwise specified.

In reaction of 3-vinylthionaphthen (I) with an excess of benzoquinone (II) for 8 hours complete aromatisation takes place,[3] and the orange-red 9-thia-1 : 2-benzofluorene-1' : 4'-quinone (IV) is produced. It is now found that a weaker solution, with a reaction

---

[1] Part I, preceding paper.
[2] Davies and Porter, *J.*, 1957, 459.
[3] Davies, Porter, and Wilmshurst, *J.*, 1957, 3366.

time of 3 hours, gives a dihydro-derivative, for which structure (V) is suggested as the red-brown colour (deep-red solution in acetic acid) indicates the presence of a quinonoid system: this product is readily dehydrogenated by chloranil to the quinone (IV). Further, an excess of vinylthionaphthen and a very short reaction time leads to a 70% yield of the pale yellow adduct (VI), which is also dehydrogenated by chloranil to the fully aromatic quinone (IV). Structure (VI) is suggested, rather than that of the theoretical first adduct (III), because the compound is not only produced in hot acetic acid, but is stable to boiling acetic acid containing hydrogen chloride, which would probably isomerise a compound (III). Another possibility is that the compound isolated is formed by enolisation of the diketone (VI), and is the quinol (VII; $R = R' = H$), whose diacetate (VII; $R = R' = Ac$) is formed by boiling acetic anhydride containing sulphuric acid. However, the original compound contains no hydroxyl groups—it is insoluble in cold sodium hydroxide solution and with cold methylmagnesium iodide gives no methane: nevertheless it is potentially enolic, for it dissolves in boiling aqueous sodium hydroxide to a clear yellow solution, from which the quinone (V) is deposited. The chemical evidence for structure (VI) is supported by the infrared spectrum which shows two carbonyl (1698·2 and 1675·3 cm.$^{-1}$), but no hydroxyl, frequencies.



3-Vinylthionaphthen also reacts readily with 1 : 4-naphthaquinone. An excess of diene produces the almost colourless adduct (VIII), which, like (VI), gives negative tests for active hydrogen and enol; an excess of the quinone leads to the dark-red quinone (IX), whose benzene and acetic acid solutions are red-purple. This compound is dehydrogenated to the light brown quinone (X) by chloranil, but not by an excess of 1 : 4-naphthaquinone, a negative result which contrasts with the oxidising action of benzoquinone to form (IV) in accord with the fact that benzoquinone is a stronger oxidant than 1 : 4-naphthaquinone.

The products (IX) and (X) give different quinol diacetates on reductive acetylation, which disposes of the possibility—not disproved by analysis—that the former is a quinhydrone. In line with this, the product (IX) contains no active hydrogen and is insoluble in boiling dilute aqueous sodium hydroxide.

Of the methods used for complete removal of oxygen from anthraquinones,[4] the most successful is reduction to the anthrone by stannous chloride,[5] followed by a modified Clemmensen reduction.[6] This technique leads also to a good yield of the fully aromatic oxygen-free compound from the quinone (X).

3-Vinylthionaphthen and juglone (5-hydroxy-1 : 4-naphthaquinone) give an adduct (XI; R = OH, R′ = H, or *vice versa*), slowly and in only 33% yield, whence juglone is not as reactive a dienophile as the parent quinone. However, even at room temperature, juglone acetate gives a 76% yield of the adduct (XII; R = OAc, R′ = H, or *vice versa*), in which migration of the double bond has not occurred (probably owing to the mild conditions employed). The adduct, in an oxidising environment, is rapidly converted by hot acetic acid containing hydrochloric acid into a stable dark red 3 : 4-dihydro-derivative (XIII; R = OAc, R′ = H, or *vice versa*), oxidation and migration of the double bond occurring. The new compound is rapidly dehydrogenated by chloranil to a quinone (XI), identical with the compound obtained by acetylation of the adduct from juglone and 3-vinylthionaphthen; thus juglone and its acetate add the diene in the same way.

Somewhat similar results have been obtained for lawsone (2-hydroxy-1 : 4-naphthaquinone) and its acetyl derivative. Lawsone does not react with 3-vinylthionaphthen in acetic acid at 100°, whereas the acetyl compound gives the quinone (X). The expected adduct containing an angular acetoxy-group apparently loses acetic acid and is dehydrogenated by excess of quinone during the reaction.

Fieser and Dunn [7] showed that with 2 : 3-dimethylbutadiene in alcohol juglone formed an adduct slightly more readily than juglone acetate. With 3-vinylthionaphthen in acetic acid the reverse is the case. It is possible that juglone does not always react as a normal naphthaquinone, since Thomson [8] has shown that it gives no hydroxyl bands in the infrared spectrum, suggesting that this is due to strong hydrogen-bonding between the 5-hydroxyl group and the neighbouring carbonyl-oxygen atom. The unreactivity of lawsone may also be partly due to hydrogen-bonding, absent from the acetyl compound.

Attention is called to the tendency in this series for 1 : 4-diketones [*e.g.*, (VI), (VIII)] to be formed rather than the isomeric dienols or quinols, even though these would be more fully conjugated. There seems to be no exact analogy among aromatic compounds, though there is a related case of isomerism in the naphthalene series: 2 : 3-dihydro-1 : 4-naphthaquinone (which is formed in small yield by heating the isomeric 1 : 4-dihydroxynaphthalene to 210° in a vacuum) is readily isomerised to the aromatic diol by mineral acid; here the quinol is more stable than the diketone, whereas the reverse seems true with our tetracyclic and pentacyclic diketones. Among derivatives of the acene series phenols tend more to form ketones as the number of rings increases: [9] however, the diketones found in our work belong to the angular series, and the carbonyl groups are not in a central ring.

Maleic anhydride and 3-vinylthionaphthen in benzene form an adduct, which, being unsaturated, is assigned structure (XIV). This rearranges in acid or alkali to the acid (XV). Aromatisation by means of selenium, followed by decarboxylation, gives dibenzothiophen.

---

[4] Clar, " Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1952, p. 107; Campbell and Gow, *J.*, 1949, 1555; Mayer, *Annalen*, 1931, **488**, 259.

[5] Cook, *J.*, 1932, 456.

[6] Martin, *J. Amer. Chem. Soc.*, 1936, **58**, 1438.

[7] Fieser and Dunn, *ibid.*, 1937, **59**, 1016.

[8] Thomson, *J.*, 1950, 1737.

[9] Ref. 4, p. 18.

3-Vinylthionaphthen and thionaphthen 1 : 1-dioxide in toluene afford a 65% yield of the tetrahydro-derivative (XVI), which is converted by lithium aluminium hydride followed by selenium into the fully aromatic compound (XVII). Desulphurisation of this gives *m*-terphenyl, whereas the possible primary adduct other than (XVI) would have led to *p*-terphenyl (αβ-addition of the diene being assumed).

3-*cyclo*Hex-1′-enylthionaphthen (XVIII) has been shown[10] to react as a diene with maleic anhydride. It is now found with benzoquinone and 1 : 4-naphthaquinone it gives the adducts (XIX) and (XX) which are crimson and light orange respectively. In both cases dehydrogenation has occurred even in the presence of excess of diene; this does not affect the *cyclo*hexene rings since the two products contain neither active hydrogen nor acidic centres. Moreover the structure (XX) is supported by the infrared spectroscopy. So far it has not proved possible to remove the oxygen from these quinones.

## EXPERIMENTAL

M. p. determinations were made in Pyrex tubes.

*Dienes.*—3-Vinylthionaphthen (I), b. p. 138—140°/18 mm., was prepared as before,[3] and also from 3-2′-bromoethylthionaphthen, of which 35 g. were refluxed for 30 min. with potassium hydroxide (8·75 g.) in 95% ethanol (330 ml.), cold diluted solution yielding to benzene 3-vinylthionaphthen (19 g., 81%), b. p. 133—134°/25 mm. The overall yield (62%) from 3-2′-hydroxyethylthionaphthen is higher than that from the previous process. The alcohol (obtained from 3-thionaphthenylmagnesium bromide and acetaldehyde), when distilled from potassium hydrogen sulphate, gave a 10% yield of 3-vinylthionaphthen and much polymer.

3-*cyclo*Hex-1′-enylthionaphthen (XVIII), b. p. 177—181°/2 mm., was prepared[10] (66%) by interaction of *cyclo*hexanone and 3-thionaphthenylmagnesium bromide, followed by dehydration.

*Reaction of* 3-*Vinylthionaphthen with Benzoquinone.*—(i) *p*-Benzoquinone (0·86 g., 0·008 mole) and 3-vinylthionaphthen (0·32 g., 0·002 mole) in glacial acetic acid (10·0 ml.) were heated on the water-bath for 3 hr. and the product, which separated on cooling, was washed with ether to remove quinhydrone. The brown residue recrystallised from benzene, giving brown needles (0·36 g., 66%) of 3 : 4-*dihydro*-9-*thia*-1 : 2-*benzofluorene*-1′ : 4′-*quinone* (V), m. p. 202—202·5° [mixed m. p. with the quinone (IV), 185—187°] (Found: C, 71·85; H, 3·8. $C_{16}H_{10}O_2S$ requires C, 72·20; H, 3·8%). The product was stable for 30 min. in boiling acetic acid containing hydrogen chloride.

(ii) Benzoquinone (1·08 g., 0·001 mole) and 3-vinylthionaphthen (2·4 g., 0·0015 mole) in acetic acid (40 ml.) were heated on the water-bath for 10 min., and after 1 hr. at room temperature the yellow precipitate was recrystallised from benzene, giving yellow needles (1·9 g., 69%) of 1 : 2 : 3 : 4-*tetrahydro*-9-*thia*-1 : 2-*benzofluorene*-1′ : 4′-*quinone* (VI), m. p. 206—207°, unchanged when refluxed for 30 min. in acetic acid saturated with hydrogen chloride (Found: C, 71·7; H, 4·6. $C_{16}H_{12}O_2S$ requires C, 71·6; H, 4·5%). No increase in yield occurred when the molar ratio was greater than 1·5. When equimolecular quantities of quinone and vinyl compound were treated under the above conditions, the yield fell to 55%.

*Proof of the Structure* (VI).—This diketone was converted by warm acetic anhydride containing a little concentrated sulphuric acid into 1′ : 4′-*diacetoxy*-3 : 4-*dihydro*-9-*thia* 1 : 2-*benzofluorene* (VII; R = R′ = Ac), colourless prisms (from benzene), m. p. 209—210° (Found: C, 68·35; H, 4·3. $C_{20}H_{14}O_4S$ requires C, 68·2; H, 4·0%). Our test for active hydrogen was instantaneous brisk evolution of gas when a cold solution of the compound in anisole was mixed with a cold solution of ethereal methylmagnesium iodide. It was negative with compound (VI). The compound was insoluble in cold sodium hydroxide solution. Boiling aqueous sodium hydroxide at once formed a deep yellow solution which soon became brown and gave a precipitate which recrystallised from glacial acetic acid in brown needles of compound (V), m. p. and mixed m. p. 201·5—202·5°.

*Dehydrogenation of Compounds* (V) *and* (VI).—Compound (VI) (0·1 g.) and chloranil (0·2 g.) in xylene (5·0 ml.) were refluxed for 8 hr., and the crystalline product from the cold solution was washed with ether and recrystallised from benzene, giving orange-red needles of 9-thia-1 : 2-benzofluorene-1′ : 4′-quinone, m. p. and mixed m. p. 197—198°. The compound (V) (0·1 g.) with chloranil (0·1 g.) gave the same quinone.

---

[10] Szmuszkovicz and Modest, *J. Amer. Chem. Soc.*, 1950, **72**, 571.

*Reaction of* 3-*Vinylthionaphthen with* 1 : 4-*Naphthaquinone*.—(i) The quinone [11] (m. p. 124—125°; 0·32 g., 0·002 mole) and 3-vinylthionaphthen (0·48 g., 0·003 mole) in glacial acetic acid (5·0 ml.) were heated on the water-bath for 10 min., then cooled for 1 hr. The yellow crystalline product recrystallised from benzene in pale yellow needles (0·4 g., 63%) of 1 : 2 : 3 : 4-*tetrahydronaphtho*(2′ : 3′-1 : 2)-9-*thiafluorene*-1′ : 4′-*quinone* (VIII), m. p. 209—210° (Found: C, 75·65; H, 4·6. $C_{20}H_{14}O_2S$ requires C, 75·45; H, 4·4%). It was unaffected for a short time in refluxing acetic acid containing hydrogen chloride, and gave no methane with methylmagnesium iodide. It gave a red solution in boiling dilute aqueous sodium hydroxide.

(ii) 3-Vinylthionaphthen (1·6 g., 0·001 mole) and 1 : 4-naphthaquinone (4·8 g., 0·003 mole) in acetic acid (50 ml.) were heated on the water-bath for 10 hr. and the dark-red crystals from the cold solution washed with ether and recrystallised from glacial acetic acid, giving dark red needles (2·2 g., 70%) of 3 : 4-*dihydronaphtho*(2′ : 3′-1 : 2)-9-*thiafluorene*-1′ : 4′-*quinone* (IX), m. p. 217—218° (Found: C, 76·1; H, 3·85. $C_{20}H_{12}O_2S$ requires C, 75·9: H, 3·8%), somewhat soluble in anisole and insoluble in dilute aqueous sodium hydroxide when boiled for a short time; the dark red anisole solution gives no methane with methylmagnesium iodide.

1′ : 4′-*Diacetoxy*-3 : 4-*dihydronaphtho*(2′ : 3′-1 : 2)-9-*thiafluorene*, needles (from benzene), m. p. 253—254°, was formed by reduction with zinc dust and anhydrous sodium acetate in acetic anhydride (Found: C, 71·6; H, 4·74. $C_{24}H_{18}O_4S$ requires C, 71·6; H, 4·5%).

*Naphtho*(2′ : 3′-1 : 2)-9-*thiafluorene*-1′ : 4′-*quinone* (X), pale brow nneedles, m. p. 273—274°, was formed (0·11 g.) when the compound (IX) (0·16 g.) and chloranil (0·13 g.) in xylene (10·0 ml.) were refluxed for 10 hr. It separated on cooling and recrystallised from acetic acid (Found: C, 76·1; H, 3·3. $C_{20}H_{10}O_2S$ requires C, 76·4; H, 3·2%). Its reductive acetylation gave 1′ : 4′-*diacetoxy*-9-*thianaphtho*(2′ : 3′-1 : 2)*fluorene*, pale yellow prisms (from benzene), m. p. 310—311° (Found: C, 71·7; H, 4·2. $C_{24}H_{16}O_4S$ requires C, 72·0; H, 4·0%).

*Reduction of Naphtho*(2′ : 3′-1 : 2)-9-*thiafluorene*-1′ : 4′-*quinone*.—To the quinone (X) (0·3 g.), suspended in refluxing glacial acetic acid (50 ml.), was added dropwise (10 min.) a solution of stannous chloride (1·2 g.) in concentrated hydrochloric acid (6·0 ml.). Refluxing was continued until the quinone was completely dissolved (2 hr.). The cold solution deposited the *anthrone*, which crystallised from benzene in orange prisms (0·15 g., 51%), m. p. 208—210° (Found: C, 79·7; H, 3·1. $C_{20}H_{12}OS$ requires C, 80·0; H, 4·0%). It (0·1 g.) was refluxed for 10 hr. with zinc dust (0·4 g.) (which had been treated with 0·1% copper sulphate solution for 5 min.) in 2N-sodium hydroxide (10 ml.) under toluene (5 ml.). The toluene layer was separated, the aqueous layer extracted once with benzene, and the residue from the combined extracts crystallised from benzene (charcoal), giving cream plates (0·05 g., 53%) of *naphtho*(2′ : 3′-1 : 2)-9-*thiafluorene*, m. p. 226—226·5° (Found: C, 84·5; H, 4·4. $C_{20}H_{12}S$ requires C, 84·5; H, 4·2%).

*Reaction of* 3-*Vinylthionaphthen with Other Quinones*.—(*a*) Juglone (2·0 g.) and 3-vinylthionaphthen (1·0 g.) in acetic acid (10·0 ml.) were heated on the water-bath for 6 hr., and the ether-washed product from the cold solution recrystallised from benzene in deep-red needles (0·75 g., 33%) of 5′(or 8′)-*hydroxynaphtho*(2′ : 3′-1 : 2)-9-*thiafluorene*-1′ : 4′-*quinone* (XI), m. p. 267—268° (decomp.) (Found: C, 72·3; H, 3·8. $C_{20}H_{12}O_3S$ requires C, 72·3; H, 3·6%).

When this quinone (0·06 g.) in acetic anhydride (2·0 ml.) containing pyridine (2 drops) was heated on the water-bath for 4 hr., the colour changed from deep-red to pale yellow. The crystals from the cold solution recrystallised from benzene in yellow needles of the *acetate*, m. p. 288—289° (decomp.) (Found: C, 71·0; H, 3·5. $C_{22}H_{12}O_4S$ requires C, 70·9; H, 3·2%).

(*b*) Juglone acetate [7] (0·5 g.), dissolved in acetic acid (7·0 ml.), was added to 3-vinylthionaphthen (0·5 g.) in acetic acid (2·0 ml.) at room temperature. Pale yellow crystals began to separate after 10 min. The solution was kept overnight, then filtered, giving yellow needles (0·66 g., 76%), m. p. 206—207°. Long heating in acetic acid gave a red colour and a less pure product, but rapid recrystallisation from acetic acid gave pale yellow needles of 1 : 2 : 3 : 10-*tetrahydro*-5′(*or* 8′)-*acetoxynaphtho*(2′ : 3′-1 : 2)-9-*thiafluorene*-1′ : 4′-*quinone* (XI), m. p. 209—210° (Found: C, 69·6; H, 4·3; O, 17·2; S, 8·5. $C_{22}H_{16}O_4S$ requires C, 70·2; H, 4·2; O, 17·0; S, 8·5%). It is readily soluble in anisole, and has no active hydrogen, it is insoluble in cold aqueous sodium hydroxide, but in boiling alkali gives a red solution.

5′(*or* 8′)-*Acetoxy*-3 : 4-*dihydronaphtho*(2′ : 3′-1 : 2)-9-*thiafluorene*-1′ : 4′-*quinone* (XIII) (0·08 g.) separated in two weeks on exposure to air of the mother-liquors from the above adduct, and crystallised from anisole or acetic acid in red-purple needles, m. p. 294—295°, which have no

---

[11] Fieser, *Org. Synth.*, Coll. Vol. II, p. 430; Coll. Vol. I, p. 383; Braude and Fawcett, *ibid.*, Vol. XXXIII, p. 50.

active hydrogen (Found: C, 70·8; H, 3·7. $C_{22}H_{14}O_4S$ requires C, 70·6; H, 3·7%). It is more readily prepared (70% yield) by atmospheric oxidation of the hydrolysate obtained by refluxing for about ½ hr. the adduct (XII) with boiling acetic acid containing a little concentrated hydrochloric acid. This oxidation with benzoquinone is immediate. The adduct (XII) (0·25 g.) and chloranil (0·36 g.) in xylene (8·0 ml.) were refluxed until a copious yellow precipitate separated (10 min.). The product (XI; R = OAc, R′ = H or *vice versa*) recrystallised from xylene in yellow needles (0·21 g., 85%), m. p. and mixed m. p. 289·5—290° (Found: C, 71·2; H, 3·4; S, 8·6. Calc. for $C_{22}H_{12}O_4S$: C, 70·9; H, 3·2; S, 8·6%).

(*c*) Lawsone acetate [12] (0·25 g.) and 3-vinylthionaphthen (0·25 g.) in acetic acid (2·5 ml.) were heated on the water-bath for 4 hr., and the product recrystallised from acetic acid, in pale-brown needles (0·15 g.) of naphtho(2′ : 3′-1 : 2)-9-thiafluorene-1′ : 4′-quinone (X), m. p. and mixed m. p. 270—271° (Found: C, 75·9; H, 3·4. Calc. for $C_{20}H_{10}O_2S$: C, 76·4; H, 3·2%). Lawsone itself was recovered when treated with 3-vinylthionaphthen under these conditions.

*Reaction of* 3-*Vinylthionaphthen with Maleic Anhydride.*—3-Vinylthionaphthen (3·2 g.) and maleic anhydride (2·0 g.) in dry benzene (35 ml.) containing quinol (0·05 g.) were refluxed for 6 hr. (water-bath). Colourless plates of 2 : 3 : 4 : 12-*tetrahydrodibenzothiophen*-3 : 4-*dicarboxylic anhydride* (XIV), m. p. 194—195°, separated on cooling (Found: C, 64·7; H, 4·1. $C_{14}H_{10}O_3S$ requires C, 65·1; H, 3·9%). This is rapidly decomposed to soluble products by boiling acetic acid. Its chloroform solution immediately decolorised a dilute solution of bromine.

The adduct (0·25 g.) was refluxed for 30 min. in acetic anhydride (2·5 ml.) and acetic acid (2·5 ml.) saturated with hydrogen chloride. The solution was cooled and diluted with ice water. The precipitate recrystallised from ethyl acetate in prisms (0·20 g.) of 1 : 2 : 3 : 4-*tetrahydrodibenzothiophen*-3 : 4-*dicarboxylic acid* (XV), m. p. 236—237° (Found: C, 61·1; H, 4·4. $C_{14}H_{12}O_3S$ requires C, 60·9; H, 4·3%). Bromine in chloroform did not decolorise the acid, which is also obtained by brief treatment of the above adduct with hot dilute sodium hydroxide solution.

A mixture of the original adduct (0·8 g.) and selenium (0·6 g.) was heated at 300—305° in a cold-finger sublimation apparatus for 6 hr., and the crystalline sublimate recrystallised from carbon tetrachloride in pale yellow needles (0·53 g.) of *dibenzothiophen*-3 : 4-*dicarboxylic anhydride*, m. p. 288—289° (Found: C, 66·0; H, 2·6. $C_{14}H_6O_3S$ requires C, 66·1; H, 2·4%). This anhydride (0·25 g.), mixed with barium hydroxide (1·0 g.) and copper bronze (0·3 g.), was heated in the sublimation apparatus at 30 mm., the temperature being slowly raised from 180° to 350° (35 min.) and kept at 350° for 30 min. The yellow sublimate was recrystallised twice from ethanol (charcoal), giving dibenzothiophen (0·03 g.), m. p. and mixed m. p. 99—100°.

*Reaction of* 3-*Vinylthionaphthen with Thionaphthen* 1 : 1-*Dioxide.*—The dioxide (0·5 g.), 3-vinylthionaphthen (1·0 g.), and quinol (20 mg.) were refluxed in toluene (4·0 ml.) for 8 hr. The product recrystallised from benzene in prisms (0·64 g., 65%) of 1 : 2 : 5 : 6-*tetrahydrodithionaphtheno*(2′ : 3′-1 : 2)(2″ : 3″-3 : 4)*benzene* 1′ : 1′-*dioxide* (XVI), m. p. 263—264° (Found: C, 66·5; H, 4·4; S, 19·3. $C_{18}H_{14}O_2S_2$ requires C, 66·3; H, 4·3; S, 19·6%).

This sulphone (1·0 g.) was extracted from a Soxhlet thimble with tetrahydrofuran (100 ml.) on to a solution of lithium aluminium hydride (1·0 g.) for 10 hr. The excess of hydride was decomposed as usual, and the dried organic layer evaporated, giving a pale brown oil (0·87 g.), which was heated with selenium (0·9 g.) at 310—315° for 7 hr. The cooled mixture was extracted with benzene, and the solution was decolorised (charcoal), yielding *dithionaphtheno*-(2′ : 3′-1 : 2)(2″ : 3″-3 : 4)*benzene* (XVII), needles (0·65 g.) [from light petroleum (b. p. 60—80°)], m. p. 165·5—166° (Found: C, 74·1; H, 3·5. $C_{18}H_{10}S_2$ requires C, 74·5; H, 3·4%). This (0·4 g.) was refluxed with Raney nickel (3·5 g.) in ethanol (100 ml.) for 10 hr.; filtration and concentration gave *m*-terphenyl (0·17 g.), m. p. and mixed m. p. 88—89°, undepressed when admixed with a genuine sample.

*Reactions of* 3-cyclo*Hex*-1′-*enylthionaphthen.*—(i) 3-*cyclo*Hex-1′-enylthionaphthen (XVIII) (2·1 g.) and *p*-benzoquinone (4·3 g.) were heated in acetic acid (20 ml.) on the water-bath for 9 hr., and the precipitate formed on cooling was washed with ethanol and recrystallised (from benzene or anisole), giving crimson needles (2·4 g., 75%) of 5′ : 6′ : 7′ : 8′-*tetrahydrophenanthra*-(9′ : 10′-2 : 3)*thionaphthen*-1′ : 4′-*quinone* (XIX), m. p. 268—269°. This has no active hydrogen atom and is not attacked on brief boiling with aqueous-alcoholic sodium hydroxide (Found: C, 75·5; H, 4·6. $C_{20}H_{14}O_2S$ requires C, 75·4; H, 4·4%). The same compound resulted (25%)

---

[12] Macbeth, Price, and Winzor, *J.*, 1935, 334.

from the similar interaction of 1 mol. of *p*-benzoquinone with 1·5 mol. of 3-*cyclo*hex-1′-enylthionaphthen.

(ii) 1 : 4-Naphthaquinone (2·4 g.) and 3-*cyclo*hex-1′-enylthionaphthen (1·0 g.) in acetic acid (12·0 ml.) at 100° during 6 hr. gave, on cooling, a very sparingly soluble precipitate of the *quinone* (XX), which recrystallised from benzene in orange needles (1·1 g., 61%), m. p. 320—321° (Found: C, 78·5; H, 4·6. $C_{24}H_{16}O_2S$ requires C, 78·3; H, 4·3%). This was similarly produced (19%) in 20 min. when excess of the thionaphthen was used. It has no active hydrogen, is not attacked by brief boiling with aqueous-alcoholic sodium hydroxide, and is recovered unchanged after 70 minutes' refluxing in acetic acid containing hydrochloric acid. Associate Professor A. N. Hambly reports that the infrared spectrum gives strong support to the structure (XX) " in that the methylene absorption is the strongest absorption in the C–H stretching region, while the carbonyl bond is single as found with quinones and not double as found with diketones."

This quinone was not reduced to the anthrone by stannous chloride and hydrochloric acid in boiling acetic or propionic acid, or by copper-coated zinc dust in boiling 2N-sodium hydroxide.

The authors are indebted to Dr. F. L. Winzor for a specimen of lawsone, Associate Professor A. N. Hambly for infrared-spectral determinations, Mr. R. G. Cooke for helpful discussions, the Anti-Cancer Council of Victoria for financial aid, and Monsanto Chemicals (Aust.) for a scholarship (to Q. N. P.). The microanalyses were made by Dr. W. Zimmerman and his staff.

UNIVERSITY OF MELBOURNE, AUSTRALIA.

[*Received, July* 9*th*, 1957.]