# 912. *The Direct Conversion of Thionaphthen into Derivatives of 9-Thiafluorene.*

By W. Davies, N. W. Gamble, and W. E. Savige.

9-Thia-3 : 4-benzofluorene (V) has been isolated by distillation of the crude product obtained from thionaphthen by hydrogen peroxide. The thionaphthen 1 : 1-dioxide (II) made essentially according to Bordwell, Lampert, and McKellin (*J. Amer. Chem. Soc.*, 1949, **71**, 1702) contained about 2% of the dioxide (III) of (V). The regulated action of heat on (II) gave 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (IV) and an isomeric substance. The structure of these compounds, except of the last, has been proved.

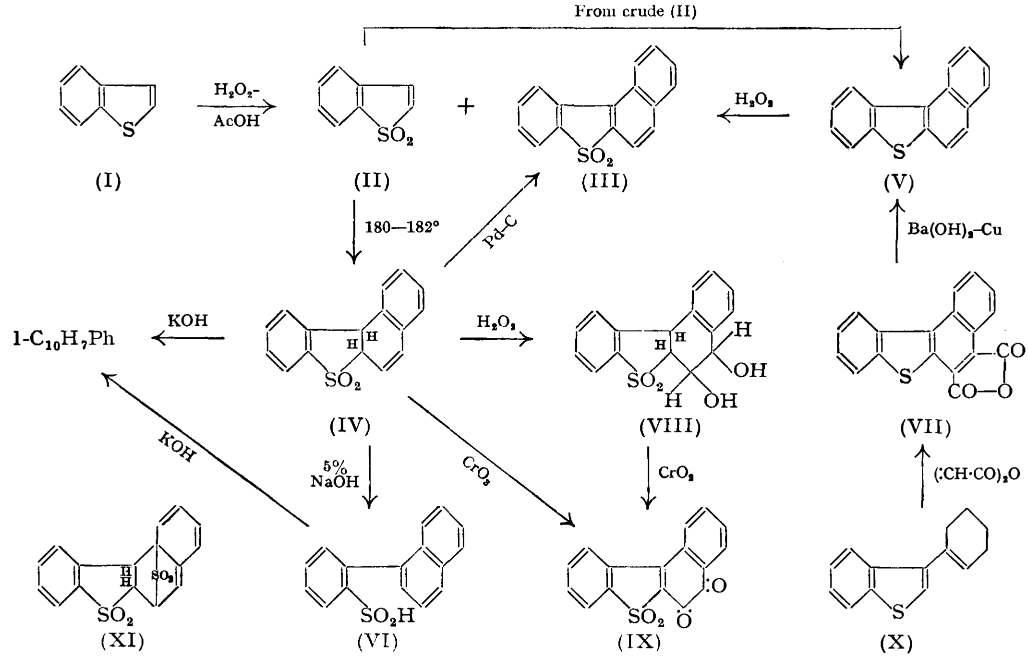
In one experiment (Savige, Thesis, Melbourne, 1951), distillation of the reaction product from thionaphthen (I) and hydrogen peroxide gave much unchanged (I) and >10% of a thiahydrocarbon $C_{16}H_{10}S$, m. p. 103·5°. The constitution, 9-thia-3 : 4-benzofluorene (V) tentatively given to this compound (*loc. cit.*) has now been verified. Repetition of the experiment gave no or very small yields of this material, a difficulty characteristic of oxidations involving free radicals, but the compound was obtained by pyrolysis of thionaphthen 1 : 1-dioxide at 195—200°.

The preparation of thionaphthen dioxide (II) has been described several times, most recently by Bordwell, Lampert, and McKellin (*J. Amer. Chem. Soc.*, 1949, **71**, 1702). We find that under their conditions sulphuric acid is also produced, together with about 2% of 3 : 4-benzo-9-thiafluorene 1 : 1-dioxide (III), the sulphone from (V). Formation of (III) is not a typical pyrolytic process, as the temperature during the oxidation does not exceed 110°. An isomer, m. p. 197°, of (III) has also been obtained in very small yield by heating (II) at 195°. However, apart from sulphur dioxide, the main pyrolysis product of (II), readily obtained in 88% yield in tetralin at 180—182°, is 10 : 11-dihydro-9-thia-3 : 4-benzofluorene 9 : 9-dioxide (IV), which has recently been prepared similarly by Bordwell, McKellin, and Babcock (*ibid.*, 1951, **73**, 5566). This paper arrived in Melbourne after the present work was complete (Gamble, Thesis, Melbourne, 1952).

The only tetracyclic compound to be directly synthesised from the thionaphthen nucleus by the American workers was (IV), which they converted by bromine into (III), whence they obtained (V) by lithium aluminium hydride. It is evident from the present work, however, that a number of tetracycles derived from two thionaphthen nuclei are obtained during the preparation and/or pyrolysis of (II). Interaction of thiophen with hydrogen peroxide is similarly complex (Davies, Gamble, James, and Savige, *Chem. and Ind.*, 1952, 804), and one of the products, $C_8H_8O_3S_2$, is readily transformed by heat into (II).

9-Thia-3 : 4-benzofluorene (V), m. p. 103·5°, was synthesised by hydrolytic decarboxylation of the aromatised adduct (VII) (Szmuskovicz and Modest, *J. Amer. Chem. Soc.*, 1950, **72**, 574) of maleic anhydride and 3-*cyclo*hex-1′-enylthionaphthen (X). The m. p. 173·7—175·2° ascribed to an impure compound thought to be (V) by Neumoyer and Amstutz (*ibid.*, 1944, **66**, 1680) is erroneous.

The structure of (IV) follows by its dehydrogenation to (III), which is obtained from (V) by hydrogen peroxide. This proof is supported by degradation of (IV) to 1-phenylnaphthalene in 79% yield by fission in concentrated alkali. 1-Phenylnaphthalene is also formed by similar treatment of 1-*o*-sulphinophenylnaphthalene (VI) which is obtained from (IV) by dilute alkali. Bordwell, McKellin, and Babcock (*loc. cit.*) effected the same degradation, but doubted the evidence thus afforded of the fine structure of (IV). We do not subscribe to their statement " The position of the double bond in (IV) has not as yet been established," since the formation of a sulphinic acid proves that (IV) has the $-SO_2\cdot\dot{C}H\cdot\dot{C}H\cdot$ group. Thus, the alkaline cleavage of some dialkyl sulphones yields an olefin and an alkanesulphinate, and phenyl 2-phenylethyl sulphone gives styrene almost quantitatively together with benzenesulphinic acid or its decomposition products (Fenton and Ingold, *J.*, 1929, 2338; 1930, 706).



It is pertinent that the sulphinic acid (VI) obtained by Bordwell, McKellin, and Babcock (*loc. cit.*) may be impure, as it has m. p. 116—118° instead of 129° : and the hydrogen content found for their dihydro-derivative, m. p. 121—122°, from (VI) is, within experimental error, that required for (VI) itself (Found : H, 4·8. Calc. for $C_{16}H_{14}O_2S$ : H, 5·2. Calc. for $C_{16}H_{12}O_2S$ : 4·5%). In any event, our proof that the hydrolysis of (IV) by mild alkali gives a sulphinic acid is doubly important, as it shows that the $SO_2H$ group (and the $SO_3H$ group formed from it by oxidation) are in the 2-position of the phenyl group and not in the naphthyl group. Moreover, fission of (III) with alkali gives a sulphonic acid identical with that obtained by oxidation of the sulphinic acid (VI) : this fission to a sulphonic acid is, when it can be effected, characteristic of completely aromatic sulphones, *e.g.*, diphenyl sulphone forms benzenesulphonic acid and benzene (Ingold and Jessop, *J.*, 1930, 707).

From this evidence of the position of the 10 : 11-hydrogen atoms in (IV) it follows that the double bond is in the 1 : 2-position, which is confirmed by oxidation of (IV) to an *o*-quinone (IX). Moreover, (IV) and hydrogen peroxide give a compound regarded as (VIII), which is also oxidised by chromic acid to (IX). The azine from the *o*-quinone (IX) and *o*-phenylenediamine is, curiously, less coloured and more soluble in glacial acetic acid than is its precursor (IX).

As Bordwell, McKellin, and Babcock point out (*loc. cit.*), the Diels-Alder adduct in the transformation of (II) into (IV) by heat is probably (XI). In hydrogen peroxide, however, there are other possibilities, for example, self-condensation of two thionaphthen nuclei may entail preliminary adducts of type (XI) but with a S or perhaps a SO bridge instead of $SO_2$. Such bridges could doubtless be readily lost in the oxidising environment, as sulphuric acid is the usual concomitant of the dimerised compound obtained by the hydrogen peroxide oxidation of thiophen or thionaphthen. It is unfortunate that attempts to prepare thionaphthen 1-oxide failed.

## EXPERIMENTAL

Thionaphthen, from L. Light & Co. Ltd., Bucks., had m. p. 31·2—31·4°, b. p. 221—222°/774 mm. (Found : S, 23·9, 23·9. Calc. for $C_8H_6S$ : S, 23·9%).

*Preparation of* 9-*Thia*-3 : 4-*benzofluorene* (V).—(i) *Oxidation of thionaphthen.* To thionaphthen (5 g.) in acetic acid (10 ml.) and acetic anhydride (1 ml.), warmed on the water-bath, 30% hydrogen peroxide (10 ml.) was added at such a rate that the mixture remained homogeneous. After 4 hours, the odour of thionaphthen was still apparent, and addition of water gave a dark oil. Extraction with chloroform, drying ($CaCl_2$), and distillation at reduced pressure (contrary to Lanfry, *Compt. rend.*, 1912, **154**, 519, thionaphthen dioxide does not sublime readily at 1 atm.) gave unchanged thionaphthen (*ca.* 3 g.), b. p. 112°/15 mm., and 9-thia-3 : 4-benzofluorene (V) (*ca.* 1 g.), b. p. 280°/15 mm., pale yellow needles, m. p. 103·5° (from light petroleum containing a few drops of benzene) (Found : C, 81·85, 82·8; H, 3·7, 4·25; S, 14·1. Calc. for $C_{16}H_{10}S$ : C, 82·05; H, 4·25; S, 13·7%).

Most subsequent experiments gave little or no yield or a very low one of (V). However, a much smaller yield of (V) was obtained as follows. To thionaphthen (5 g.), acetic acid (20 ml.), and acetic anhydride (1 ml.), at *ca.* 97° (water-bath), hydrogen peroxide (30% ; 1 ml.) was added. After 5 minutes the solution became pink, and in 15 minutes deep brown-red. A further 2½ ml. of peroxide were added in ½-ml. portions at 15 minute intervals and heating was discontinued after a total of 4½ hours; the solution was chocolate-brown and a small amount of heavy black oil had separated. After 12 hours the product was poured into water (300 ml.) and extracted with chloroform (3 × 50 ml.). Drying ($MgSO_4$) and distillation gave thionaphthen (*ca.* 2 g.), b. p. 108—112°/25 mm., m. p. and mixed m. p. 32°, then 9-thia-3 : 4-benzofluorene (0·5 g.), b. p. *ca.* 220/0·2 mm., which when recrystallised from aqueous alcohol or light petroleum (b. p. 70—95°) was identical (mixed m. p.) with the above specimen.

(ii) *By the action of heat on thionaphthen dioxide* (II). The dioxide (2 g.) was heated at 195—200° for 1 hour, the black glass-like solid which formed on cooling was powdered and extracted with boiling benzene (100 ml.), and to the hot filtered solution absolute alcohol (100 c.c.) was added. The filtrate from the dark green solid which separated on cooling was allowed to evaporate at room temperatures, leaving pale brown needles (*ca.* 0·1 g.) which recrystallised in needles (m. p. 103·5°) identical (mixed m. p.) with the original specimen of (V) (Found : C, 81·85; H, 4·4; S, 13·5%).

(iii) *Rational synthesis.* 3-Bromothionaphthen (21 g.; made according to Crook and Davies, *J.*, 1937, 1698) and a few drops of methyl iodide on this occasion reacted vigorously in ether with magnesium (2·5 g.; contrast Crook and Davies, and Szmuzkovicz and Modest, *locc. cit.*), and the reagent formed in 3 hours condensed sufficiently with *cyclo*hexanone (10·6 g.) in 8 hours to give a 66% yield of 3-*cyclo*hex-1′-enylthionaphthen (X). The adduct with maleic anhydride required heating with sulphur at 260° for 1·25 hours (contrast Szmuszkovicz and Modest, *loc. cit.*) before evolution of hydrogen sulphide ceased. The sublimed product (0·5 g.; orange needles) was thoroughly ground with crystalline barium hydroxide (2 g.) and copper bronze (0·7 g.) and heated at 200° in a horizontal Pyrex tube until all water of crystallisation had been expelled. A capillary tube was then attached to the Pyrex tube which was heated at *ca.* 350° and gentle suction applied until no more yellow oil distilled away from the hot part of the tube. The oil solidified to long yellow needles, m. p. 99—101° (0·37 g.), and when crystallised from ethanol had m. p. 102—103°, alone or mixed with (V).

*Other Attempted Syntheses of* 9-*Thia*-3 : 4-*benzofluorene*.—(i) *From* 1-*phenylnaphthalene*. Two compounds with approximately the desired m. p. were obtained by the interaction of 1-phenylnaphthalene (2 g.) and sulphur (0·6 g.). To this mixture at 120° powdered anhydrous aluminium chloride (0·08 g.) was added during 1 hour, and the temperature raised to 140° during 3¼ hours. Though evolution of hydrogen sulphide had not ceased, the mixture was cooled, and extracted with boiling water (2 × 5 ml.), and then ethanol (8 × 5 ml.). The alcoholic extract yielded a brown residue (0·7 g.), which after five recrystallisations from light petroleum (b. p. 30—90°), in which it is easily soluble, gave *di*-1-*phenylnaphth*-x-*yl sulphide* as colourless plates with constant m. p. 99—100° (Found : C, 87·7; H, 5·4; S, 7·5. $C_{32}H_{22}S$ requires C, 87·7; H, 5·0; S, 7·3%). When the temperature was raised to 260° during 8 hours (no more hydrogen sulphide evolved), the alcoholic extract gave yellow needles (m. p. 103—105°), mixed m. p. with (V) 70—80°, in insufficient amount to admit of complete purification (Found : C, 90·8; H, 5·8%).

(ii) *From diazotised* 2-*aminophenyl* β-*naphthyl sulphide*. β-*Naphthyl* o-*nitrophenyl sulphide*, yellow needles (from alcohol), m. p. 92—93°, separated (3·7 g.; 90% yield) in 12 hours at room temperature after 4 hours' refluxing of *o*-chloronitrobenzene (2·25 g.) and naphthalene-2-thiol (2·25 g.) in 30% aqueous sodium hydroxide solution (7 ml.) and ethanol (5 ml.) (Found : C, 68·45; H, 3·9; S, 11·6. $C_{16}H_{11}O_2NS$ requires C, 68·3; H, 3·9; S, 11·4%). Attempted reduction with aqueous-alcoholic sodium hydrosulphite (dithionite) gave much unchanged material, tin and hydrochloric acid gave naphthalene-2-thiol, and hot ammoniacal aqueous-alcoholic ferrous sulphate produced a yellow solid, m. p. 144—146°; no primary aromatic amine was isolated.

β-Naphthyl *o*-nitrophenyl sulphide (3 g.) was reduced when added slowly to acetic acid (95%, 10 ml.) and iron filings (7 g.) on the water-bath, and heating continued for an hour whilst the volume was kept constant by addition of water (10 ml.). A further 20 ml. of water was finally added, the solution neutralised ($Na_2CO_3$), and the precipitate washed with boiling alcohol (3 × 50 ml.), yielding o-*aminophenyl* β-*naphthyl sulphide* (93%), orange-yellow needles, m. p. 74—75° (from aqueous alcohol) (Found : C, 76·7; H, 5·2; N, 5·4. $C_{16}H_{13}NS$ requires C, 76·5; H, 5·2; N, 5·6%). This base in dilute sulphuric acid readily gave a diazo-solution, which yielded only tars on addition of copper powder or when it was added to boiling 50% sulphuric acid or to sodium naphthalene-1-sulphonate (cf. Hodgson and Marsden, *J.*, 1940, 209).

*Attempted Preparation of Thionaphthen* 1-*Oxide*.—Thionaphthen and fuming nitric acid in acetic acid at <40° gave only the steam-volatile 3-nitrothionaphthen, m. p. 79° (55%) (Found : C, 53·9; H, 2·7; S, 18·0. Calc. for $C_8H_5O_2NS$ : C, 53·6; H, 2·8; S, 17·9%). Use of concentrated nitric and sulphuric acids at <40° gave a tar. Chlorine in carbon tetrachloride at 0° attacked the nucleus and not the sulphur atom, giving 3 : 5-dichlorothionaphthen (66%), m. p. 55·5° (Schlesinger and Mowry, *J. Amer. Chem. Soc.*, 1951, **73**, 2614, give m. p. 55·5—56·5°) (Found : C, 47·5; H, 2·2; S, 16·1. Calc. for $C_8H_4O_2SCl_2$ : C, 47·5; H, 2·0; S, 15·8%).

*Oxidation of Thionaphthen with Hydrogen Peroxide*.—To (I) (50 g.) in acetic acid (300 ml.) 30% hydrogen peroxide (225 ml.) was added, and the solution was refluxed for 15 minutes (care). The temperature throughout was between 106° and 110°. Pouring the cooled solution into cold water (1 l.) gave a pale yellow precipitate which was collected after 12 hours, washed with water, extracted with boiling water (3 × 1 l.), and filtered at the b. p. The filtrates on cooling gave almost white needles of the sulphone, m. p. 140—141° (46·4 g.), and concentration of the mother-liquors to 400 ml. gave a further 4·6 g. The water-insoluble yellow residue was dissolved in boiling absolute alcohol (200 ml.), which was filtered hot and on cooling gave yellow needles, m. p. 232—233° (0·65 g.) and on evaporation a further 0·35 g. Recrystallisation from absolute alcohol gave 9-thia-3 : 4-benzofluorene 9 : 9-dioxide, pale yellow needles, m. p. 233·5—234° (Bordwell, McKellin, and Babcock, *loc. cit.*, 1951, record m. p. 228—229°) (Found: C, 72·0; H, 3·8; S, 12·2. Calc. for $C_{16}H_{10}O_2S$: C, 72·2; H, 3·75; S, 12·0%). The m. p. was undepressed on admixture with the sulphone (m. p. 234°) obtained by heating synthetic (V) for 15 minutes with hydrogen peroxide in acetic acid.

10 : 11-*Dihydro*-9-*thia*-3 : 4-*benzofluorene* 1 : 1-*Dioxide* (IV).—Sulphur dioxide was formed when approx. equimolar quantities of thionaphthen (I) and its dioxide (II) were heated at 185—190°. After 15 minutes the product was distilled, and (I) was removed (b. p. 60—70°/0·2 mm.); the fraction, b. p. 240°/0·2 mm., solidified and after being washed with hot light petroleum had m. p. 176—179°. Recrystallisation (from alcohol) gave colourless needles, m. p. 182°, readily soluble in acetone and alcohol, very sparingly soluble in light petroleum (b. p. 70—95°); the crystals had a pale blue fluorescence and the solutions a strong purple fluorescence in ultra-violet light (Found: C, 71·6; H, 4·5; S, 11·6. Calc. for $C_{16}H_{12}O_2S$: C, 71·65; H, 4·5; S, 11·9%) (Bordwell, McKellin, and Babcock, *locc. cit.*, record m. p. 181—182° and 183—184°).

The process is a preparative one when 12 g. each of (I) and of (II) are heated together at 180—190° for an hour until the evolution of gas has almost ceased; (I) (10·9 g.) is distilled off in steam, and the residue filtered hot. The filtrate on cooling gives pale pink needles of essentially pure (II) (m. p. 138—139°; 2·8 g.) and the precipitate (m. p. 175—179°; 7·0 g.) gives pure (IV) (from ethanol). The best yield (8·2 g.) is obtained when (II) (11·5 g.) is heated with tetralin (6 ml.) for 90 minutes in a bath of boiling aniline and the crystals collected on cooling. The dihydro-compound (IV) was not easily dehydrogenated, as it was recovered unchanged from refluxing xylene containing chloranil (6 hours), aqueous ethanol containing potassium acetate and iodine (5 hours), and *p*-cymene containing 5% palladium–charcoal (6 hours). 20% Palladium–charcoal in boiling cymene gave, after filtration hot, a mixture of yellow crystals which, when recrystallised very slowly from ethanol, were seen to consist of colourless cubes and yellow needles. The cubes which were removed by hand were unchanged (IV) (m. p. and mixed m. p. 181—182°) and the needles on recrystallisation from ethanol had m. p. 234° alone and when mixed with 9-thia-3 : 4-benzofluorene 1 : 1-dioxide (III) (Found: C, 72·2; H, 3·95. Calc. for $C_{16}H_{10}O_2S$: C, 72·2; H, 3·75%).

*Oxidation of* 10 : 11-*Dihydro*-9-*thia*-3 : 4-*benzofluorene* 1 : 1-*Dioxide* (IV).—The oxide is stable to boiling aqueous neutral potassium permanganate, but is attacked by permanganate containing sodium carbonate, and by permanganate in dry acetone. Apart from unchanged (IV), no organic compound was isolated. However, 1 : 2-*dihydro*-1 : 2-*diketo*-9-*thia*-3 : 4-*benzofluorene* 1 : 1-*dioxide* (IX), orange crystals (0·3 g.), m. p. 329—330° (from 2-methoxy-ethanol), was formed exothermally when (IV) (1·0 g.) was heated with chromic acid (1·5 g.) in acetic acid (9·5 ml.) and water (0·5 ml.) (Found: C, 65·3; H, 2·9; S, 10·9. $C_{16}H_8O_4S$ requires C, 64·9; H, 2·7; S, 10·8%). A suspension of this in hot glacial acetic acid reacted immediately with *o*-phenylenediamine, giving the *quinoxaline*, m. p. 296° (from alcohol) (Found: C, 71·8; H, 3·3. $C_{22}H_{12}O_2N_2S_2$ requires C, 71·7; H, 3·3%). Reductive acetylation (acetic anhydride, 5 ml.; anhydrous sodium acetate, 0·1 g.; zinc dust, 0·2 g.; 4 hours) yielded 1 : 2-*diacetoxy*-9-*thia*-3 : 4-*benzofluorene* 1 : 1-*dioxide* which crystallised from ethanol in colourless needles, m. p. 280—281° (Found: C, 62·6; H, 4·2. $C_{20}H_{16}O_6S$ requires C, 62·5; H, 4·2%), very soluble in anisole or benzene, less so in ethanol, and still less in light petroleum (b. p. 100—120°). These solutions in ultra-violet light give a fluorescence which in ethanol or light petroleum is pale blue, but in benzene is true blue and so intense that it is visible in diffused daylight.

*Interaction of* (IV) *with Hydrogen Peroxide*.—Hydrogen peroxide (4·5 ml. of 30%) in acetic acid (6 ml.) containing (IV) (1·0 g.) was heated under reflux. After an hour the solution was cooled and deposited white flakes (0·85 g.), m. p. 197—199°, of 10 : 11-*dihydro*-1 : 2-*dihydroxy*-9-*thia*-3 : 4-*benzofluorene* 1 : 1-*dioxide* (VIII), m. p. 201° [from light petroleum (b. p. 100—150°)] (Found: C, 63·2; H, 4·65. $C_{16}H_{14}O_4S$ requires C, 63·6; H, 4·6%). Equal weights of this and chromic acid in hot acetic acid immediately gave orange crystals, m. p. 327—329° [328—330° when mixed with (IX)].

*Degradation of* (IV).—The dioxide (IV) (1 g.) gradually dissolved in boiling aqueous sodium hydroxide (5%; 30 ml.) and, after 1 hour, was concentrated to about 15 ml., cooled, and acidified with concentrated hydrochloric acid as soon as crystallisation of the colourless sodium sulphinate began. The precipitated brown viscous oil solidified at 0° and after being washed had m. p. 126—128° (0·75 g.). After recrystallisation from acetone and then acetone–light petroleum 1-o-*sulphinophenylnaphthalene*, m. p. 129°, separated in colourless needles which in several days become superficially brown (Found: C, 71·3; H, 4·5; S, 11·8. Calc. for $C_{16}H_{12}O_2S$: C, 71·65; H, 4·45; S, 11·9%). It dissolved in saturated sodium hydrogen carbonate solution, and was characterised as a sulphinic acid by formation of a red-brown precipitate with neutral aqueous-alcoholic ferric chloride, production of a violet colour with anisole in cold concentrated sulphuric acid, and extensive precipitation, by a moderate excess of sodium hydroxide, of the sodium salt from its solution in cold water.

1-*Phenylnaphthalene*.—When equal weights of (IV) and powdered potassium hydroxide were very carefully heated until fusion just occurred, the yield of (VII) was 92%, and no sulphur dioxide was observed on acidification of the aqueous solution of the fusion mixture, and no 1-phenylnaphthalene was formed. This, however, was the main product, b. p. 185°/25 mm., $n_D^{16 \cdot 5}$ 1·6678 (1·2 g.), when (IV) (2 g.) and powdered potassium hydroxide (2 g.) were fused in a small distilling flask and heated until no more liquid distilled. The phenylnaphthalene was further purified by separating it (by centrifuge) in crystalline form from the solution in absolute alcohol cooled in carbon dioxide–acetone and then had b. p. 182°/15 mm., $n_D^{18}$ 1·6692. With fuming nitric acid in acetic acid at room temperature it gave 4-nitro-1-phenylnaphthalene, of which the m. p. (126—127°) could not be improved, although the m. p. 132° is recorded, probably of a purer specimen (Beilstein, 2nd Suppl., Vol. V, p. 603) (Found : C, 77·1; H, 4·35; N, 5·8. Calc. for $C_{16}H_{11}O_2N$ : C, 77·1; H, 4·4; N, 5·6%). Authentic 1-phenylnaphthalene (Weiss, *Org. Synth.*, **24**, 84) (from α-tetralone) had $n_D^{20}$ 1·6682, and both specimens gave a mononitro-derivative, m. p. and mixed m. p. 126—127°. With bromine (5 drops) in carbon disulphide (5 ml.) the hydrocarbon gave 1-*p*-bromophenylnaphthalene, plates (from ethanol), m. p. 75—76° (cf. Beilstein, *loc. cit.*) (Found : C, 67·6; H, 3·95; Br, 29·0. Calc. for $C_{16}H_{11}Br$ : C, 67·8; H, 3·9; Br, 28·3%).

1-o-*Sulphophenylnaphthalene*.—A suspension of (IV) (1·6 g.) in 5% sodium hydroxide solution (15 ml.) became clear when refluxed for 15 minutes, and then a hot concentrated solution of potassium permanganate was added until the colour became permanent. The colour was discharged with sulphur dioxide and the filtered solution acidified with concentrated hydrochloric acid. On cooling, the solution deposited 1-o-*sulphophenylnaphthalene*, plates (1·7 g.), m. p. 146—147° (from benzene) (Found : C, 60·2; H, 4·9; S, 9·8. $C_{16}H_{12}O_3S,2H_2O$ requires C, 60·0; H, 5·0; S, 10·0%), very soluble in hot and moderately soluble in cold water, and slightly soluble in chloroform. The m. p. of the hydrated acid when kept for 8 months was 131—136°.

This acid, whose potassium salt is sparingly soluble in cold water, displaced carbon dioxide from carbonates, and tests for a sulphinic acid were negative. It was obtained and identified by mixed m. p. when (III) (0·2 g.) was gently heated with potassium hydroxide (0·6 g.) and the mixture cooled as soon as a reaction was apparent. Fusion with potassium hydroxide at higher temperature for 15 minutes gave an impure phenol.

*Action of Heat on Thionaphthen* 1 : 1-*Dioxide in the Absence of Solvent*.—The sulphone (2 g.) was heated to 195°, the evolution of sulphur dioxide ceasing in 10 minutes, and after a further 10 minutes the product was cooled, dissolved in chloroform, and boiled with charcoal. The filtrate yielded a residue of which the benzene-insoluble portion crystallised from methyl alcohol in pale brown needles, m. p. 197° (Found : C, 71·6; H, 3·9; S, 12·1. $C_{16}H_{10}O_2S$ requires C, 72·2; H, 3·8; S, 12·0%). Both the solid *substance* and the solution fluoresced yellow in ultra-violet light.

The authors are indebted to Dr. Emily F. M. Stephenson for helpful discussions, and to the Dunlop Rubber Company of Australia for a research scholarship (to N. W. G.). Most of the microanalyses were made in the Organic Micro Analytical Laboratory of the Division of Industrial Chemistry (C.S.I.R.O.) by Dr. W. Zimmermann and his staff.

THE ORGANIC CHEMISTRY LABORATORY,
UNIVERSITY OF MELBOURNE.

[*Received, July* 7*th*, 1952.]