514. *Polymerisation of Thiophen Derivatives. Part V.* The Self-condensation of* 4 : 5- *and* 6 : 7-*Benzothionaphthen* 1 : 1-*Dioxides. A New Route to* 1-1′- *and* 4-2′-*Naphthylphenanthrene.*

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The condensations mentioned in the title give 10 : 11-dihydro-9-thia-5 : 6-benzonaphtho(1′ : 2′-3 : 4)- (IX) and -7 : 8-benzonaphtho(2′ : 1′-3 : 4)-fluorene 9 : 9-dioxide (XII), respectively. These products, with alkali, give the corresponding naphthylphenanthrenes.

Part IV of this series [1] described the self-condensation of the sulphones from thionaphthen and its 3- and 5-bromo- and 3-chloro-derivatives, to give tetracyclic monosulphones, usually derivatives of 9-thia-3 : 4-benzofluorene. The present work describes an extension of the process, namely, the production of hexacyclic structures by self-condensation of the tricyclic sulphones, 4 : 5- (I) and 6 : 7-benzothionaphthen 1 : 1-dioxide (XI).

Preparation of the initial sulphone (I) presents difficulties. Though thionaphthen and many of its simple derivatives are converted into their sulphones by hydrogen peroxide in acetic acid, this and other oxidising agents degrade 4 : 5-benzothionaphthen (which is readily prepared by cyclisation of 2-naphthylthioacetaldehyde acetals). Presumably the 6 : 7-double bond in 4 : 5-benzothionaphthen is very readily oxidised. Accordingly indirect methods of preparing the sulphone have been sought. Since butadiene and sulphur dioxide readily give a dihydrothiophen dioxide,[2] and 1-vinylnaphthalene readily combines with maleic anhydride,[3] it was expected that sulphur dioxide and 1-vinylnaphthalene could form a dihydro-4 : 5-benzothionaphthen 1 : 1-dioxide, dehydrogenation of which would give the desired sulphone (I). However, despite the use of a polymerisation inhibitor, the sulphur-containing product is polymeric and amorphous.

Another approach, starting from tetralin, is the synthesis of the tetrahydro-sulphide (III), in which the sensitivity of the 6 : 7-bond to oxidation should be small and therefore permit the oxidative conversion of the sulphide (III) into the tetrahydro-sulphone (IV), dehydrogenation of which should yield the desired sulphone (I). Indeed, the acetal (V) is cyclised in good yield and the product has the correct empirical formula, but it is a mixture, presumably of the desired sulphide (III) and its linear isomer, the unknown tetrahydrothiophanthrene. This mixture, and also that of the derived sulphones, is difficult to separate, and the process has therefore been relinquished in favour of a synthesis, which though circuitous and containing an ambiguous step, is very successful.

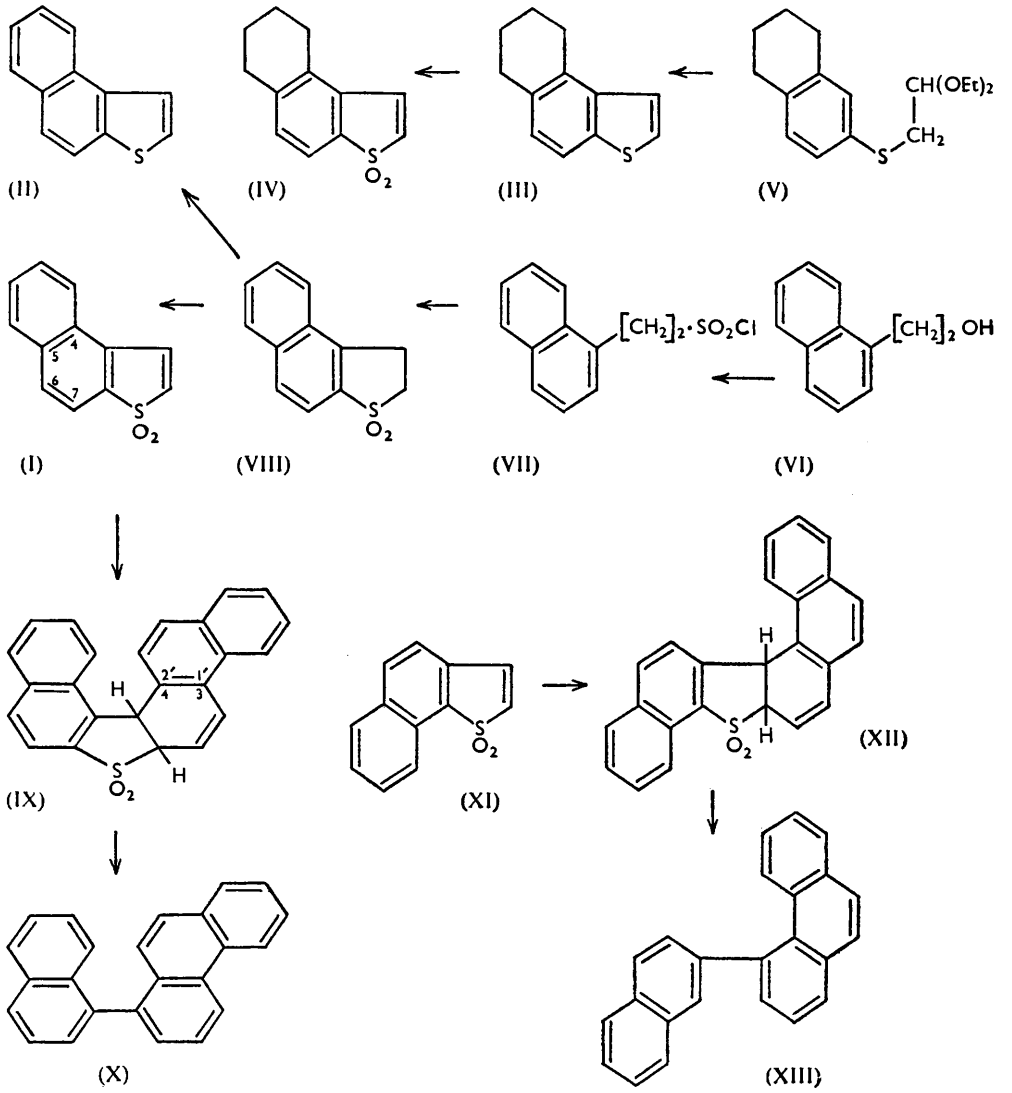
2-1′-Naphthylethanol (VI) was converted into the bromide and thence by sodium sulphite and phosphorus pentachloride into the sulphonyl chloride (VII). Cyclisation of this with aluminium chloride in nitrobenzene yields the 2 : 3-dihydro-derivative (VIII), which is dehydrogenated with *N*-bromosuccinimide to the required sulphone (I). That cyclisation has occurred in the 2- and not the *peri*-position is shown by reduction of the sulphone (VIII) with lithium aluminium hydride, followed by dehydrogenation with chloranil, to give 4 : 5-benzothionaphthen (II). A different proof of the structure of the dihydro-compound (VIII) has been given by Truce and Toren [4] who synthesised it in the same way and whose paper appeared after the above work was complete.[5] The only poor yields in this synthesis are in the cyclisation (43%) and the dehydrogenation (47%; about 80% if allowance is made for recovered starting material).

4 : 5-Benzothionaphthen 1 : 1-dioxide in solution in boiling xylene gives a 75% yield of 10 : 11-dihydro-9-thia-5 : 6-benzonaphtho(1′ : 2′-3 : 4)fluorene 9 : 9-dioxide (IX) which is converted by potassium hydroxide in diethylene glycol into 1-1′-naphthylphenanthrene

* Part IV, *J.*, 1955, 1565.

[1] Davies, James, Middleton, and Porter, *J.*, 1955, 1565.
[2] Backer and Blaas, *Rec. Trav. chim.*, 1942, **61**, 789.
[3] " Organic Reactions," Wiley, New York, 1954, Vol. IV, p. 34.
[4] Truce and Toren, *J. Amer. Chem. Soc.*, 1954, **76**, 695.
[5] Porter, Thesis, Melbourne, Feb., 1954.

(X). For comparison, a specimen of this naphthylphenanthrene has been made by interaction of 1-naphthylmagnesium bromide with 1 : 2 : 3 : 4-tetrahydro-1-oxophenanthrene, followed by dehydration and dehydrogenation with sulphur.[6] 1-1′-Naphthylphenanthrene



has also been prepared by Bachmann and Deno [7] by dehydrogenation of dimerised 1-vinylnaphthalene, and by Campbell [8] by decarboxylation of dimerised β-1-naphthylpropiolic acid.

The preparation of the other tricyclic sulphone required, 6 : 7-benzothionaphthen 1 : 1-dioxide (XI), has also been indirect. Though the corresponding sulphide, 6 : 7-benzothionaphthen, has been isolated from coal tar,[9] and prepared from the corresponding thioindoxyl,[10] and also been synthesised in an indirect manner,[11] none of these processes is

[6] Cf. Haworth, *J.*, 1932, 1129.
[7] Bachmann and Deno, *J. Amer. Chem. Soc.*, 1949, **71**, 3062.
[8] Campbell, *J.*, 1954, 3659.
[9] Kreuber and Raeithel, *Ber.*, 1953, **86**, 366.
[10] Carruthers, *J.*, 1953, 4186.
[11] Szmuszkovicz and Modest, *J. Amer. Chem. Soc.*, 1950, **72**, 571.

convenient on a moderately large scale. Direct synthesis from 1-naphthylthioacetaldehyde diethyl acetal seemed inapplicable in view of the evidence [12] that cyclisation took place in the *peri*-position, though this result has since [13] been shown to be incorrect. Moreover, it seemed likely that 6 : 7-benzothionaphthen would, like its isomer (II), resist oxidation to its sulphone, which has not been described. Accordingly, (5-tetralylthio)acetic acid was made so that cyclisation, reduction, oxidation to the sulphone, and dehydrogenation would yield the sulphone (XI). However, this route was abandoned and a synthesis analogous to that of the isomeric sulphone (I), starting from 2-bromonaphthalene, was found to give 6 : 7-benzothionaphthen 1 : 1-dioxide. One noteworthy fact is that sodium 2-2′-naphthylethanesulphonate has, for a sodium salt, the very low solubility in boiling water of about 3%.

A rather higher temperature (about 175°) is required for the self-condensation of the sulphone (XI) than for its isomer (I) but the yield is excellent (84%). 10 : 11-Dihydro-9-thia-7 : 8-benzonaphtho(2′ : 1′-3 : 4)fluorene 9 : 9-dioxide (XII), with alkali, affords 4-2′-naphthylphenanthrene (XIII), identical with a specimen, kindly supplied by Dr. A. D. Campbell,[8] who prepared it from β-2-naphthylpropiolic acid. This identification shows that cyclisation of 2-2′-naphthylethanesulphonyl chloride formed the sulphone (XI) and not the (unlikely) linear isomer.

Though naphthyl-phenanthrenes have recently been synthesised by methods other than those now described, it is seen that the present work may be useful for the synthesis of large aromatic molecules [cf. Campbell's syntheses [8] of 2 : 3-benzoperylene and naphtho-(2′ : 3′-1 : 2)pyrene]. Its utility depends on the accessibility of the thionaphthen dioxides, and this varies for different compounds. It should be stated that a much more direct synthesis of 6 : 7-benzothionaphthen 1 : 1-dioxide (XI) than the present is described elsewhere.[13]

The direct dehydrogenation of 2 : 3-dihydro-sulphones by *N*-bromosuccinimide has not been recorded previously; it is of value with 2 : 3-dihydrothionaphthen sulphone and its derivatives. The conditions, including the use of benzoyl peroxide, are essentially those used by Karrer and Schmid [14] in the bromination of toluene. In this way the dioxides of thionaphthen and 4 : 5- and 6 : 7-benzothionaphthen have been prepared from the corresponding 2 : 3-dihydro-derivatives. The last-named gives a by-product, 3-bromo-6 : 7-benzothionaphthen 1 : 1-dioxide, which with one mol. of piperidine readily forms the 3-piperidino-dioxide. Had the bromine been in the 2-position addition of piperidine would be expected and excess of piperidine would be required to eliminate hydrogen bromide, as in the simpler case of 3-bromothionaphthen 1 : 1-dioxide.[15] 2 : 3-Dihydro-4 : 5-benzothionaphthen 1 : 1-dioxide (VIII) also forms a by-product, 2-bromo-2 : 3-dihydro-4 : 5-benzothionaphthen 1 : 1-dioxide, a substance containing positive bromine, readily reconvertible into the parent compound (VIII), and showing properties which may throw light on the mechanism of dehydrogenation by *N*-bromosuccinimide.

Experimental

Synthesis of 4 : 5-*Benzothionaphthen* 1 : 1-*Dioxide* (I).—2-1′-*Naphthylethanesulphonyl chloride* (VII). 2-1′-Naphthylethanol (VI), b. p. 130—132/0·2 mm., made from 1-naphthylmagnesium bromide and ethylene oxide,[16] with phosphorus tribromide [17] gave 2-1′-naphthylethyl bromide. This (98 g.) was refluxed and stirred for 15 hr. with sodium sulphite heptahydrate (170 g.) in water (700 ml.). After cooling, the yield of (dried) sodium 2-1′-naphthylethanesulphonate was 81 g. (76%). Of this, 80 g. were mixed with phosphorus pentachloride (66 g.), kept at room temperature for 30 min., then heated on the steam-bath for 30 min. An ethereal extract of the product precipitated by ice-water yielded 2-1′-naphthylethanesulphonyl chloride (48 g., 60%), prisms (from ether–light petroleum), m. p. 48—48·5° (Found : C, 56·6; H, 4·3. Calc. for $C_{12}H_{11}O_2ClS$: C, 56·8; H, 4·5%). Truce and Toren [4] give m. p. 48—49°, and m. p. 171—173°

[12] Dikshit and Tilak, *Proc. Indian Acad. Sci.*, 1951, **33**, *A*, 78.
[13] Banfield, Davies, Ennis, Middleton, and Porter, preceding paper.
[14] Karrer and Schmid, *Helv. Chim. Acta*, 1946, **29**, 573.
[15] Bordwell and Albisetti, *J. Amer. Chem. Soc.*, 1948, **70**, 1558.
[16] Wilds, *J. Amer. Chem. Soc.*, 1942, **64**, 1421.
[17] Hoch, *Bull. Soc. chim. France*, 1938, **5**, 264.

for the corresponding amide, needles (from aqueous alcohol), m. p. 172·5—173° (Found : C, 61·4; H, 5·7. Calc. for $C_{12}H_{13}O_3NS$: C, 61·3; H, 5·6%). The *anilide* formed needles (from aqueous alcohol), m. p. 133·5—134° (Found : N, 4·35. $C_{18}H_{17}O_3NS$ requires N, 4·5%).

2 : 3-*Dihydro*-4 : 5-*benzothionaphthen* 1 : 1-*dioxide* (VIII). The above sulphonyl chloride (40 g.) in nitrobenzene (75 ml.) was added to a cold solution of powdered aluminium chloride (24 g.) in nitrobenzene (200 ml.), and the mixture kept at room temperature for 1 hr. and then at 70° for 2 hr. The complex was decomposed with dilute hydrochloric acid, and the nitrobenzene was removed by steam. The aqueous filtrate deposited 2 : 3-dihydro-4 : 5-benzothionaphthen 1 : 1-dioxide (3·7 g.), needles, m. p. 178—178·5° (lit.,[4] m. p. 177—178°) (Found : C, 66·5; H, 4·75. Calc. for $C_{12}H_{10}O_2S$: C, 66·1; H, 4·6%). The residue was extracted with hot benzene (3 × 300 ml.), the concentrated extracts were clarified with carbon and diluted with light petroleum (b. p. 60—100°), and the precipitate crystallised from methanol, to give pure sulphone (14·8 g., 43%).

4 : 5-*Benzothionaphthen* 1 : 1-*dioxide* (I). The preceding dioxide (6·0 g.) was refluxed with *N*-bromosuccinimide (4·8 g.) and benzoyl peroxide (0·1 g.) in dry carbon tetrachloride (150 ml.) for 8 hr., the solvent removed, and the residue dissolved in hot benzene. Succinimide separated, the benzene filtrate was chromatographed on alumina, and the eluate from the first band (pale yellow with a light green fluorescence in ultraviolet light) gave 4 : 5-*benzothionaphthen* 1 : 1-*dioxide*, pale yellow needles (2·7 g.) (Found : C, 66·5; H, 3·65. $C_{12}H_8O_2S$ requires C, 66·7; H, 3·7%). It melts, with the evolution of sulphur dioxide, at 136—137° or 141—142°, according to the rate of heating, then resolidifies to form the crude sulphone (IX) which melts to a black liquid at about 222° (see below).

The precipitated crude succinimide (2·8 g.) was extracted with dilute sodium hydroxide solution, and the alcoholic solution of the residue gave 2-*bromo*-2 : 3-*dihydro*-4 : 5-*benzothionaphthen* 1 : 1-*dioxide* (0·9 g.), needles, m. p. 220° (decomp.) (Found : C, 48·4; H, 3·4; Br, 27·0. $C_{12}H_9O_2BrS$ requires C, 48·5; H, 3·0; Br, 27·0%). This was unaffected by refluxing pyridine or triethylamine–benzene, but with a hot solution of sodium iodide in acetone it rapidly gave iodine and 2 : 3-dihydro-4 : 5-benzothionaphthen 1 : 1-dioxide, and the last compound was also formed by debromination by boiling tetralin. Hot alcoholic potassium hydroxide converted the bromine compound in low yield into 2 : 3-*dihydro*-3- or -2-*hydroxy*-4 : 5-*benzothionaphthen* 1 : 1-*dioxide*, needles, m. p. 182·5—183° (Found : C, 62·05; H, 4·5. $C_{12}H_{10}O_3S$ requires C, 61·8; H, 4·3%).

Proof of structure. 2 : 3-Dihydro-4 : 5-benzothionaphthen 1 : 1-dioxide (0·5 g.) in ether (20 ml.) was refluxed with lithium aluminium hydride (0·3 g.) for 6 hr., and after interaction with dilute hydrochloric acid the ether layer yielded 2 : 3-dihydro-4 : 5-benzothionaphthen (0·3 g.), plates (from aqueous alcohol), m. p. 86·5—87° (Truce and Toren report m. p. 88—89°) (Found : C, 77·5; H, 5·5. Calc. for $C_{12}H_{10}S$: C, 77·4; H, 5·4%). This (0·2 g.) was refluxed with chloranil (0·3 g.) in sulphur-free xylene (5 ml.) for 6 hr., and the cooled solution filtered, diluted with benzene (15 ml.), and chromatographed on alumina. The first band was colourless but with a blue fluorescence in ultraviolet light, and gave 4 : 5-benzothionaphthen identical with the cyclisation product of 2-naphthylthioacetaldehyde diethyl acetal.[13]

Self-condensation of 4 : 5-*Benzothionaphthen* 1 : 1-*Dioxide* (I).—The sulphone (2·5 g.) was refluxed in xylene (50 ml.) until evolution of sulphur dioxide ceased (4 hr.), the solvent was removed under reduced pressure, and the residue crystallised from benzene in prisms (1·6 g., 75%) of 10 : 11-*dihydro*-9-*thia*-5 : 6-*benzonaphtho*(1′ : 2′-3 : 4)*fluorene* 9 : 9-*dioxide* (IX), m. p. 226° (Found : C, 78·1; H, 4·3; S, 8·7. $C_{24}H_{16}O_2S$ requires C, 78·3; H, 4·35; S, 8·7%).

1-1′-*Naphthylphenanthrene.*—The dioxide (IX) (0·1 g.) was refluxed for 10 min. in diethylene glycol (0·5 ml.) containing potassium hydroxide (0·5 g.). The mixture was diluted with water (50 ml.); the oil from the ethereal extract solidified when triturated with alcohol, giving a good yield of 1-1′-naphthylphenanthrene, plates, m. p. 115—116°, identical (mixed m. p.) with a specimen made as follows: β-1′-Naphthoylpropionic acid, prepared from naphthalene, succinic anhydride, and aluminium chloride and readily separated from the isomeric acid,[18] was reduced in good yield to γ-1-naphthylbutyric acid by a modification [19] of the Clemmensen method. This acid was cyclised in 75% sulphuric acid [6] to 1 : 2 : 3 : 4-tetrahydro-1-oxophenanthrene, of which 4·0 g. in ether (35 ml.) was added to 1-naphthylmagnesium bromide made from 1-bromonaphthalene (4·3 g.) and magnesium (0·6 g.) in ether (10 ml.). The mixture was diluted with benzene (10 ml.) and refluxed for 4 hr. The organic layer formed on acidification with dilute

[18] Robinson and Slater, *J.*, 1941, 376.
[19] Martin, *J. Amer. Chem. Soc.*, 1936, **58**, 1438.

hydrochloric acid gave the oily tertiary alcohol which was dehydrated by anhydrous formic acid at 100° during 1 hr. Naphthalene (about 0·5 g.) was removed by steam-distillation of the solution diluted with water, and the benzene solution of the residual oil was dried ($MgSO_4$). Removal of the benzene gave an oil which solidified when triturated with light petroleum and then crystallised from ethanol in needles (2·1 g.) of 3 : 4-*dihydro*-1-1′-*naphthylphenanthrene*, m. p. 124—125° (Found: C, 94·0; H, 6·1. $C_{24}H_{18}$ requires C, 94·1; H, 5·9%). This (1·0 g.) was heated with sulphur (0·9 g.) at 250° for 1 hr., and the benzene solution of the residue chromatographed on alumina. From the colourless band which had a blue fluorescence in ultraviolet light, prisms, m. p. 116° (from ethanol), of 1-1′-naphthylphenanthrene were obtained (Found: C, 94·5; H, 5·1. Calc. for $C_{24}H_{16}$: C, 94·7; H, 5·3%). Its reported m. p.[8] is 115°.

Synthesis of 6 : 7-*Benzothionaphthen* 1 : 1-*Dioxide* (XI).—2-2′-Naphthylethanol, m. p. 66—67°, b. p. 128—130°/0·2 mm., was prepared in 64% yield, and converted into the corresponding bromide, m. p. 55—56°, b. p. 116—118°/0·2 mm., as described for the 1-isomer. The bromide (18·5 g.) was refluxed with sodium sulphite heptahydrate (30 g.) in water (100 ml.) for 12 hr. Some *sodium* 2-2′-*naphthylethanesulphonate* separated in plates from the boiling solution and on cooling a total of 12·3 g. was obtained (Found: C, 56·05; H, 4·4. $C_{12}H_{11}O_3SNa$ requires C, 55·8; H, 4·3%). The dried salt (8·0 g.) was heated for 1½ hr. on the water-bath with phosphorus pentachloride (6·6 g.) and phosphorus oxychloride (3·0 g.). 2-2′-*Naphthylethanesulphonyl chloride* obtained by treatment with crushed ice, crystallised from benzene–light petroleum in prisms (5·8 g.) m. p. 66—66·5° (Found: C, 56·6; H, 4·8. $C_{12}H_{11}O_2ClS$ requires C, 56·8; H, 4·5%). The *amide*, needles (from aqueous alcohol), had m. p. 200—200·5° (Found: N, 5·6. $C_{12}H_{13}O_2NS$ requires N, 5·9%).

2 : 3-*Dihydro*-6 : 7-*benzothionaphthen* 1 : 1-*dioxide*. The above sulphonyl chloride (5·0 g.) in dry nitrobenzene was cyclised in the same way as the isomer, and the filtrate and residue gave 2 : 3-*dihydro*-6 : 7-*benzothionaphthen* 1 : 1-*dioxide*, needles (2·9 g.) (from methanol), m. p. 187·5—188° (Found: C, 65·8; H, 4·4. $C_{12}H_{10}O_2S$ requires C, 66·1; H, 4·6%).

Dehydrogenation. This dioxide (5·7 g.) was refluxed for 12 hr. with *N*-bromosuccinimide (5·0 g.) and benzoyl peroxide (50 mg.) in dry carbon tetrachloride (250 ml.), the solvent removed, and the residue dissolved in hot benzene. The succinimide which separated on cooling was discarded and the filtrate chromatographed on alumina. The bands were visible in ultraviolet light. The products of the least firmly adsorbed band are discussed below. The third band gave unchanged 2 : 3-dihydro-6 : 7-benzothionaphthen 1 : 1-dioxide (1·9 g.), and the second band 6 : 7-*benzothionaphthen* 1 : 1-*dioxide* (XI) (3·0 g.), yellow plates (from methanol), m. p. 181—182° (decomp.) to 194—195° (decomp.) according to the rate of heating (Found: C, 66·3; H, 3·7. $C_{12}H_8O_2S$ requires C, 66·7; H, 3·7%).

The first band gave pale yellow needles (0·3 g.) (from ethanol) of 3-*bromo*-6 : 7-*benzothionaphthen* 1 : 1-*dioxide*, m. p. 244·5—245° (Found: C, 48·8; H, 2·6; S, 10·8. $C_{12}H_7O_2BrS$ requires C, 48·8; H, 2·4; S, 10·85%). This gives no iodine with sodium iodide in acetone but the bromine is replaced when one mol. of piperidine is used as follows: The dioxide (0·07 g.) and piperidine (0·02 g.) were refluxed in alcohol for 45 min. The cooled solution was diluted with water, and the precipitated 3-1′-*piperidino*-6 : 7-*benzothionaphthen* 1 : 1 *dioxide* crystallised from benzene–light petroleum in prisms, m. p. 171·5—172° (Found: C, 68·5; H, 5·6. $C_{17}H_{17}O_2NS$ requires C, 68·2; H, 5·7%).

Self-condensation of 6 : 7-*Benzothionaphthen* 1 : 1-*Dioxide* (XI).—This dioxide (2·7 g.) was refluxed in technical *o*-dichlorobenzene (27 ml.) until the evolution of sulphur dioxide ceased (5 hr.). The solvent was removed under reduced pressure, and the residue crystallised from methanol in prisms (1·9 g., 84%) of 10 : 11-*dihydro*-9-*thia*-7 : 8-*benzonaphtho*(2′ : 1′-3 : 4)-*fluorene* 9 : 9-*dioxide* (XII), m. p. 166—167° (Found: C, 78·6; H, 4·5; S, 8·9. $C_{24}H_{16}O_2S$ requires C, 78·3; H, 4·35; S, 8·7%). When it (0·1 g.) was heated with potassium hydroxide in diethylene glycol, it gave needles of 4-2′-naphthylphenanthrene, m. p. 105—106° alone or mixed with a specimen kindly supplied by Dr. A. D. Campbell.[8]

Synthesis of Tetrahydrobenzothionaphthen.—Tetralin-6-sulphonyl chloride, m. p. 57—58°, was prepared as described by Schroeter.[20] Reduction with zinc dust and sulphuric acid [21] gave 68% of 6-mercaptotetralin, b. p. 161—162°/35 mm. The thiol (25 g.) was added to the still-reacting mixture of ethanol (200 ml.) and sodium (7·5 g.). Chloroacetal (37·5 ml.) and sodium bromide (2·5 g.) were added and the mixture was refluxed for 6 hr. The mixture was extracted with sodium hydroxide solution (2%; 150 ml.) and with ether. Evaporation of the ether and

[20] Schroeter, *Annalen*, 1922, **426**, 83.
[21] Adams and Marvel, *Org. Synth.*, **1**, 71.

distillation gave 6-*tetralylthioacetaldehyde diethyl acetal* (26·5 g.), b. p. 160—161°/0·5 mm. (Found: S, 11·1. $C_{16}H_{24}O_2S$ requires S, 11·5%). This acetal (25 g.) was added slowly below the surface of a mixture of phosphoric acid (*d* 1·75; 90 ml.) and phosphoric oxide (150 g.) at 160°/0·2 mm. A vigorous reaction occurred and a yellow oil distilled. Redistillation gave a mixture of tetrahydrobenzothionaphthens (9·8 g.), b. p. 119—121°/0·3 mm. (Found: C, 77·1; H, 6·0; S, 17·0. Calc. for $C_{12}H_{12}S$: C, 76·6; H, 6·4; S, 17·0%).

Oxidation was attempted under a number of conditions, with hydrogen peroxide in glacial acetic acid, but in no case gave appreciable amounts of crystals.

Synthesis of (5- *and* 6-*Tetralylthio*)*acetic Acid.*—Tetralin (50 g.) was added dropwise to stirred chlorosulphonic acid, at $< -5°$. Then the mixture was stirred at $-5°$ for 1 hr. and allowed to come to room temperature. The oily sulphonyl chlorides, precipitated by crushed ice, were extracted with carbon tetrachloride. Evaporation of the dried ($MgSO_4$) extract gave a mixture of tetralin-5- and -6-sulphonyl chloride (68 g.). The mixture was reduced as described for the 6-isomer, giving a mixture (69%) of the corresponding thiols, b. p. 161—164°/33 mm.

This mixture (20 g.) was added to a solution of chloroacetic acid (14·5 g.) and sodium hydroxide (12 g.) in water (250 ml.). The solution was heated on the water-bath for 1 hr., cooled, and acidified. The precipitated acids were crystallised from aqueous alcohol (yield, 25·0 g., 93%).

The mixed acids (20 g.) were dissolved in a 5% potassium hydroxide solution (80 ml.), and 40% potassium hydroxide solution (40 ml.) was added. The acidified precipitate gave (6-tetralylthio)acetic acid, needles (from aqueous alcohol), m. p. 78·5—79° (9·2 g.), and the filtrate on acidification gave (5-tetralylthio)acetic acid, needles (from aqueous alcohol), m. p. 133—134° (9·0 g.). Schroeter reports m. p. 79—80° and 133—135° respectively. The separation by means of the ammonium salts as used by Schroeter is unsatisfactory.

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