513. *The Synthesis of Thionaphthen Derivatives. Part I. The Cyclisation of Arylthioacetaldehyde Diethyl Acetals.*

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Cyclisation of various arylthioacetaldehyde diethyl acetals has been examined and the most reliable, although not infallible, reagent is the mixture of phosphoric oxide and phosphoric acid first used by Tilak [1] with the corresponding dimethyl acetals. Tilak's so-called naphtho(1′ : 9′ : 8′-2 : 3 : 4)thiapyran (VII) from 1-naphthylthioacetaldehyde dimethyl acetal is now found to be 6 : 7-benzothionaphthen (VI).

The preparation of thionaphthens by reduction of the corresponding thioindoxyls, often stated [2-4] to be satisfactory, sometimes suffers serious disadvantages in that (*a*) cyclisation of the phenylthioglycollic acids to the thioindoxyls is complicated by oxidation,[5] intermolecular condensation [as shown by the formation of (*p*-acetylphenylthio)acetic acid (II)

[1] Tilak, *Proc. Indian Acad. Sci.*, 1950, **32**, *A*, 390.
[2] Steinkopff, " Die Chemie des Thiophens," Steinkopff, Leipzig, 1941.
[3] Hartough and Meisel, " Compounds with Condensed Thiophen Ring Systems," Interscience, New York, 1954.
[4] Elderfield, " Heterocyclic Compounds," Wiley, 1951, Vol. II, p. 146.
[5] Smiles and Hutchinson, *J.*, 1912, **101**, 573.

from (phenylthio)acetic acid (I) [6]], or fission of a carbon–sulphur bond (minimised by use of basic cyclising agents [7]), (*b*) the thioindoxyl is readily oxidised in air to the thioindigo, and (*c*) reduction to the thionaphthen is difficult to control.[4, 8] Several recent preparations have started with the now commercially available thionaphthen but this is usually useful only for derivatives which contain at least one substituent in the thiophen ring. A different approach, begun by us in 1948, was from arylthioacetaldehyde diethyl acetals, $ArS{\cdot}CH_2{\cdot}CH(OEt)_2$.

These acetals are readily prepared from chloroacetaldehyde diethyl acetal and the sodium aryl sulphide, a method already known [9] for the phenylthio-compound. Use of the more expensive bromoacetal [1] is unnecessary. Most of our acetals have been characterised by conversion into the *p*-nitrophenylhydrazones of the corresponding aldehydes, which, however, were not themselves isolated.

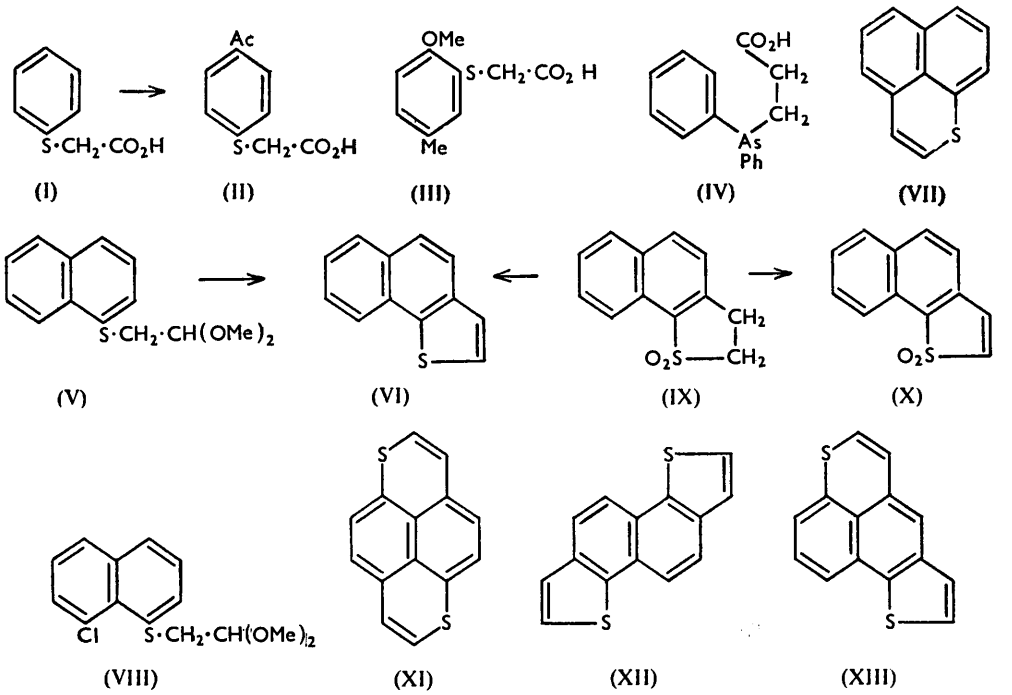
Autenrieth [9] attempted to convert phenylthioacetaldehyde diethyl acetal into thionaphthen, but found that decomposition occurred on the use of hydrochloric acid, zinc chloride, acetic anhydride, or concentrated sulphuric acid; it is now found that the last reagent destroys thionaphthen. The problem is more difficult than the cyclodehydration of the corresponding ether $PhO{\cdot}CH_2{\cdot}CH(OEt)_2$, as an alkoxy-group would be expected to activate the *ortho*-position more strongly than an alkylthio-group. Moreover, the more drastic cyclodehydration conditions required for the sulphur compound are likely to bring about a fission of one of the sulphur–carbon bonds. For example, hydrogen iodide brought about such a fission with (6-methoxy-3-methylphenylthio)acetic acid (III), though the methoxy-group was not hydrolysed.[10] During the present work it has been found that acidic reagents readily cause fission of various arylthioacetals, and the fission products contain, apart from tar, the original thiol or the corresponding disulphide. Thus, di-2-naphthyl disulphide is the principal compound formed when the 2-naphthylthio-acetal is heated with pyridine hydrobromide at 180° for 2 hours, and the *p*-tolylthio-acetal gives thiocresol and di-*p*-tolyl disulphide when heated with dry oxalic acid at 210° for 5 hours. Another probable source of by-products from the thioacetal process is the condensation of the thionaphthen derivative, as it is formed, with unused aldehyde or acetal: *e.g.*, 2-formylthiophen and thiophen form tri-2-thienylmethane when refluxed with phosphoric oxide in ether.[11]

The comparison between aryloxy- and arylthio-compounds is paralleled with derivatives of nitrogen and arsenic: (2-carboxyethyl)diphenylarsine (IV) and related compounds cannot be cyclised,[12] although the corresponding nitrogen compounds readily gave 1 : 2 : 3 : 4-tetrahydro-4-oxo-1-phenylquinoline, etc., by conventional methods. Moreover, some acidic reagents cause fission between the arsenic atom and the side chain in (IV), behaviour which is similar to that of the above sulphur compounds.

Stannic chloride in chloroform at room temperature cyclises 2-naphthylthioacetaldehyde diethyl acetal to 4 : 5-benzothionaphthen (about 90% yield), and the 3 : 4-dimethoxyphenylthio-analogue into 5 : 6-dimethoxythionaphthen (about 20% yield), the respective structures being proved by desulphurisation to 1-ethylnaphthalene and to an oil whose oxidation gives veratric acid. The Experimental section describes the partly successful use of various cyclisation agents, the search for which was relinquished when Tilak [1] described the almost invariably successful use of a mixture of phosphoric oxide and syrupy phosphoric acid. This agent has found extensive general application [13] since its inception,[14] and, in general, is sufficiently mild to permit Tilak's method of cyclising at a temperature high enough to remove the sensitive thionaphthen, as soon as it is formed, by continuous distillation under reduced pressure. Even this process, however,

[6] Dann and Kokurudz, *Chem. Ber.*, 1953, **86**, 1452.
[7] Dalgleish and Mann, *J.*, 1954, 899; D.R.-P. 184,496, 190,674, 367,493, 543,286.
[8] Carruthers, *J.*, 1953, 4187.
[9] Autenrieth, *Ber.*, 1891, **24**, 164.
[10] Gibson and Smiles, *J.*, 1923, 2388.
[11] Nahke, *Ber.*, 1897, **30**, 2038.
[12] Cookson and Mann, *J.*, 1949, 71.
[13] Evans and Smith, *J.*, 1954, 785.
[14] Koebner and Robinson, *J.*, 1938, 1994.

occasionally gives varying or low yields as a result of slight changes in molecular structure and/or cyclisation conditions. Thus, Rabindran, Sunthankar, and Tilak [15] obtained from *p*-bromophenylthioacetaldehyde dimethyl acetal only a 13% yield of 5-bromothionaphthen, whereas the diethyl acetal is now found to give a 49% yield; on the other hand, cyclisation of *p*-methoxyphenylthioacetaldehyde diethyl acetal seems even more difficult than that of the corresponding dimethyl acetal.[16]



Either 6 : 7-benzothionaphthen (VI) or naphtho(1′ : 9′ : 8′-2 : 3 : 4)thiapyran (VII) could be formed by cyclisation of the acetal (V), which was converted by Tilak [17] into a cyclic sulphide, whose picrate had m. p. 177—178°. Since the compound obtained by cyclisation of 8-chloro-1-naphthylthioacetaldehyde dimethyl acetal (VIII), followed by replacement of chlorine by hydrogen, gave a picrate of m. p. 140·5—141·5°, it was accepted that cyclisation of (V) had taken place in the *peri*-position. We therefore chose an indirect method for the synthesis of the sulphone (X); it was made *via* 2 : 3-dihydro-6 : 7-benzothionaphthen 1 : 1-dioxide (IX), obtained by the cyclisation of 2-2′-naphthylethanesulphonyl chloride.[18] The dihydro-sulphone (IX), on successive reaction with lithium aluminium hydride and chloranil, gives a compound (m. p. 27—28°), the properties of which agree with those recorded for 6 : 7-benzothionaphthen [8, 19] but not with those of the linear thiophanthrene,[20] m. p. 189°, which would have been expected had the cyclisation of 2-2′-naphthylethanesulphonyl chloride produced the linear isomeride of (IX). Now the sulphide produced from (IX) is identical (mixed m. p.) with the purified sulphide obtained by cyclisation of the acetal (V) by Tilak's method, and the 2 : 4 : 7-trinitrofluorenone derivatives are identical. The m. p. of the picrates of the identical sulphides obtained by the cyclisation of (V) and the corresponding diethyl acetal agrees essentially with those of the picrate of 6 : 7-benzothionaphthen obtained in other ways.[8, 19] Moreover, the

[15] Rabindran, Sunthankar, and Tilak, *Proc. Indian Acad. Sci.*, 1952, **34**, *A*, 405.
[16] Tilak, *ibid.*, 1951, **33**, *A*, 35.
[17] *Idem*, *ibid.*, p. 71.
[18] Davies and Porter, following paper.
[19] Kruber and Raeithel, *Chem. Ber.*, 1953, **86**, 366.
[20] Mayer, *Annalen*, 1931, **488**, 259.

acetal cyclisation product (VI) is directly oxidised to its sulphone, identical with the synthetic sulphone (X).

The m. p. (13—19°) of the crude cyclised product of the acetal (V), and also its conversion into the 2 : 4 : 7-trinitrofluorenone derivative in 87% yield, show that the compound is almost homogeneous, and the amount of thiapyran (VII) must therefore be very small or nil. A possible explanation of the error may be that Tilak's picrate (m. p. 177—178°) of the supposed " thiapyran " is actually another form of the known picrate (m. p. about 144°) of 6 : 7-benzothionaphthen. The picrate of 6 : 7-benzothionaphthen is inferior for characterisation to the 2 : 4 : 7-trinitrofluorenone derivative, which crystallises with little dissociation and melts without decomposition. It is pertinent that there are not two picrates of the isomeric 4 : 5-benzothionaphthen;[21] the " picrate " melting at 116—117° is 4 : 5-benzothionaphthen itself.

As a result of the above work on the cyclisation of the acetal (V), reconsideration should be given to the course of cyclisation of 1 : 8-naphthalenebis(thioacetaldehyde dimethyl acetal). The product, because of its orange colour and its absorption spectrum, is thought by Tilak [17] to be " 1 : 6-dithiapyrene " (XI) (formed by cyclisation in the *peri*-position), and not the isomeric dithienonaphthalene (XII) which was expected to be colourless. Visible colour is sometimes associated with persistent impurities : for example, the 6 : 7-benzothionaphthen synthesised in a diffierent manner is reported [22] to be yellow, though the pure compound is colourless.[19] The absorption spectrum seems stronger evidence that the compound is not a dithienonaphthalene, though the possibility that it is (XIII), with one thiapyran and one thiophen group, has apparently been overlooked. In any event, as the pure cyclisation product is obtained in less than 3·7% yield, the elucidation of its structure will require more evidence than is at present available.

Though the acetal (V) cyclises in only about 35% yield to the sulphide (VI), which is oxidised into its sulphone in about 28% yield, this process is nevertheless so far the best for preparing 6 : 7-benzothionaphthen 1 : 1 dioxide (X) from common materials. Only partial degradation occurs during the oxidation, and this compares with the successful preparation, by means of chromic acid, of the 4 : 5-quinone of 6 : 7-benzothionaphthen in about 14% yield.[19] These results contrast with the essentially complete degradation of 4 : 5-benzothionaphthen (under the same conditions), indicating that in this isomer or its corresponding sulphone, the 6 : 7-bond is most susceptible to oxidation. The above and similar differences in stability among isomers in this series are of interest for comparison with the analogous aromatic hydrocarbons.

Experimental

Preparation of Arylthioacetaldehyde Diethyl Acetals.—Two methods used for the preparation of the acetals are exemplified in the preparation of the *p*-tolylthio-compound, as follows :

(i) Sodium (17 g., 1·4 g.-atom) was added to ethanol (300 ml.), and *p*-thiocresol (65 g., 1 mole) was added to the still-reacting solution. Chloroacetal (88 ml., 1·4 mole) was gradually added to the cooled mixture with agitation during 15 min. After several hours at 0° and then 2 days at room temperature, most of the alcohol was distilled off and the residue diluted with water (500 ml.). The dried ($MgSO_4$) ethereal extract gave the acetal, b. p. 170·5—172°/18 mm. (53%).

(ii) Refluxing one-tenth of the above quantities for 6 hr. gave the *acetal* (71%), b. p. 171°/18 mm., n_D^{24} 1·5155 (Found : C, 65·2; H, 8·2. $C_{13}H_{20}O_2S$ requires C, 65·0; H, 8·3%). p-*Tolylthioacetaldehyde* p-*nitrophenylhydrazone*, yellow needles (from ethanol), m. p. 123·5—124·5°, was formed when the acetal (0·1 g.) was refluxed for 3 min. with ethanol (5 ml.) and 2N-hydrochloric acid (3 ml.) and the solution then shaken at about 60° for a few minutes with an excess of *p*-nitrophenylhydrazine in dilute hydrochloric acid (Found : C, 60·25; H, 5·05; N, 13·9. $C_{15}H_{15}O_2N_3S$ requires C, 59·8; H, 5·0; N, 13·95%).

Similarly were prepared : The o-*tolylthio-acetal* [prepared by method (i); 3 days at room temperature; 48% yield], b. p. 164—166°/18 mm. (Found : C, 65·45; H, 7·95%). o-*Tolylthioacetaldehyde* p-*nitrophenylhydrazone*, yellow prisms (from alcohol), m. p. 121—121·5° (Found : N, 14·1%).

[21] Ref. 3, p. 308.
[22] Szmuszkovicz and Modest, *J. Amer. Chem. Soc.*, 1950, **72**, 571.

The m-*tolylthio-acetal* [method (i); 7 days at room temperature; 39% yield], b. p. 160—163°/17 mm. (Found: C, 65·5; H, 8·2; S, 13·6. $C_{13}H_{20}O_2S$ requires C, 65·0; H, 8·3; S, 13·35%). m-*Tolylthioacetaldehyde* p-*nitrophenylhydrazone*, orange rods, m. p. 125—127° (Found: N, 14·0%).

The p-*methoxyphenylthio-acetal* [method (i); 3 days at room temperature; 62% yield], b. p. 192—194°/19 mm. (Found: C, 60·5; H, 7·4. $C_{13}H_{20}O_3S$ requires C, 61·0; H, 7·8%). p-*Methoxyphenylthioacetaldehyde* p-*nitrophenylhydrazone*, orange plates (from ethanol), m. p. 107—108° (Found: C, 56·8; H, 4·8; OMe, 9·75. $C_{15}H_{15}O_3N_3S$ requires C, 56·8; H, 4·75; OMe, 9·75%).

The 3 : 4-dimethoxyphenylthioacetal [method (i); 5 days at room temperature; 70% yield], b. p. 170—172°/0·4 mm. 3 : 4-*Dimethoxyphenylthioacetaldehyde* p-*nitrophenylhydrazone*, yellow needles (from alcohol), m. p. 129·5—130·5° (Found: C, 55·5; H, 4·95; N, 12·4; OMe, 18·25. $C_{16}H_{17}O_4N_3S$ requires C, 55·0; H, 4·9; N, 12·1; OMe, 17·9%).

The 2-*naphthylthio-acetal* [method (ii); refluxing for 6 hr.; 78% yield], b. p. 157—160°/0·3 mm. (Found: C, 69·6; H, 6·9; S, 11·9. $C_{16}H_{20}O_2S$ requires C, 69·6; H, 7·25; S, 11·6%).

The 1-*naphthylthio-acetal*, prepared (77%) as above except that 0·1 mole of sodium bromide was added, had b. p. 145—148°/0·2 mm. (Found: C, 70·3; H, 6·7; S, 12·2%). 1-*Naphthylthioacetaldehyde* p-*nitrophenylhydrazone* formed yellow crystals, m. p. 160—161° (Found: N, 12·4. $C_{18}H_{15}O_2N_3S$ requires N, 12·5%).

The p-*bromophenylthio-acetal* [method (ii) from bromoacetaldehyde diethyl acetal; refluxing for 3 hr.; 60% yield], b. p. 195—196°/19 mm. (Found: C, 47·1; H, 5·7. $C_{12}H_{17}O_2SBr$ requires C, 47·2; H, 5·6%). p-*Bromophenylthioacetaldehyde* p-*nitrophenylhydrazone*, orange needles, m. p. 141° (Found: N, 13·6. $C_{14}H_{11}O_4N_4SBr$ requires N, 13·6%).

Cyclisation of Acetals.—To 2-naphthylthioacetaldehyde diethyl acetal (2 g.) in dry chloroform (20 ml.), anhydrous stannic chloride (2 ml.) was added with cooling. After 24 hr. at room temperature dilute hydrochloric acid was added. The chloroform layer, after drying, yielded a residue from which hot ethanol (75 ml.) extracted almost pure 4 : 5-benzothionaphthen which was precipitated by water (300 ml.) in 92% yield (m. p. 104—107°). Pure material (plates, m. p. 111—112°) was obtained by sublimation at 100°/20 mm. or more rapidly by distillation in 30 volumes of ethylene glycol in which the benzothionaphthen is sparingly soluble when cold (Found: C, 78·25; H, 4·5; S, 17·1. Calc. for $C_{12}H_8S$: C, 78·3; H, 4·35; S, 17·3%). When purified by means of the picrate it has m. p. 113—114°. The m. p. of the coal-tar product[19] was 116°, and those of the synthetic products of Carruthers[8] and of Tilak[17] were 112° and 116—117° respectively. The last-named obtained it in a yield of about 55% by cyclisation of 2-naphthylthioacetaldehyde dimethyl acetal with polyphosphoric acid.

2-Naphthylthioacetaldehyde diethyl acetal has been used in examining the cyclising effect of various reagents. (i) The acetal (1 g.) was refluxed for 2 hr. in acetic acid (3 ml.) containing fused zinc chloride (3 g.), allowed to cool, and poured into water, and the crude 4 : 5-benzothionaphthen (0·27 g., 41%) purified as above. (ii) The acetal (1 g.) was refluxed in ethanol (6 ml.) with powdered fused zinc chloride (4 g.) for 4 hr. The mixture gave 4 : 5-benzothionaphthen (0·26 g.,39% yield) when poured into dilute hydrochloric acid. (iii) When fused zinc chloride was used alone at 150—190° the yields were much lower. (iv) The acetal (5 g.) was heated with anhydrous oxalic acid (7·5 g.) at 190° for 30 min., cooled, and extracted with boiling water, to give 4 : 5-benzothionaphthen (82%). (v) The acetal (1 g.) was heated with phosphoric oxide (0·33 g.) at 160° for 45 min. Digestion with water yielded 4 : 5-benzothionaphthen (0·27 g., 40%). (vi) Among unsuccessful reagents used were boron trifluoride in ether, concentrated sulphuric acid, and toluene-*p*-sulphonic acid.

Removal of Sulphur from 4 : 5-*Benzothionaphthen.*—4 : 5-Benzothionaphthen (0·5 g.) did not lose sulphur when refluxed with stirring for 5 hr. with Raney nickel (5 g.) in ethanol (150 ml.); but when it (0·18 g.) was refluxed in ethylene glycol (25 ml.) for 3½ hr. with Raney nickel (2 g.), then diluted with water and extracted with chloroform, 1-ethylnaphthalene was obtained, identified as the picrate, m. p. 96—97°, mixed m. p. 97—98°. The authentic sample of 1-ethylnaphthalene was prepared by the method of Gilman and Hoyle[23] from 1-naphthylmagnesium bromide and diethyl sulphate.

To 3 : 4-dimethoxyphenylthioacetaldehyde diethyl acetal (2·6 g.) in chloroform (60 ml.) was carefully added a solution of stannic chloride (2 g.) in chloroform (20 ml.). After 30 min. at room temperature the red solution was poured into water (100 ml.), and crude 5 : 6-*dimethoxythionaphthen* (0·4 g., 23%) was precipitated. Distillation in the vapour of ethylene glycol or

[23] Gilman and Hoyle, *J. Amer. Chem. Soc.*, 1922, **14**, 2623.

sublimation at 120°/15 mm. gave prisms, m. p. 100—101° (Found : C, 62·1 ; H, 5·2. $C_{10}H_{10}O_2S$ requires C, 61·8 ; H, 5·2%). The yield was about 13% when reaction was for 10 min.

Among unsuccessful reagents used were zinc chloride (alone and with glacial acetic acid), oxalic acid, stannic chloride, and concentrated sulphuric acid.

Degradation of 5 : 6-*Dimethoxythionaphthen.*—5 : 6-Dimethoxynaphthen was desulphurised in the same way as 4 : 5-benzothionaphthen to a sweet-smelling oil which on oxidation with potassium permanganate in aqueous sodium carbonate gave needles, m. p. 178·5—179·5°. The mixed m. p. with veratric acid (m. p. 181—182°) was 180·5—181°.

The method of cyclisation (13% yield) of *p*-bromophenylthioacetaldehyde dimethyl acetal by polyphosphoric acid [15] was applied to the corresponding diethyl acetal (9·5 g.) which gave 5-bromothionaphthen (3·3 g., 49%), m. p. 47°. *p*-Methoxyphenyl- and *o*-, *m*-, and *p*-tolylthioacetaldehyde dimethyl acetal, which correspond to the above described four arylthioacetaldehyde diethyl acetals, have been successfully cyclised by Tilak [1] by polyphosphoric acid.

Preparation of 6 : 7-*Benzothionaphthen* (VI).—(i) *From* 2 : 3-*dihydro*-6 : 7-*benzothionaphthen* 1 : 1-*dioxide* (IX). The dioxide (2·8 g.) in a Soxhlet thimble was continuously extracted for 10 hr. with dry ether (100 ml.) containing lithium aluminium hydride (2·0 g.), excess of which was decomposed with ether containing ethanol, and then with dilute hydrochloric acid. The dried ($CaCl_2$) ether layer yielded an oil (1·5 g.), distillation of which gave 2 : 3-*dihydro*-6 : 7-*benzothionaphthen* (1·2 g.), b. p. 183—185°/18 mm. (Found : C, 77·3; H, 5·6. $C_{12}H_{10}S$ requires C, 77·4; H, 5·4%). The *picrate*, m. p. 132—132·5°, formed dark red needles (from alcohol), the red alcoholic solution of which became yellow when boiled (Found : N, 9·7. $C_{18}H_{13}O_7N_3S$ requires N, 10·1%).

A mixture of 2 : 3-dihydro-6 : 7-benzothionaphthen (0·50 g.), chloranil (0·8 g.), and xylene (15 ml.) was refluxed for 7 hr., and the filtrate diluted with benzene was chromatographed on alumina. The first eluate (faint blue fluorescence in ultraviolet light) gave a pale yellow oil (0·43 g.) which with 2 : 4 : 7-trinitrofluorenone (0·8 g.) in ethanol gave a derivative which recrystallised from ethanol in orange-yellow needles, m. p. 198·5° (0·6 g., 51%). This was decomposed (in 90% yield) in benzene solution on an alumina column and the first eluate gave an oil (0·20 g. ; overall yield, 40%) which solidified at room temperature to give crystals, m. p. 27—28° (6 : 7-benzothionaphthen [8]).

(ii) *From* 1-*naphthylthioacetaldehyde acetals.* 1-Naphthylthioacetaldehyde dimethyl acetal (9·9 g.) was dropped during 15 min. below the surface of a mixture of phosphoric oxide (65 g.) and phosphoric acid (65 ml. ; *d* 1·75) at 180°/0·5 mm. After a further 10 minutes' heating the mixture was poured into water and steam-distilled, and the ethereal extract, dried after washing with aqueous sodium hydroxide, gave 2·6 g. (35%) of a pale yellow oil which crystallised and had m. p. 13—19°. Its picrate, brown-yellow needles, had the m. p. (143—144°) recorded [8] for the picrate of 6 : 7-benzothionaphthen synthesised in a different way.

The cyclisation product (0·17 g.) was mixed with a boiling solution of 2 : 4 : 7-trinitrofluorenone (0·40 g.) in ethanol (100 ml.). The 6 : 7-*benzothionaphthen*–2 : 4 : 7-*trinitrofluorenone derivative*, which was formed on cooling, recrystallised in orange-yellow needles (0·40 g., 87%), m. p. 198—198·5° (Found : C, 60·4; H, 2·7. $C_{12}H_8S$,$C_{13}H_5O_7N_3$ requires C, 60·0; H, 2·6%). This compound (0·34 g.) in benzene was decomposed on an alumina column to give an almost colourless oil (0·12 g.) which after crystallisation had m. p. 25—27°, not depressed on admixture with the above 6 : 7-benzothionaphthen, m. p. 27—28°.

6 : 7-*Benzothionaphthen* 1 : 1-*Dioxide.*—A mixture of the above 6 : 7-benzothionaphthen (0·90 g.), glacial acetic acid (11 ml.), and hydrogen peroxide (3·2 ml. ; 100-vol.) was heated on the water-bath for 4 hr., and the cold solution poured into water (100 ml.). The precipitate, formed overnight, crystallised from methanol in pale yellow plates (0·24 g., 23%), m. p. 179—180° (Found : C, 66·8; H, 3·8. Calc. for $C_{12}H_8O_2S$: C, 66·7; H, 3·7%). It was identical (mixed m. p.) with the 6 : 7-benzothionaphthen sulphone (X) ultimately derived from 2-bromonaphthalene.[18] The yellow colour of both specimens could not be removed by crystallisation.

1-Naphthylthioacetaldehyde diethyl acetal, cyclised under the above conditions, gave a 20% yield of 6 : 7-benzothionaphthen, of which the picrate and 2 : 4 : 7-trinitrofluorenone derivative were identical with the above.

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