935. *Derivatives of Thionaphthen. Part II.* Thionaphthen Derivatives formed by Cyclisation of Acetonyl Aryl Sulphides and Aryl Phenacyl Sulphides.*

By J. E. Banfield, W. Davies, N. W. Gamble, and S. Middleton.

Cyclisation of phenacyl phenyl sulphide gives, not the expected 3-phenylthionaphthen, but 2-phenylthionaphthen (32% yield), whose structure has been proved by synthesis and degradation. 2-Phenylthionaphthen derivatives are similarly formed by the cyclisation of phenacyl *m*- and *p*-tolyl sulphides and 4-methoxyphenacyl phenyl sulphide. The compounds described [1] as 6-hydroxy- and 6-methoxy-3-phenylthionaphthen are now also found to be derivatives of 2-phenylthionaphthen. On the other hand, cyclisation of acetonyl phenyl sulphide is known to give 3-methylthionaphthen, without rearrangement. Various other substituted thionaphthens have been synthesised.

In early attempts to synthesise thionaphthen derivatives by the cyclodehydration of arylthio-ketones Delisle,[2] and Delisle and Schwalm,[3] used respectively acetonyl phenyl sulphide, $PhS{\cdot}CH_2{\cdot}COMe$, and ethyl (phenylthio)acetoacetate, $PhS{\cdot}CH(CO_2Et){\cdot}COMe$. Success was first achieved by Fries, Heering, Hemmecke, and Siebert [1] who cyclised *m*-hydroxyphenyl phenacyl sulphide and its methyl ether (I) with concentrated sulphuric acid to form what has hitherto been accepted as 6-hydroxy-3-phenylthionaphthen and its methyl ether (II). These two cyclisations, the only ones recorded until 1949, were doubtless aided by the

* Part I, Banfield, Davies, Ennis, Middleton, and Porter, *J.*, 1956, 2603.

[1] Fries, Heering, Hemmecke, and Siebert, *Annalen*, 1937, **527**, 110.
[2] Delisle, *Annalen*, 1890, **260**, 250.
[3] Delisle and Schwalm, *Ber.*, 1892, **25**, 2980.

activation of the position *para* to the strongly nucleophilic hydroxyl or methoxyl group, and do not justify the implication of a general synthesis given by Elderfield.[4] Such a general synthesis was begun [5] in 1948, by the preparation and attempted cyclisation of arylthio-ketones $ArS{\cdot}CH_2{\cdot}COR$ (R = aryl or occasionally methyl). This work was anticipated to a slight extent by Werner [6] who prepared ten arylthio-ketones, nine of which had the formula $Ar{\cdot}S{\cdot}CHR{\cdot}COMe$ (R = Me or H) and only one, $PhS{\cdot}CH_2{\cdot}COPh$, was of the phenacyl type. Werner, using phosphoric oxide or zinc chloride, successfully cyclised six of these to thionaphthen derivatives, all containing a 3-methyl substituent, but his efforts to cyclise phenacyl phenyl sulphide were unsuccessful.

The arylthio-ketones used were prepared by condensing 2-halogeno-ketones with arenethiols in the presence of base, but the process is more complicated than preparation of arylthioacetaldehyde acetals from the thiol and chloroacetaldehyde (Part I). First, when the ketone is phenacyl chloride and the base sodium hydroxide in ethanol, some of the phenacyl chloride is, despite the presence of the thiol, converted into " β-chlorodiphenacyl," [7] $C_{16}H_{13}O_2Cl$. Secondly, the 2-halogeno-ketones contain a positive halogen which can have an undesirable oxidising action on the thiol: thus, the interaction of phenacyl chloride and sodium *p*-tolyl sulphide in boiling methanol forms, not the desired sulphide, but acetophenone and phenacyl *p*-tolyl sulphoxide.[8] Similarly condensation of ethyl αα-dichloroacetoacetate and sodium thiophenoxide gave diphenyl disulphide and ethyl αβ-diacetylfumarate.[9] In the present work the oxidising effect in strong alkali of the positive halogen in phenacyl chloride has been repeatedly seen in the formation of large amounts of the diaryl disulphides.

Though these difficulties have been overcome with *p*-tolylthiomagnesium iodide in ether,[10] and by the rapid condensation at low temperatures of the very reactive phenacyl bromide with thiophenol in the presence of sodium methoxide,[11] it is now found that a very convenient condensing reagent for phenacyl chloride is boiling pyridine, the excess of which acts as solvent. It is particularly useful with *p*-acetamidothiophenol and other compounds containing groups sensitive to alkali.

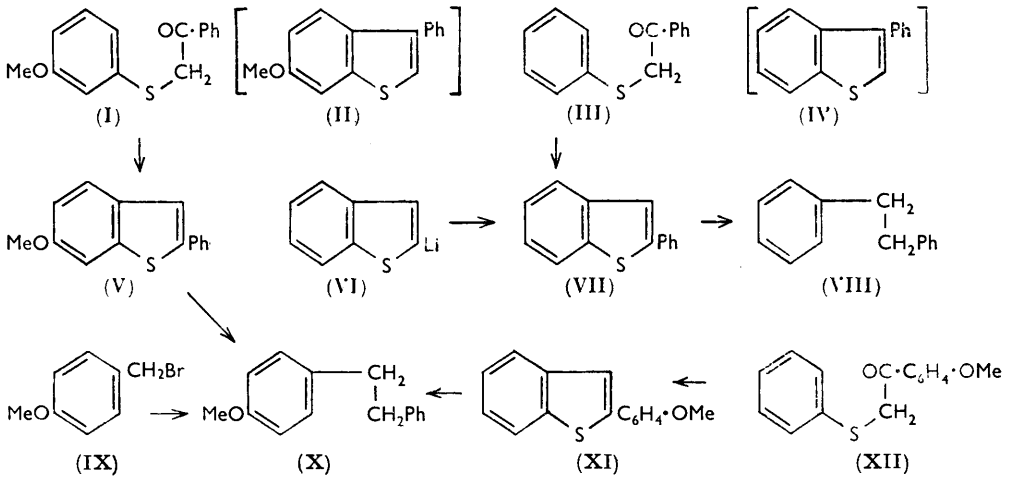
Arylthio-ketones are more resistant to acidic dehydrating agents than are arylthioacetaldehyde acetals, but like them readily suffer fission between the sulphur atom and the side chain, the original thiol or the disulphide from it being isolated. Oxalic acid is generally too weak a reagent, and concentrated sulphuric acid under ordinary conditions is too strong, though it is successful in cyclising 1-naphthyl phenacyl sulphide. It was independently found by some of the present workers and by Werner that phosphoric oxide and fused zinc chloride are often effective cyclising agents, but that they failed with phenacyl phenyl sulphide. However, this sulphide is cyclised (32% yield) by the prolonged use of polyphosphoric acid, which has so far been little used with compounds of this type. Many of the aryl phenacyl sulphides prepared resisted attempts to cyclise them with zinc chloride or phosphoric oxide, but polyphosphoric acid has not yet been tried with them.

The cyclisation of phenacyl phenyl sulphide (III) and some related compounds is now found to be subject to a rearrangement not previously observed in the synthesis of derivatives of thionaphthen. Polyphosphoric acid converts it in 32% yield into 2-phenylthionaphthen (VII), together with tar; 3-phenylthionaphthen (IV) has not been isolated from the product. Desulphurisation of the product (VII) with Raney nickel gives dibenzyl (VIII) (nitrated to 4 : 4′-dinitrodibenzyl, and oxidised to benzoic acid). Had 3-phenylthionaphthen (IV) been formed, desulphurisation would have given 1 : 1-diphenylethane, Ph_2CHMe, oxidation of which is known to yield benzophenone.[12] The 2-phenyl structure (VII) is further proved by synthesis of the compound from fluorobenzene and

[4] Elderfield, " Heterocyclic Compounds," Wiley, New York, 1950, Vol. II, p. 146.
[5] Banfield, Thesis, Melbourne, 1950.
[6] Werner, *Rec. Trav. chim.*, 1949, **68**, 509.
[7] Beilstein, " Handbuch der Organischen Chemie," Vol. XIX, p. 54.
[8] Kohler and Potter, *J. Amer. Chem. Soc.*, 1936, **58**, 2166.
[9] Otto and Rossing, *Ber.*, 1890, **23**, 756.
[10] Gilman and King, *J. Amer. Chem. Soc.*, 1925, **47**, 1136.
[11] Krollpfeiffer, Hartmann, and Schmidt, *Annalen*, 1949, **563**, 21.
[12] Beilstein, *op. cit.*, Vol. V, p. 60.

2-thionaphthenyl-lithium (VI), the constitution of the latter having been proved by its carboxylation to thionaphthen-2-carboxylic acid.[13]

A repetition of the cyclisation of *m*-methoxyphenyl phenacyl sulphide (I) with concentrated sulphuric acid by Fries *et al.*[1] gave a small amount of their product, m. p. 59°, but this compound is more easily obtained by the use of polyphosphoric acid. The product is desulphurised to give 4-methoxydibenzyl (X) identical with a specimen synthesised from 4-methoxybenzyl bromide and benzylmagnesium chloride. The cyclisation has therefore formed 6-methoxy-2-phenylthionaphthen (V) and not 6-methoxy-3-phenylthionaphthen



(II), desulphurisation of which would yield 1-*p*-methoxyphenyl-1-phenylethane. Had cyclisation occurred in the position *ortho* to methoxyl group, the resulting thionaphthen derivative would have yielded either 2-methoxydibenzyl or 1-*o*-methoxyphenyl-1-phenylethane on desulphurisation. Further, since demethylation of the compound, m. p. 59°, gave [1] the hydroxyphenylthionaphthen obtained by cyclisation of *m*-hydroxyphenyl phenacyl sulphide, it follows that the compound described by Fries [1] as 6-hydroxy-3-phenylthionaphthen is the 2-phenyl derivative.

Rearrangement also occurs in the cyclisation of 4-methoxyphenacyl phenyl sulphide (XII). The product must be 2-*p*-methoxyphenylthionaphthen (XI), for this also on desulphurisation gives 4-methoxydibenzyl (X).

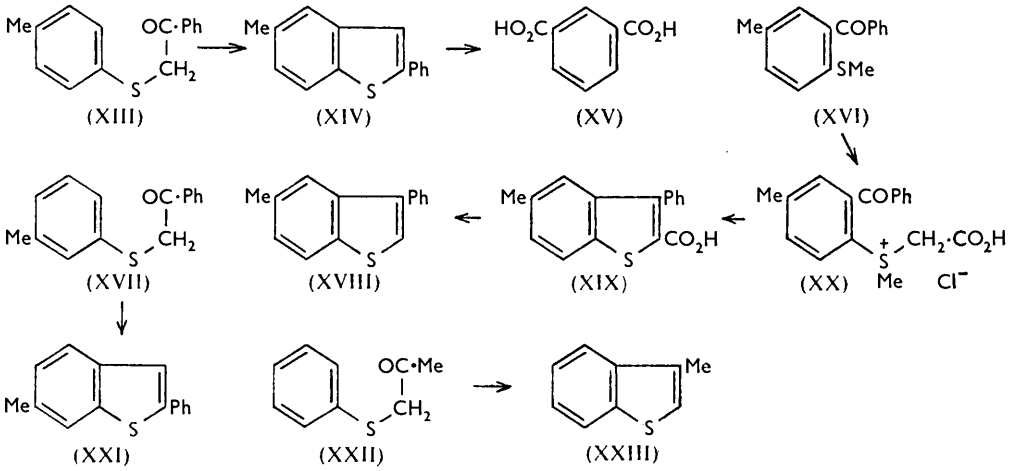
Similarly phenacyl *p*-tolyl sulphide (XIII) cyclises to form 5-methyl-2-phenylthionaphthen (XIV), desulphurisation of which gives a hydrocarbon (not characterised) considered to be 1-phenyl-2-*m*-tolylethane since it is oxidised to *iso*phthalic acid (XV) and benzoic acid; no *m*-benzoylbenzoic acid was obtained though this would be expected had the cyclisation product been 5-methyl-3-phenylthionaphthen (XVIII) whose derived hydrocarbon would be 1-phenyl-1-*m*-tolylethane. Now 5-methyl-3-phenylthionaphthen (XVIII) has been synthesised [14] by decarboxylation of 5-methyl-3-phenylthionaphthen-2-carboxylic acid (XIX) prepared unambiguously from 5-methyl-2-(methylthio)benzophenone (XVI). In confirmation of the structure (XVIII), it is now found that the oil obtained by this method yields *m*-benzoylbenzoic acid on desulphurisation and oxidation.

Four thionaphthen derivatives can theoretically be obtained by the cyclisation of phenacyl *m*-tolyl sulphide (XVII), where ring closure might occur *para* or *ortho* to the methyl group. 6-Methyl-2-phenylthionaphthen (XXI) should give 4-methyldibenzyl on reductive desulphurisation, and this would be oxidised to benzoic and terephthalic acid; these are indeed the only acids obtained from the homogeneous thionaphthen derivative formed in this cyclisation, and prove the structure (XXI).

[13] Shirley and Cameron, *J. Amer. Chem. Soc.*, 1950, **72**, 2788.
[14] Krollpfeiffer, Schneider, and Wissner, *Annalen*, 1950, **566**, 147.

Finally, the cyclisation of acetonyl phenyl sulphide (XXII) has been shown by Werner [6] to give 3- and not 2-methylthionaphthen, so that there is so far no evidence that rearrangement occurs in the cyclisation of $ArS{\cdot}CH_2{\cdot}COR$ where R is alkyl.

It has been proved that rearrangement occurs with each of the five compounds $Ar'S{\cdot}CH_2{\cdot}COAr$ examined. The yields are moderate (26—68%), and a considerable amount of tar is formed. Fries *et al.* cyclised the sulphide (I) in 55—60% yield, but the details in their paper are so vague that a repetition of their process by the present workers



has given only a minute yield of the product (V). In the cyclisation of arylthioacetaldehyde diethyl acetals (Part I), where there is no possibility of rearrangement, slight changes in conditions can cause much tar-formation and a great fall in yield. Hence it is felt that in the cyclisation of aryl phenacyl sulphides the moderate yield of the thionaphthen derivative is due to the imperfections of the process itself, rather than to the presence in the tar of much of the " normal " 3-arylthionaphthen derivative, of which so far none has been isolated. Probably the 3- are more easily fusible than the 2-arylthionaphthen derivatives [cf. the oily 5-methyl-3-phenylthionaphthen (XVIII) with 5-methyl-2-phenylthionaphthen (XIV), m. p. 158—158·5°], and this would render the isolation of the 3-aryl derivatives more difficult. Nevertheless, the present work indicates that the 2-aryl- are probably the main, if not the only, thionaphthen derivatives formed.

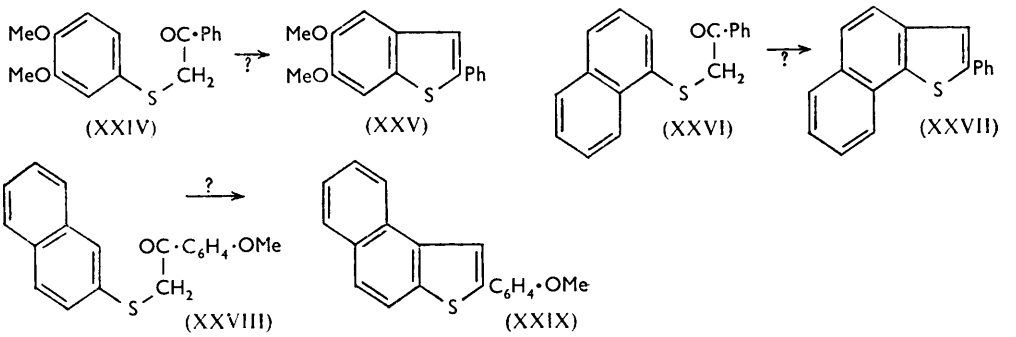
Our work leads to a tentative generalisation that in the cyclisation of $ArS{\cdot}CH_2{\cdot}COR$ rearrangement occurs when R is a simple aryl and not when R is a simple alkyl group.

Accordingly the cyclisation products of acetonyl *o*- and *p*-tolyl sulphides are regarded as 3 : 7- and 3 : 5-dimethylthionaphthen respectively. Since Sunthankar and Tilak [15] have shown that the cyclisation of *m*-tolylthioacetaldehyde dimethyl acetal gives 6-methylthionaphthen, acetonyl *m*-tolyl sulphide should form 3 : 6-dimethylthionaphthen. It is remarkable that in the cyclisation of the three tolylthioacetaldehyde dimethyl acetals and the three acetonyl tolyl sulphides, the smallest yield of thionaphthen derivative is obtained from the *p*-tolyl type.

On the other hand, if rearrangement is assumed, the structures of a number of cyclisation products from various aryl phenacyl sulphide derivatives are considered definite for the following reasons. Since 3 : 4-dimethoxyphenylthioacetaldehyde diethyl acetal cyclises at a position *para* to one of the methoxyl groups (Part I), the product from 3 : 4-dimethoxyphenyl phenacyl sulphide (XXIV) should be 5 : 6-dimethoxy-2-phenylthionaphthen (XXV). By analogy, 5 : 6-dimethoxy-2-*p*-methoxyphenylthionaphthen should be the product from 3 : 4-dimethoxyphenyl 4-methoxyphenacyl sulphide. As cyclisation occurs in the 2- and not the *peri*-position with 1-naphthylthioacetaldehyde dimethyl and diethyl acetals (Part I)

[15] Sunthankar and Tilak, *Proc. Indian Acad. Sci.*, 1950, **32**, *A*, 396.

and with 3-1′-naphthylthiobutan-2-one,[6] it is likely that 1-naphthyl phenacyl sulphide (XXVI) would form 2-phenyl-6 : 7-benzothionaphthen (XXVII), and that 4-methoxyphenacyl 1-naphthyl sulphide would similarly give 2-*p*-methoxyphenyl-6 : 7-benzothionaphthen. Finally, 2-naphthylthioacetaldehyde diethyl acetal is known to cyclise in the



1-position (Part I), hence 4-methoxyphenacyl 2-naphthyl sulphide (XXVIII) should yield 2-*p*-methoxyphenyl-4 : 5-benzothionaphthen (XXIX).

Experimental

Preparation of Acetonyl Aryl Sulphides.—These have been made by using as condensation agent (a) aqueous alkali or (p) pyridine, as exemplified in the preparation of acetonyl phenyl sulphide.

Method (*a*). Thiophenol (11·0 g.) was added to a solution of sodium hydroxide (4·0 g.) in water (12·0 g.) under nitrogen, and bromoacetone (8·5 ml., 1·01 mol.) added, with stirring and ice-cooling, during ½ hr. After 2 hr. the mixture yielded to ether slightly impure acetonyl phenyl sulphide, m. p. 25—30°, b. p. 160—165°/22 mm. (8·8 g., 53%).

Method (*p*). Bromoacetone (5·0 ml., 1·31 mol.) was slowly added to a solution of thiophenol (5·0 g., 1 mol.) in pyridine (25 ml.), and after 5 min. the solution was heated on the water-bath for 10 min. The cooled solution, acidified with hydrochloric acid, yielded to ether acetonyl phenyl sulphide, m. p. 30—33°, b. p. 165—175°/28 mm. (4·8 g., 64%). Delisle [2] records m. p. 34—35°.

The following *acetonyl sulphides* were made essentially as above, though in method (a) a larger amount (about 1·2 mol.) of bromoacetone was used. The yields are calculated on the thiol. In the method (p) the reactants were sometimes kept at room temperature for many hours, but were not heated for more than ¼ hr.

o-*Tolyl* (p, 3 days; 60%), b. p. 161—164°/22 mm., n_D^{16} 1·5750 (Found : C, 66·6; H, 6·7; S, 18·2. $C_{10}H_{12}OS$ requires C, 66·7; H, 6·7; S, 17·8%).

m-Tolyl (p, 5 min.; 49%), b. p. 158—164°/19 mm., n_D^{18} 1·5674. Newell and Calaway [16] record b. p. 133—135°/7 mm.

p-Tolyl (purified through the bisulphite compound) (a, 55%; p, ¼ hr.; 58%), b. p. 164—168°/22 mm., n_D^{26} 1·5610. Delisle [2] records b. p. 150—157°/18 mm.

p-*Methoxyphenyl* (p, 5 min.; 55%), b. p. 180—182°/18 mm., n_D^{16} 1·5718 (Found : C, 61·6; H, 6·2; S, 16·8. $C_{10}H_{12}O_2S$ requires C, 61·2; H, 6·1; S, 16·3%).

3 : 4-*Dimethoxyphenyl* (p, 1 hr.; 61%), b. p. 210—214°/28 mm., n_D^{15} 1·5778 (Found : C, 57·8; H, 6·3; S, 14·6. $C_{11}H_{14}O_3S$ requires C, 58·4; H, 6·2; S, 14·2%).

p-*Acetamidophenyl* (p, ½ hr., then heated for 1 min.; 68%), needles (from ethanol), m. p. 151° (Found : C, 59·05; H, 5·9; S, 14·4. $C_{11}H_{13}O_3NS$ requires C, 59·2; H, 5·8; S, 14·3%).

2-*Naphthyl* (a, 58%; p, 24 hr.; 96% yield of product, m. p. 37—40°, about 98% pure) (separated from a trace of non-volatile di-2-naphthyl disulphide, m. p. and mixed m. p. 138·5—139·5° by distillation with ethylene glycol at ordinary pressure), plates, m. p. 46—46·2° (from light petroleum) (Found : C, 72·3; H, 5·5; S, 14·5. $C_{13}H_{12}OS$ requires C, 72·2; H, 5·5; S, 14·8%).

1-*Naphthyl* (p, 12 hr.; 22%), b. p. 167—177°/0·4 mm. (Found : C, 72·5; H, 5·7; S, 14·5%).

[16] Newell and Calaway, *J. Amer. Chem. Soc.*, 1947, **69**, 116.

Preparation of Aryl Phenacyl Sulphides.—The thiol (1 mol.), usually dissolved in 1½—4 times its weight of pyridine, was refluxed with phenacyl chloride (1 mol.) for the time indicated. Similar heating is desirable to improve the low yields of some of the above acetonyl aryl sulphides, especially when derived from *o*-substituted thiols. The following *aryl phenacyl sulphides* were prepared : phenyl (6 hr.; 95%), b. p. 173—177°/0·5 mm., m. p. 52—53° (from ethanol); cf. Delisle.[2]

o-*Tolyl* (4 hr.; 50%), m. p. 65—66° (from light petroleum) (Found : C, 74·4; H, 5·8. $C_{15}H_{14}OS$ requires C, 74·4; H, 5·8%).

m-*Tolyl* (6 hr.; 72%), b. p. 176—182°/0·35 mm., plates (from light petroleum), m. p. 45° (Found : C, 74·1; H, 5·6; S, 13·5. $C_{15}H_{14}OS$ requires C, 74·4; H, 5·8; S, 13·2%).

p-Tolyl (4 hr.; 86%), b. p. 184—185°/0·1 mm., m. p. 35—36° (from ethanol). Gilman and King [10] record m. p. 37°.

p-*Methoxyphenyl* (9 hr.; 78%), b. p. 196—198°/0·2 mm., n_D^{16} 1·6229 (Found : C, 69·3; H, 5·45; S, 12·4. $C_{15}H_{14}O_2S$ requires C, 69·8; H, 5·45; S, 12·4%).

3 : 4-*Dimethoxyphenyl* (5 hr. ; 95%), b. p. 222—227°/0·5 mm., needles (from ethanol), m. p. 70—70·5 (Found : C, 66·75; H, 5·8; S, 11·0. $C_{16}H_{16}O_3S$ requires C, 66·7; H, 5·5; S, 11·2%).

p-*Acetamidophenyl* (½ hr.; 72%), needles (from ethanol), m. p. 121·5° (Found : N, 5·2; S, 11·6. $C_{16}H_{15}O_2NS$ requires N, 4·9; S, 11·2%).

2-*Naphthyl* (4 hr.; 66%), m. p. 96·5—97·5° (from ethanol) (Found : C, 77·9; H, 5·1; S, 12·0. $C_{18}H_{14}OS$ requires C, 77·7; H, 5·05; S, 11·5%).

1-*Naphthyl* (5 hr.; 74%), prisms (from ethanol), m. p. 83·5—84° (Found : C, 77·6; H, 5·15; S, 11·65%), of which the pale straw colour could not be removed by carbon.

m-Methoxyphenyl (6 hr.; 81%), m. p. 46—47°. Fries *et al.*[1] report m. p. 47°. The 2 : 4-*dinitrophenylhydrazone* recrystallised from alcohol in prisms, m. p. 153—154° (Found : N, 12·5. $C_{21}H_{18}O_5N_4S$ requires N, 12·8%).

The following were prepared without the use of pyridine.

p-Nitrophenyl phenacyl sulphide, identical with the product (m. p. 118°) of Waldron and Reid [17] who used sodium hydroxide, was obtained in 90% yield by using alcoholic ammonia (several hours at room temperature).

2 : 4-*Dinitrophenyl phenacyl sulphide* (good yield) began to separate in 1 min. after addition of phenacyl chloride to a warm solution of 2 : 4-dinitrothiophenol in alcoholic sodium hydroxide. Crystallised from ethanol, it had m. p. 170—171° (Found : C, 53·0; H, 3·45; N, 8·9. $C_{14}H_{10}O_5N_2S$ requires C, 52·8; H, 3·15; N, 8·8%).

The following aryl 4-*methoxyphenacyl sulphides* were prepared from 4-methoxyphenacyl chloride and the corresponding thiophenol in pyridine as described above :

Phenyl (4 hr.; 84%), plates (from ethanol), m. p. 89—90° (Found : C, 69·5; H, 5·5. $C_{15}H_{14}O_2S$ requires C, 69·8; H, 5·4%). The 2 : 4-*dinitrophenylhydrazone* formed needles (from alcohol), m. p. 169—170° (Found : N, 12·5. $C_{21}H_{18}O_5N_4S$ requires N, 12·8%).

3 : 4-*Dimethoxyphenyl* (4 hr.; 90%), needles, m. p. 46·5—47·5° (from ether–light petroleum) (Found : OMe, 29·25. $C_{17}H_{18}O_4S$ requires OMe, 29·3%). The p-*nitrophenylhydrazone* was orange plates (from ethanol), m. p. 164—165° (Found : C, 61·05; H, 5·4; N, 9·45. $C_{23}H_{23}O_5N_3S$ requires C, 60·9; H, 5·1; N, 9·3%).

1-*Naphthyl* (4 hr.; 68%), cream-coloured needles, m. p. 71° (from ethanol) (Found : OMe, 10·1. $C_{19}H_{16}O_2S$ requires OMe, 10·05%) [p-*nitrophenylhydrazone*, light yellow needles (from ethanol), m. p. 148·5° (Found : C, 68·0; H, 4·95; N, 9·55. $C_{25}H_{21}O_3N_3S$ requires C, 67·7; H, 4·75; N, 9·5%)].

2-*Naphthyl* (4 hr.; 95%), plates (from ether–light petroleum), m. p. 95·5° (Found : OMe, 10·2%) [p-*nitrophenylhydrazone*, light golden plates (from ethanol), m. p. 159—160° (Found : N, 9·4%)].

o-*Tolyl* (5 hr.; 85%), pale yellow prisms (from aqueous ethanol), m. p. 50° (Found : OMe, 11·5. $C_{16}H_{16}O_2S$ requires OMe, 11·4%) [p-*nitrophenylhydrazone*, golden-yellow plates (from ethanol), m. p. 162—163° (Found : N, 10·6. $C_{22}H_{21}O_3N_3S$ requires N, 10·3%)].

p-*Dimethylaminophenyl* (4 hr.; 70%), pale brown plates (from aqueous ethanol), m. p. 69—70° (Found : OMe, 10·1. $C_{17}H_{19}O_2NS$ requires OMe, 10·3%) [p-*nitrophenylhydrazone*, golden plates (from ethanol), m. p. 184—185° (Found : N, 12·85. $C_{23}H_{24}O_3N_4S$ requires N, 12·8%)].

Conversion of Acetonyl Aryl Sulphides into Thionaphthens.—3-Methylthionaphthen was readily prepared by Werner's method,[6] the action of phosphoric oxide at 160—190° or zinc chloride at 190° on acetonyl phenyl sulphide. However, appreciable amounts were recovered

[17] Waldron and Reid, *ibid.*, 1923, **45**, 240.

unchanged (25% after ¾ hour's heating with 0·33 part of phosphoric oxide at 160°, and 21% after ¾ hour's heating with 1½ parts of zinc chloride at 190°). The following were prepared.

3 : 7-*Dimethylthionaphthen* (60%), b. p. 122—124°/12 mm., m. p. 30—31°, n_D^{15} 1·6090, from equal weights of acetonyl *o*-tolyl sulphide and phosphoric oxide at 190° for ¾ hr. (Found : C, 74·1; H, 6·1; S, 19·6. $C_{10}H_{10}S$ requires C, 74·1; H, 6·2; S, 19·7%).

3 : 6-*Dimethylthionaphthen* (63%), b. p. 133—134°/18 mm., n_D^{18} 1·6158, from the *m*-tolyl sulphide similarly at 170° for 1½ hr. and then at 190° for ½ hr. (also, in 53% yield, from 1 part of ketone and 2 parts of zinc chloride for 7 hr. at 160—170°) (Found : S, 19·0%) [*picrate*, orange needles (from ethanol), m. p. 134·5—135·5° (Found : C, 49·1; H, 3·6; N, 11·2; S, 8·15. $C_{16}H_{13}O_7N_3S$ requires C, 49·1; H, 3·3; N, 10·75; S, 8·2%)].

3 : 5-Dimethylthionaphthen, b. p. 125—126°/14 mm., n_D^{15} 1·6010, in 27% yield from the *p*-tolyl sulphide similarly at 190° for ¾ hr. (a smaller yield was obtained by the use of equal parts of zinc chloride and the ketone at 170° for 40 min., then at 200° for 10 min., some thio-*p*-cresol being obtained also) (Found : C, 73·6; H, 6·2; S, 20·3%) [picrate, orange needles (from ethanol), m. p. 113—114° (from ethanol) (cf. ref. 11) (Found : N, 10·8%).

3-*Methyl*-6 : 7-*benzothionaphthen* (62%), m. p. 60·5—61·5°, b. p. 140—144°/0·3 mm., from the 1-naphthyl sulphide (1·4 g.) similarly at 190° for ¾ hr. (Found : C, 78·7; H, 5·1; S, 16·05. $C_{13}H_{10}S$ requires C, 78·8; H, 5·05; S, 16·1%) [*picrate*, orange prisms (from benzene–light petroleum), m. p. 125·5—127·5° (decomp.) (Found : S, 7·3; N, 10·1. $C_{19}H_{13}O_7N_3S$ requires S, 7·5; N, 9·85%)].

3-*Methyl*-4 : 5-*benzothionaphthen* (95%), m. p. 58·5—59·5°, b. p. 150—170°/0·5 mm. (accompanied by sublimation), from the 2-naphthyl sulphide with 4 times its weight of zinc chloride at 180° for ½ hr., then at 190° for ½ hr. (Found : C, 79·2; H, 5·2; S, 16·2%) [yellow *picrate* (from benzene–light petroleum), m. p. 152—153° (Found : S, 7·45; N, 10·1%)].

5 : 6-*Dimethoxy*-3-*methylthionaphthen* (83%), m. p. 107—107·5° (from light petroleum) from the 3 : 4-dimethoxyphenyl sulphide (5·6 g.) and phosphoric oxide (1·9 g.) at 170—175° for ½ hr. (the product was extracted with chloroform) (Found : C, 63·7; H, 5·95; S, 15·7; OMe, 29·6. $C_{11}H_{12}O_2S$ requires C, 63·5; H, 5·8; S, 15·4; OMe, 29·8%).

The *p*-methoxy- and *p*-acetamido-phenyl sulphides could not be cyclised with zinc chloride or with phosphoric oxide.

Cyclisation of Aryl Phenacyl Sulphides and their Derivatives.—In these cyclisations, times and temperatures are important.

(i) *Phenacyl phenyl sulphide.* The sulphide (5 g.), phosphoric oxide (35 g.), and phosphoric acid (20 ml.; *d* 1·75) were heated at 180—190° for 3 hr., and the cold mixture poured into water. Ether extracted 2-phenylthionaphthen (1·5 g., 32%), prisms, m. p. 175—176° (Found : C, 80·1; H, 4·8; S, 15·0. Calc. for $C_{14}H_{10}S$: C, 80·0; H, 4·8; S, 15·2%). Horton [18] gives m. p. 175·5—176°.

This product (0·8 g.) was refluxed with Raney nickel (8 g.) in ethylene glycol (30 ml.) for 8 hr., and the hot filtrate poured into water (250 ml.). The precipitate was washed twice with chloroform (75 ml.) and each washing was then used to extract the aqueous solution. The chloroform extract was dried ($MgSO_4$) and yielded a brown fragrant oil which was separated into two parts. One part was refluxed for 15 min. with water (10 ml.), powdered potassium permanganate (0·5 g.), and sodium carbonate (0·2 g.), the cold solution was clarified by sulphur dioxide, and benzoic acid separated (m. p. and mixed m. p. 120—121°). The second part was shaken with cold fuming nitric acid (2 ml.) for a few minutes, and the mixture was diluted with water, giving pale yellow prisms (from ethanol) of 4 : 4′-dinitrodibenzyl, m. p. 178—179°, mixed m. p. 179—180°.

A solution of thionaphthenyl-lithium was prepared by Shirley and Cameron's method [13] from *n*-butyl bromide (20 g.), lithium (2·45 g.), and thionaphthen (10 g.). To this solution was added freshly distilled fluorobenzene (6·3 g.) and after 24 hr. at room temperature, lithium fluoride separated. The mixture was poured into water (400 ml.), and the dried (Na_2SO_4) ethereal extract gave an oil from which excess of fluorobenzene and butyl bromide were removed under reduced pressure. The residual solid was fractionally crystallised from ethanol, to give prisms, m. p. and mixed m. p. 175—176°, of 2-phenylthionaphthen (8·6 g., 55% based on thionaphthen), and also needles (0·02 g., m. p. 260—262°) of (presumably) 2 : 2′-dithionaphthenyl which is recorded [13,19] as having m. p. 262°.

(ii) *Phenacyl* m-*tolyl sulphide.* By the same procedure phenacyl *m*-tolyl sulphide and

[18] Horton, *J. Org. Chem.*, 1949, **14**, 761.
[19] Fries and Hemmecke, *Annalen*, 1929, **470**, 1.

polyphosphoric acid gave prisms (28%) (from ethanol), m. p. 184—184·5°, of 6-*methyl*-2-*phenylthionaphthen* (Found: C, 80·4; H, 5·5; S, 14·0. $C_{15}H_{12}S$ requires C, 80·3; H, 5·35; S, 14·3%). Desulphurisation and oxidation as before gave two acids, the less soluble (in alcohol) of which was esterified to give dimethyl terephthalate, m. p. 138—139°, mixed m. p. 138—140°. The other acid was benzoic acid (m. p. and mixed m. p. 120—121°).

(iii) *Phenacyl* p-*tolyl sulphide*. With polyphosphoric acid as before, this sulphide afforded prisms (from ethanol), m. p. 158—158·5°, of 5-*methyl*-2-*phenylthionaphthen* (26%) (Found: C, 80·3; H, 5·4; S, 14·1%). Desulphurisation and oxidation as before gave *iso*phthalic acid, needles (from ethanol), m. p. >300° (anilide, m. p. 246—248°, mixed m. p. 248—250°), and benzoic acid.

(iv) 5-Methyl-3-phenylthionaphthen, b. p. 155—157°/0·4 mm., was prepared by the method of Krollpfeiffer *et al.*,[14] who record b. p. 162°/1 mm. It was desulphurised and oxidised as was 2-phenylthionaphthen, giving needles (from ethanol), m. p. 161—162°; *m*-benzoylbenzoic acid has m. p. 162°.

(v) m-*Methoxyphenyl phenacyl sulphide*. With polyphosphoric acid (at 190° for 3 hr.) or cold concentrated sulphuric acid, this sulphide gave 6-*methoxy*-2-*phenylthionaphthen*, prisms (from ethanol), m. p. 58—59° (not the 3-phenyl derivative as reported by Fries *et al.*,[1] who also report m. p. 59°).

The product (0·5 g.) was refluxed in absolute ethanol (150 ml.) with Raney nickel (8 g.) for ½ hr., the alcoholic solution filtered whilst hot, and the filtered metal washed with hot ethanol. The concentrated alcohol solution, after clarification (charcoal), yielded 4-methoxydibenzyl, m. p. 58—60° alone or mixed m. p. with an authentic specimen.

4-Methoxybenzyl bromide (from 4-methoxybenzyl alcohol; cf. Woodward[20] who used 3-methoxybenzyl alcohol) was treated with benzylmagnesium chloride as described by Späth,[21] affording 4-methoxydibenzyl, m. p. 60—61° (78%).

(vi) 3 : 4-*Dimethoxyphenyl phenacyl sulphide*. The sulphide with phosphoric oxide at 190° for ½ hr. gave (probably) 5 : 6-*dimethoxy*-2-*phenylthionaphthen*, needles (from 80% ethanol), m. p. 116·5—117° (27%) (Found: C, 70·8; H, 5·1; S, 11·9; OMe, 23·2. $C_{16}H_{14}O_2S$ requires C, 71·2; H, 5·2; S, 11·9; OMe, 23·0%). The same product was obtained in 21% yield by the use of zinc chloride at 180° for ¾ hr.

(vii) 1-*Naphthyl phenacyl sulphide*. The sulphide (1 g.) was added gradually with stirring to cold concentrated sulphuric acid (15 ml.) and after 30 min. the deep red solution was poured on ice. The oil was extracted with light petroleum (b. p. 90—100°) in a continuous extractor for 2 hr. After removal of the petroleum the residual oil was dissolved in ether (50 ml.), light petroleum (50 ml.; b. p. 70—90°) added, and the mixture chromatographed on alumina. A broad yellow band (yellow fluorescence in ultraviolet light) was developed with ether, and its yellow eluate gave yellow needles, m. p. 50—56° (0·4 g.). Recrystallisation from ethanol or sublimation yielded yellow needles, m. p. 56—57°, regarded as 2-*phenyl*-6 : 7-*benzothionaphthen* (Found: C, 82·8; H, 4·8; S, 12·3. $C_{18}H_{12}S$ requires C, 83·1; H, 4·6; S, 12·3%).

(viii) 4-*Methoxyphenacyl phenyl sulphide*. With polyphosphoric acid at 190° for 1 hr. this gave 2-p-*methoxyphenylthionaphthen*, prisms (from ethanol), m. p. 193—194° (44%) (Found: C, 75·1; H, 5·2. $C_{15}H_{12}OS$ requires C, 75·0; H, 5·0%), desulphurised as for the methoxy-compound in (V) above to 4-methoxydibenzyl, m. p. and mixed m. p. 59—61°.

(ix) 3 : 4-*Dimethoxyphenyl* 4-*methoxyphenacyl sulphide*. When heated with an equal weight of anhydrous zinc chloride at 175—180° for 40 min., the sulphide gave a black glass from which light petroleum (b. p. 30—90°) extracted a crystalline product which was recrystallised from light petroleum (b. p. 100—150°) to give colourless needles, m. p. 85—86°, regarded as 5 : 6-dimethoxy-2-*p*-methoxyphenylthionaphthen (53%). No picrate could be obtained from ethyl alcohol or benzene as solvent but it was obtained (red needles, m. p. 96—97°) by fusing equimolecular proportions of the compound and picric acid. Attempts to recrystallise this picrate resulted in its dissociation.

(x) 4-*Methoxyphenacyl* 1-*naphthyl sulphide*. Equal weights of this sulphide and zinc chloride were heated at 180° for 1 hr., the solid product powdered and boiled with water, and the aqueous suspension yielded to chloroform probably 2-p-*methoxyphenyl*-6 : 7-*benzothionaphthen* (64%), plates (from light petroleum), m. p. 164—165° (Found: OMe, 10·6. $C_{19}H_{14}OS$ requires OMe, 10·7%).

(xi) 4-*Methoxyphenacyl* 2-*naphthyl sulphide*. With zinc chloride at 170—175° for 1 hr. this

[20] Woodward, *J. Amer. Chem. Soc.*, 1940, **62**, 1481.
[21] Späth, *Monatsh.*, 1913, **34**, 2009.

sulphide similarly gave pale brown needles, m. p. 157—158°, regarded as 2-p-*methoxyphenyl*-4 : 5-*benzothionaphthen* (68%) (Found : C, 78·9; H, 4·85; OMe, 10·6. $C_{19}H_{14}OS$ requires C, 78·6; N, 4·8; OMe, 10·7%). A picrate was obtained (m. p. 150—151°) as for 2-*p*-methoxyphenyl-5 : 6-benzothionaphthen above, but it also could not be recrystallised.

(xii) *Unsuccessful cyclisations.* Concentrated sulphuric acid at room temperatures and phosphoric oxide at 190° for ¾ hr., partly converted 2-naphthyl phenacyl sulphide into di-2-naphthyl disulphide (m. p. 139°). Anhydrous oxalic acid and stannic chloride were ineffective.

The following phenacyl sulphides could not be cyclised by the use of phosphoric oxide at 190° for 1 hr. : *o*-tolyl, *p*-acetamidophenyl, *p*-nitrophenyl, and 2 : 4-dinitrophenyl. Similarly, the following 4-methoxyphenacyl sulphides could not be cyclised by the use of sulphuric acid, stannic chloride, phosphoric oxide, or zinc chloride : *o*- and *p*-tolyl, *p*-acetamidophenyl.

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