## 758. *Extrusion of Sulphur. Part I. Formation of Phenanthrenes from Dibenzo*[b,f]*thiepins.*

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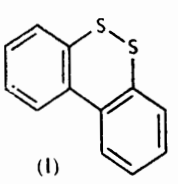
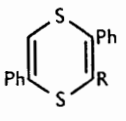
Derivatives of dibenzo[*b*,*f*]thiepin are prepared from 2-arylthio-5-nitrobenzaldehydes *via* 2-arylthio-5-nitrophenylpyruvic acids and yield phenanthrene derivatives by extrusion of sulphur.

A number of isolated observations contribute to the view that a thia-atom is fairly readily extruded from a heterocycle if the ring contraction involved leads to an aromatic structure. For example, phenothiazine [1] and several of its benzo-derivatives [2] when heated with copper yield the corresponding carbazoles. The reported similar conversion of phenoxathiin into dibenzofuran [3] has not been confirmed,[4] but thianthren [5] and the cyclic disulphide (I) [6] each yields dibenzothiophen. Thianthrens are thermally stable compounds but *p*-dithiins of type (II; R = H, CHO, or $NO_2$) are converted by heat or by treatment with phosphorus oxychloride into derivatives of thiophen.[7] A particularly ready extrusion is found for the compound (III) which yields naphthalene-2 : 3-dicarboxylic acid when heated in aqueous methanol.[8] That extrusion is not restricted to the bivalent sulphur atom is shown by the preferential elimination of the oxidised sulphur from *p*-dithiin 1 : 1-dioxides,[7] from thianthren 5-oxide,[9] and from cyclic thiolsulphonates allied to the disulphide (I).[10] Moreover, the *endo*-sulphones which are presumably formed as adducts by the interaction of certain thiophen 1 : 1-dioxides and acetylenic dienophils, decompose *in situ* with elimination of sulphur dioxide and formation of benzene derivatives.[11] To these examples of sulphur extrusion we now add the conversion of certain dibenzo[*b*,*f*]thiepins into phenanthrenes by the action of heat in presence of copper.


(I)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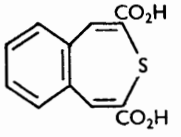
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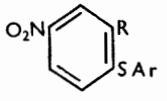
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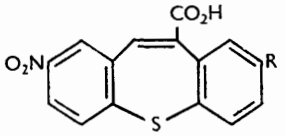
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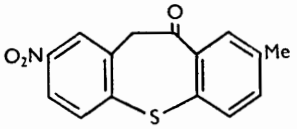
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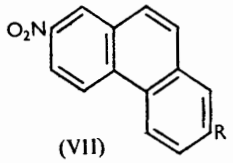
(VII)

Derivatives of dibenzo[*b*,*f*]thiepin were prepared from 2-arylthio-5-nitrobenzaldehydes (IV; R = CHO) by reactions which closely correspond to those described for the synthesis of dibenz[*b*,*f*]oxepins.[12] In general the intermediate 2-arylthio-5-nitrophenylpyruvic acids

[1] Goske, *Ber.*, 1887, **20**, 232.
[2] Ris, *Ber.*, 1886, **19**, 2240; Kym, *Ber.*, 1890, **23**, 2458.
[3] Ferrario, *Bull. Soc. chim.*, 1911, [iv], **9**, 536.
[4] Suter, McKenzie, and Maxwell, *J. Amer. Chem. Soc.*, 1936, **58**, 717; Gilman, Van Ess, Willis, and Stuckwisch, *ibid.*, 1940, **62**, 2606.
[5] Cullinane, Morgan, and Plummer, *Rec. Trav. chim.*, 1937, **56**, 627.
[6] Barber and Smiles, *J.*, 1928, 1141; Armarego and Turner, *J.*, 1956, 1665.
[7] Parham and Traynelis, *J. Amer. Chem. Soc.*, 1954, **76**, 4960; 1955, **77**, 68.
[8] Scott, *ibid.*, 1953, **75**, 6332; Dimroth and Lenke, *Chem. Ber.*, 1956, **89**, 2608.
[9] Gilman and Swayampati, *J. Amer. Chem. Soc.*, 1955, **77**, 3387.
[10] Armarego and Turner, *J.*, 1957, 13.
[11] Bailey and Cummins, *J. Amer. Chem. Soc.*, 1954, **76**, 1932 *et seq.*; Duck, *Research*, 1955, **8**, S47.
[12] Preceding paper.

(IV; R = $CH_2$·CO·$CO_2H$) were less smoothly cyclised by polyphosphoric acid than were their 2-aryloxy-analogues, and use of hydrobromic acid in acetic acid was sometimes preferred. Satisfactory yields of the carboxylated thiepin, cf. (V), were obtained from the pyruvic acid (IV; R = $CH_2$·CO·$CO_2H$) where the aryl group (Ar) was phenyl, *p*-tolyl, or 1-naphthyl, but the reaction failed when the aryl group was *p*-methoxyphenyl or 2-naphthyl. 5-Nitro-2-*p*-tolylthiophenylpyruvic acid was converted, *via* its oxime and the derived benzyl cyanide, into 5-nitro-2-*p*-tolylthiophenylacetic acid which was cyclised to the ketone (VI).

When the thiepin (V; R = Me) was heated with copper in quinoline decarboxylation was accompanied by extrusion of sulphur. That the product was a phenanthrene derivative followed from its oxidation, without loss of carbon, first to a phenanthraquinone and then to a derivative of diphenic acid. It is formulated as 2-methyl-7-nitrophenanthrene (VII; R = Me), other structures conceivably formed by union of the aryl nuclei at centres not originally linked to sulphur being considered unlikely. This is supported by the identification of 2-nitrophenanthrene (VII; R = H) as the product of a similar reaction applied to the thiepin (V; R = H). 2-Nitrophenanthrene was first prepared impure by Schmidt and Heinle[13] and was recently obtained pure by Bavin and Dewar.[14] Our specimen had the m. p. recorded by the latter workers and was further characterised by oxidation to the known 2-nitrophenanthraquinone.[15]

Despite the close homologous relation between the two thiepins (V; R = H) and (V; R = Me) there was an appreciable difference in the ease with which they were converted into phenanthrene derivatives. Treatment of the thiepincarboxylic acid (V; R = H) under various conditions usually afforded 2-nitrodibenzo[*b*,*f*]thiepin, with varying small amounts of 2-nitrophenanthrene and of 2-nitro-9-phenanthroic acid. The decarboxylated thiepin (V; R = H, H for $CO_2H$) was likewise convertible into 2-nitrophenanthrene, but again in poor yield. On the other hand the thiepincarboxylic acid (V; R = Me) afforded moderately good yields (*ca.* 50%) of 2-methyl-7-nitrophenanthrene and only traces of 2-methyl-8-nitrodibenzo[*b*,*f*]thiepin were detected. A similar difference was also found when the methyl esters of (V; R = H) and (V; R = Me) were briefly treated with copper in boiling diethyl phthalate. Thereby methyl 2-nitro-9-phenanthroate and methyl 7-methyl-2-nitro-9-phenanthroate were obtained in 39 and 55% yield respectively and, having regard to reliability and ease of manipulation, this appears at present to be the best pathway from the dibenzothiepin to the phenanthrene series.

## Experimental

Throughout petroleum refers to light petroleum (b. p. 60—80°).

*5-Nitro-2-p-tolylthiophenylpyruvic Acid.*—5-Nitro-2-*p*-tolylthiobenzaldehyde[16] (1 mol.), aceturic acid (1 mol.), and fused sodium acetate (1 mol.) were heated with acetic anhydride under reflux (1 hr.). The solution was cooled and, after 15 hr., afforded *2-methyl-4-(5-nitro-2-p-tolylthiobenzylidene)-5-oxazolone*, m. p. 188—189° (from petroleum–benzene; yield 55%) (Found: C, 61·1; H, 4·0. $C_{18}H_{14}O_4N_2S$ requires C, 61·0; H, 3·95%). The pure oxazolone (0·3 g.) was heated (15 hr.) with a mixture of acetic acid (7·5 c.c.), concentrated hydrochloric acid (2 c.c.), and water (4 c.c.) affording *5-nitro-2-p-tolylthiophenylpyruvic acid* as lemon-yellow crystals, m. p. 143° (from benzene–methanol; yield 90%) (Found: C, 57·8; H, 4·0; N, 4·2. $C_{16}H_{13}O_5NS$ requires C, 58·0; H, 3·9; N, 4·2%). The *oxime* had m. p. 169° (decomp.) (from benzene–methanol) (Found: C, 55·6; H, 4·2. $C_{16}H_{14}O_5N_2S$ requires C, 55·5; H, 4·05%).

*5-Nitro-2-p-tolylthiophenylacetic Acid.*—The foregoing oxime (3 g.), when heated with acetic anhydride (60 c.c.) for 2 hr. followed by concentration of the solution *in vacuo*, afforded *5-nitro-2-p-tolylthiobenzyl cyanide*, m. p. 80° (from benzene–petroleum; yield 60%) (Found: C, 63·2; H, 4·4. $C_{15}H_{12}O_2N_2S$ requires C, 63·3; H, 4·2%). This (10 g.) was hydrolysed (9 hr.) in hot acetic acid (100 c.c.) and hydrochloric acid (100 c.c.) giving *5-nitro-2-p-tolylthiophenylacetic acid*,

[13] Schmidt and Heinle, *Ber.*, 1911, **44**, 1488.
[14] Bavin and Dewar, *J.*, 1955, 4477.
[15] Schmidt and Spoun, *Ber.*, 1922, **55**, 1194.
[16] Campbell, Dick, Ferguson, and Loudon, *J.*, 1941, 747.

m. p. 126° (from benzene–petroleum; yield 70%) (Found: C, 59·5; H, 4·3. $C_{15}H_{13}O_4NS$ requires C, 59·4; H, 4·3%).

2-p-*Tolylthiophenylacetic Acid*.—A solution of the 5-nitro-compound (0·5 g.) in water (60 c.c.) containing potassium carbonate (0·35 g.) was hydrogenated with palladised strontium carbonate as catalyst. Neutralisation of the filtered solution afforded 5-*amino*-2-p-*tolylthiophenylacetic acid*, m. p. 127° (from ethanol–water) (Found: C, 66·2; H, 5·4. $C_{15}H_{15}O_2NS$ requires C, 65·9; H, 5·5%), which formed the *hydrochloride*, m. p. 209° (decomp.), from dilute hydrochloric acid (Found: C, 58·0; H, 5·5. $C_{15}H_{16}O_2NClS$ requires C, 58·1; H, 5·2%). A diazotised solution of the amino-acid in hydrochloric acid was treated with an excess of hypophosphorous acid. After 20 hr. the precipitated 2-p-*tolylthiophenylacetic acid* was collected as straw-coloured needles, m. p. 112° (from benzene–petroleum) (Found: C, 69·9; H, 5·4. $C_{15}H_{14}O_2S$ requires C, 69·8; H, 5·4%).

10 : 11-*Dihydro*-8-*methyl*-2-*nitro*-10-*oxodibenzo*[b,f]*thiepin* (VI) was obtained (yield, 75%) as yellow needles, m. p. 161° (from methanol), by cyclisation of 5-nitro-2-*p*-tolylthiophenylacetic acid by polyphosphoric acid (1½ hr. at 100°) (Found: C, 63·4; H, 4·1. $C_{15}H_{11}O_3NS$ requires C, 63·15; H, 3·9%). Its solution in benzene was colourless. With hydroxylamine hydrochloride in pyridine it afforded the *oxime*, m. p. 191° (from benzene–petroleum) (Found: C, 60·3; H, 4·0. $C_{15}H_{12}O_3N_2S$ requires C, 60·0; H, 4·0%).

8-*Methyl*-2-*nitrodibenzo*[b,f]*thiepin*-10-*carboxylic Acid* (V; R = Me).—(*a*) 5-Nitro-2-*p*-tolylthiophenylpyruvic acid was cyclised in polyphosphoric acid first at 160° (5 min.) and then at 100° (2 hr.). Addition of water to the cooled mixture gave the thiepin, m. p. 268° (from benzene–methanol; yield, 70%). (*b*) A solution of the pyruvic acid (10 g.) in a mixture of hydrobromic acid (48%; 20 c.c.) and acetic acid (35 c.c.) was heated under reflux for 5 hr. After 12 hr. at 18° the resultant greenish-brown needles (8·8 g.; m. p. 269°) were recrystallised (charcoal) from acetic acid affording the *thiepin*, m. p. 276° (Found: C, 61·1; H, 3·5. $C_{16}H_{11}O_4NS$ requires C, 61·3; H, 3·5%). Heated for 12 hr. with methanol (250 c.c.) and concentrated sulphuric acid (2 c.c.) the thiepincarboxylic acid (5 g.) gave the corresponding *methyl ester*, m. p. 183° (from methanol–methyl acetate) (Found: C, 62·6; H, 4·0. $C_{17}H_{13}O_4NS$ requires C, 62·4; H, 4·0%).

2-*Methyl*-7-*nitrophenanthrene* (VII; R = Me).—(*a*) 8-Methyl-2-nitrodibenzothiepin-10-carboxylic acid (2 g.), copper bronze (10 g.), and pure quinoline (50 c.c.) were heated under reflux for 4 hr. The cooled mixture was diluted with benzene and filtered, and the filtrate washed with dilute sulphuric acid, again filtered, and then washed in turn with water, aqueous sodium carbonate, and water. 2-*Methyl*-7-*nitrophenanthrene* was recovered from the solution as pale yellow crystals, m. p. 192° (from benzene–methanol) (Found: C, 75·85; H, 4·6. $C_{15}H_{11}O_2N$ requires C, 75·95; H, 4·6%). A solution of the compound in hot acetic acid was slowly treated with an aqueous solution of chromic acid (in slight excess) affording 2-*methyl*-7-*nitrophenanthraquinone*, m. p. 230° (decomp.) (from benzene–methanol) (Found: C, 67·5; H, 3·5. $C_{15}H_9O_4N$ requires C, 67·4; H, 3·4%). To a suspension of this quinone (0·2 g.) in methanol (2 c.c.) containing hydrogen peroxide (30%; 0·5 c.c.) 4N-sodium hydroxide (1 c.c.) was added, with thorough shaking, and thereafter more hydrogen peroxide (1 c.c.). After 15 hr. the methanol was removed and the residue acidified affording 4-*methyl*-4′-*nitrodiphenic acid*, m. p. 186° (from benzene–methanol) (Found: C, 59·7; H, 4·0. $C_{15}H_{11}O_6N$ requires C, 59·8; H, 3·7%).

(*b*) The thiepincarboxylic acid (V; R = Me) (0·5 g.), copper bronze (0·5 g.), and diethyl phthalate (3 c.c.) were heated (30 min.) at 250° under nitrogen. The mixture was diluted with benzene and filtered through charcoal, and the solvents distilled off *in vacuo*. The resultant dark viscous oil was extracted several times with petroleum, and the combined extracts were chromatographed on alumina and eluted with petroleum. Successive eluates afforded in small quantity (i) 8-*methyl*-2-*nitrodibenzo*[b,f]*thiepin* as yellow needles, m. p. 117° (from methanol) (Found: C, 67·0; H, 3·8; N, 5·1. $C_{15}H_{11}O_2NS$ requires C, 66·9; H, 4·1; N, 5·2%); (ii) a solid mixture which was not resolved by crystallisation; (iii) 2-methyl-7-nitrophenanthrene, m. p. and mixed m. p. 192°.

*Methyl* 7-*Methyl*-2-*nitro*-9-*phenanthroate*.—The methyl ester (0·5 g.) of compound (V; R = Me), copper bronze (0·5 g.), and diethyl phthalate (3 c.c.) were boiled for 7½ min. under nitrogen. The cold mixture was diluted with benzene, poured on to (alkali-free) alumina and eluted with benzene. Addition of petroleum to the concentrated eluate gave a yellow solid from which, after renewed chromatography, *methyl* 7-*methyl*-2-*nitro*-9-*phenanthroate* was obtained as cream-coloured crystals (0·25 g.), m. p. 188° (from methyl acetate) (Found: C, 69·3; H, 4·5. $C_{17}H_{13}O_4N$ requires C, 69·1; H, 4·4%). It was hydrolysed by boiling acetic–hydrochloric acid

to *7-methyl-2-nitro-9-phenanthroic acid*, m. p. 291° (from acetonitrile) (Found: C, 68·2; H, 3·8. $C_{16}H_{11}O_4N$ requires C, 68·3; H, 3·9%).

*5-Nitro-2-phenylthiobenzaldehyde*.—To a solution of 2-chloro-5-nitrobenzaldehyde (45 g.) and thiophenol (25 g.) in ethanol (500 c.c.) and water (200 c.c.) stirred and maintained at 60°, potassium carbonate was added in portions (18 × 1 g.) during 20 min. and stirring was continued for 40 min. The crystalline product was washed with water affording *5-nitro-2-phenylthiobenzaldehyde*, m. p. 105° (from ethyl acetate; yield, 48 g.) (Found: C, 60·4; H, 3·5. $C_{13}H_9O_3NS$ requires C, 60·2; H, 3·5%).

*2-Nitrodibenzo*[b,f]*thiepin-10-carboxylic Acid* (V; R = H).—5-Nitro-2-phenylthiobenzaldehyde and aceturic acid afforded (yield, 55%) *2-methyl-4-(5-nitro-2-phenylthiobenzylidene)-5-oxazolone*, m. p. 190° (from benzene) (Found: C, 60·0; H, 3·8. $C_{17}H_{12}O_4N_2S$ requires C, 60·0; H, 3·5%), which was hydrolysed to *5-nitro-2-phenylthiophenylpyruvic acid*, m. p. 146° (from benzene–petroleum; yield, 90%) (Found: C, 56·9; H, 3·55. $C_{15}H_{11}O_5NS$ requires C, 56·8; H, 3·5%). This acid was cyclised by polyphosphoric acid (5 min. at 160°, then 2 hr. at 100°), affording *2-nitrodibenzo*[b,f]*thiepin-10-carboxylic acid*, m. p. 248° (from benzene–methanol; yield, 65%) (Found: C, 60·4; H, 3·3. $C_{15}H_9O_4NS$ requires C, 60·2; H, 3·0%). Cyclisation by procedure (*b*) described for the analogue (V; R = Me), but here prolonged to 12 hr., gave a purer product in 75% yield. Esterification as described for the analogue gave the *methyl ester*, m. p. 156° (from methyl acetate–methanol) (Found: C, 61·5; H, 3·5. $C_{16}H_{11}O_4NS$ requires C, 61·3; H, 3·5%).

*Decomposition of 2-Nitrodibenzo*[b,f]*thiepin-10-carboxylic Acid* (V; R = H).—(*a*) When the thiepincarboxylic acid was treated (4 hr.) with copper bronze or cuprous oxide in boiling quinoline, as described under (*a*) for compound (VII; R = Me), *2-nitrodibenzo*[b,f]*thiepin* was isolated as yellow crystals, m. p. 110° (from methanol; yield, 45—50%) (Found: C, 65·6; H, 3·7. $C_{14}H_9O_2NS$ requires C, 65·9; H, 3·5%).

(*b*) The same thiepin, m. p. and mixed m. p. 110°, was the only crystalline product (yield, 49%) when the acid was treated as described under (*b*) for compound (VII; R = Me).

(*c*) When the reaction time in experiment (*a*), with cuprous oxide, was extended to 9 hr. and the product before chromatography was separated into basic, neutral, and acidic fractions, the neutral fraction afforded a small quantity of yellow needles, m. p. 117° depressed by admixture with 2-nitrodibenzothiepin and unchanged by admixture with 2-nitrophenanthrene, cf. (*d*).

(*d*) The thiepincarboxylic acid (2 g.) was placed under a coil of freshly-reduced copper wire (10 g.) and the whole heated (5 min.) at 300—310° in nitrogen. Products of the vigorous reaction were trapped and washed out in boiling benzene from which, after concentration, a carboxylic acid crystallised, cf. (*f*). The filtrate, purified on alumina and eluted with benzene, afforded 2-nitrophenanthrene (0·07 g.), micro-m. p. 120° (from benzene) (Found: C, 75·5; H, 4·1; N, 6·45. Calc. for $C_{14}H_9O_2N$: C, 75·3; H, 4·1; N, 6·3%). This, on being oxidised with chromic acid in acetic acid, gave 2-nitrophenanthraquinone which was identified by its infrared spectrum and mixed micro-m. p., 265—269°, with an authentic specimen prepared as described by Schmidt and Spoun.[15]

(*e*) The thiepincarboxylic acid (0·5 g.) and copper bronze (0·4 g.) were heated in boiling diethyl phthalate (2 c.c.) for 15 min. The cooled mixture was diluted with benzene, filtered, washed with aqueous sodium carbonate and then with water, and refiltered, hot, through charcoal. The tarry residue, obtained by removing the solvents *in vacuo*, was extracted with boiling methanol from which 2-nitrophenanthrene was recovered and purified by chromatography (0·07 g.; m. p. 120°). When the reaction mixture was heated for only 5 min., 2-nitrodibenzothiepin was obtained.

(*f*) The carboxylic by-product from (*d*), combined with the acidic fraction from (*c*), afforded *2-nitro-9-phenanthroic acid* as pale yellow needles, micro-m. p. 266° (from acetic acid) (Found: C, 67·5; H, 3·3. $C_{15}H_9O_4N$ requires C, 67·4; H, 3·4%). This was identified by oxidation to 2-nitrophenanthraquinone and also by comparison with a sample prepared from the methyl ester (below).

*Decomposition of 2-Nitrodibenzo*[b,f]*thiepin*.—The thiepin (0·25 g.) and copper bronze (0·25 g.) were heated in boiling diethyl phthalate (1·5 c.c.) for 7½ min. under nitrogen. Dilution of the cold mixture with benzene, followed by filtration through charcoal and concentration *in vacuo*, gave a red oil which partially solidified when rubbed with methanol. The solid, purified by chromatography in petroleum on alumina, afforded 2-nitrophenanthrene (0·04 g.), m. p. and mixed m. p. 120°, and some unchanged thiepin.

*Methyl 2-nitro-9-phenanthroate*, cream-coloured crystals, m. p. 161° (from methyl acetate), was obtained in 39% yield from methyl 2-nitrodibenzo[*b*,*f*]thiepin-10-carboxylate by the method described for the 7-methyl homologue (Found: C, 68·6; H, 3·8. $C_{16}H_{11}O_4N$ requires C, 68·3; H, 3·9%). The ester was hydrolysed by boiling acetic–hydrochloric acid to 2-nitro-9-phenanthroic acid, m. p. and mixed m. p. 265°.

2-p-*Methoxyphenylthio-5-nitrophenylpyruvic Acid.*—2-p-*Methoxyphenylthio-5-nitrobenzaldehyde*, m. p. 89° (from aqueous acetic acid), prepared from 2-chloro-5-nitrobenzaldehyde and sodium *p*-methoxyphenyl sulphide (Found: C, 58·1; H, 4·1. $C_{14}H_{11}O_4NS$ requires C, 58·1; H, 3·8%), was converted by reaction with aceturic acid into 2-*methyl*-4-(2-p-*methoxyphenylthio-5-nitrobenzylidene*)-5-*oxazolone*, m. p. 206° (from benzene) (Found: C, 58·5; H, 4·0. $C_{18}H_{14}O_5N_2S$ requires C, 58·4; H, 3·8%), and hence into 2-(p-*methoxyphenylthio*)-5-*nitrophenylpyruvic acid*, m. p. 174° (from benzene–methanol) (Found: C, 55·1; H, 3·7. $C_{16}H_{13}O_6NS$ requires C, 55·3; H, 3·7%), which formed an *oxime*, m. p. 167° (decomp.) (from benzene–methanol) (Found: C, 52·9; H, 4·1. $C_{16}H_{14}O_6N_2S$ requires C, 53·0; H, 3·9%), but could not be cyclised by polyphosphoric acid.

2-2′-*Naphthylthio-5-nitrophenylpyruvic Acid.*—2-2′-*Naphthylthio-5-nitrobenzaldehyde*, m. p. 108° (from acetic acid), prepared from 2-chloro-5-nitrobenzaldehyde and naphthalene-2-thiol (Found: C, 66·25; H, 3·6. $C_{17}H_{11}O_3NS$ requires C, 66·0; H, 3·6%), was converted into 2-*methyl*-4-(2-2′-*naphthylthio-5-nitrobenzylidene*)-5-*oxazolone*, m. p. 193° (from benzene–petroleum) (Found: C, 64·65; H, 3·8. $C_{21}H_{14}O_4N_2S$ requires C, 64·6; H, 3·6%), and hence into 2-2′-*naphthylthio-5-nitrophenylpyruvic acid*, m. p. 153° (from benzene) (Found: C, 62·35; H, 3·8. $C_{19}H_{13}O_5NS$ requires C, 62·1; H, 3·5%). Attempts to cyclise this acid by polyphosphoric acid failed, starting material being recovered in diminished quantity.

10-*Nitrobenzo*[b]*naphtho*[2,1-f]*thiepin-7-carboxylic Acid.*—2-1′-*Naphthylthio-5-nitrobenzaldehyde*, m. p. 123° (from acetic acid), prepared from 2-chloro-5-nitrobenzaldehyde and naphthalene-1-thiol (Found: C, 66·2; H, 3·6%), was converted by reaction with aceturic acid into 2-*methyl*-4-(2-1′-*naphthylthio-5-nitrobenzylidene*)-5-*oxazolone*, m. p. 195° (from benzene–petroleum) (Found: C, 64·55; H, 3·8%), and hence into 2-1′-*naphthylthio-5-nitrophenylpyruvic acid*, m. p. 171° (from benzene–methanol) (Found: C, 62·4; H, 3·7%), which afforded the *oxime*, m. p. 194° (from benzene–methanol) (Found: C, 59·7; H, 3·8. $C_{19}H_{14}O_5N_2S$ requires C, 59·7; H, 3·7%). When the pyruvic acid in polyphosphoric acid was heated first at 230° for a few minutes and then at 100° for 3 hr. it afforded 10-*nitrobenzo*[b]*naphtho*[2,1-f]*thiepin-7-carboxylic acid* as yellow needles m. p. 274° (decomp.) (from benzene–methanol) (Found: C, 65·55; H, 3·5. $C_{19}H_{11}O_4NS$ requires C, 65·3; H, 3·2%).

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