98. *Methyl β-Naphthyl Sulphide.*

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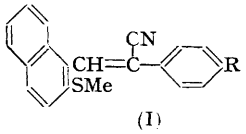
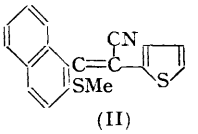
Methyl β-naphthyl sulphide undergoes reactions similar to those of the β-naphthyl ether (formylation, Friedel–Crafts reaction), although less readily. Numerous sulphur-containing naphthalene derivatives have been prepared.

In the framework of a study of the reactivity of naphthalene derivatives, the little-known behaviour of methyl β-naphthyl sulphide has been examined. Although the *N*-methylformanilide method for aldehyde syntheses had frequently been applied to naphthyl ethers (cf. *Org. Synth.*, 1940, **20**, 12), it had not been extended to the corresponding derivatives of thionaphthols. Methyl β-naphthyl sulphide has now been found thus to give 2-methylthio-1-naphthaldehyde; its reactivity, however, was lower than that of its oxygen analogue, as witnessed by the relatively low yield (about 35%) obtained in the usual conditions.

2-Methylthio-1-naphthaldehyde was completely resistant to demethylation by pyridine hydrochloride, a characteristic shared by other thiophenol ethers (cf. Buu-Hoï and Hoán, *J. Org. Chem.*, 1952, **17**, 350) and parallel to their resistance to rearrangement (cf. Buu-Hoï, Le Bihan, Binon, and Xuong, *ibid.*, 1951, **16**, 988). In other reactions, it closely resembled its oxygen analogue. Wolff–Kishner reduction yielded methyl 1-methyl-2-naphthyl sulphide; alkali-catalysed condensation with arylacetonitriles readily gave a series of diversely substituted αβ-diarylacrylonitriles (I), and similar acrylonitriles (II) and (III) were obtained with 2-thienyl- and 3-thionaphthenyl-acetonitrile (see Table 1).



(I)



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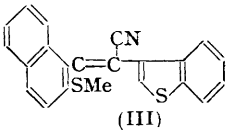

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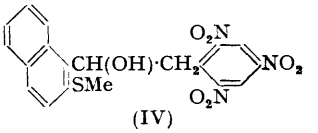
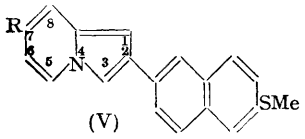


(IV)

Piperidine-catalysed condensation with 2 : 4 : 6-trinitrotoluene, on the other hand, yielded, instead of the expected stilbene, the alcohol (IV), dehydration of which was probably sterically hindered. Other reactions of 2-methylthio-1-naphthaldehyde investigated were the formation of a cinchoninic acid by β-naphthylamine and pyruvic acid, preparation of a thiosemicarbazone, and, from the latter compound and α-halogenated fatty acids, of the corresponding 4-keto-2-thiazolinylhydrazones (cf. Chabrier, *Bull. Soc. chim.*, 1947, **14**, 797; Buu-Hoï and Hoán, *J.*, 1951, 1834).

In Friedel–Crafts ketone syntheses, methyl β-naphthyl sulphide closely resembled its oxygen analogue; with acetyl chloride and aluminium chloride in nitrobenzene a single ketone was obtained, which was probably 6-methylthio-2-acetonaphthone, from analogy with the behaviour of neroline in similar conditions (Haworth and Sheldrick, *J.*, 1934, 864). The other conceivable site of substitution, position 1, was excluded on the ground that the substituted naphthylamine obtained by Beckmann degradation of the ketoxime readily underwent Doebner reactions with pyruvic acid and various aldehydes to give cinchoninic acids, proof that the *ortho*-position was free. Propionylation of methyl β-naphthyl sulphide similarly gave a single ketone, probably 6-methylthio-2-propionaphthone; succinoylation yielded a keto-acid, probably β-(6-methylthio-2-naphthoyl)-propionic acid, Wolff–Kishner reduction of which afforded an acid, probably, γ-(6-methylthio-2-naphthyl)butyric acid.

Several reactions of these two ketones were studied. A Willgerodt–Kindler reaction with 6-methylthio-2-acetonaphthone gave 6-methylthio-2-naphthylacetic acid, and Wolff–Kishner reduction readily yielded 6-ethyl-2-naphthyl methyl sulphide, which could be further acetylated to a single ketone, possibly 6-ethyl-2-methylthio-1-acetonaphthone. Crude 2-ω-bromo-6-methylthioacetonaphthone, obtained by side-chain bromination in the usual way, underwent Tschitschibabin reactions with α-picoline and 2 : 4-lutidine (Tschitschibabin, *Ber.*, 1927, **60**, 1607; Borrows, Holland, and Kenyon, *J.*, 1946, 1069, 1083; Buu-Hoï and Hoán, *Rec. Trav. chim.*, 1949, **68**, 452) to give 2-(6-methylthio-2-naphthyl)- (V; R = H) and 7-methyl-2-(6-methylthio-2-naphthyl)pyrrocoline (V; R = Me), and with 2-aminopyridine (Tschitschibabin, *Ber.*, 1925, **58**, 1704; 1926, **59**, 2048; Tschitschibabin and Plaschenkowa, *Ber.*, 1931, **64**, 2842; Buu-Hoï and Hoán, *loc. cit.*) to give 2-(6-methylthio-2-naphthyl)glyoxalino[1 : 2-*a*]pyridine (VI). Fischer cyclisation of the phenylhydrazones of 6-methylthio-2-acetonaphthone and -2-propionaphthone gave 2-(6-methylthio-2-naphthyl)- (VII; R = H) and 3-methyl-2-(6-methylthio-2-naphthyl)-indole (VII; R = Me).



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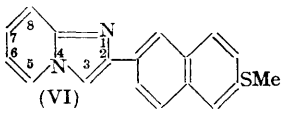

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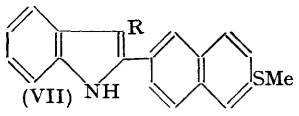

(VII)

The ketones described in this work gave positive Pfitzinger reactions; the cinchoninic acids and quinolines obtained therefrom by decarboxylation are listed in Table 2, together with the cinchoninic acids prepared by the Doebner reactions. Table 3 lists the various 4-keto-2-thiazolinylhydrazones prepared from the thiosemicarbazones of 2-methylthio-1-naphthaldehyde and 6-methylthio-2-acetonaphthone.

Experimental

2-Methylthio-1-naphthaldehyde.—Methyl β-naphthyl sulphide (30 g.), *N*-methylformanilide (28 g.), and phosphorus oxychloride (31 g.) were heated for 6 hours on a water-bath; after cooling, the product was poured on ice and taken up in toluene, and the organic layer washed with dilute hydrochloric acid, then with water, and dried (Na_2SO_4); the solvent was removed, and the residue vacuum-fractionated, giving the *aldehyde* (12 g.), b. p. 220°/20 mm., pale yellow leaflets, m. p. 65° (from ethanol) (Found: C, 71·2; H, 5·0. $C_{12}H_{10}OS$ requires C, 71·3; H, 5·0%). 18 G. of unchanged methyl β-naphthyl sulphide were recovered. The substance was recovered unchanged after 10 minutes' boiling with redistilled pyridine hydrochloride. Its *thiosemicarbazone* formed pale yellow needles, m. p. 171°, from ethanol (Found: C, 56·5; H, 4·6. $C_{13}H_{13}N_3S_2$ requires C, 56·7; H, 4·7%).

Methyl 1-Methyl-2-naphthyl Sulphide.—The foregoing aldehyde (3 g.), 85% hydrazine hydrate (3 g.), and diethylene glycol (50 c.c.) were heated at 100° for 5 minutes, then refluxed for 2 hours with potassium hydroxide (3 g.) with removal of water. After cooling, water was added, and the solid *sulphide* obtained washed and recrystallised from ethanol as leaflets (2 g.), m. p. 48° (Found: C, 76·5; H, 6·6. $C_{12}H_{12}S$ requires C, 76·6; H, 6·4%), giving a picrate as silky crimson needles, m. p. 107°, from ethanol.

1-(2-Methylthio-1-naphthyl)-2-(2 : 4 : 6-trinitrophenyl)ethan-1-ol (IV).—An equimolecular mixture of 2-methylthio-1-naphthaldehyde and 2 : 4 : 6-trinitrotoluene in ethanol was boiled with 2 drops of piperidine and left overnight; the solid *alcohol* obtained crystallised as shiny brownish needles, m. p. 81°, from ethanol (Found: C, 52·7; H, 3·5. $C_{19}H_{15}O_7N_3S$ requires C, 53·1; H, 3·5. $C_{19}H_{13}O_6N_3S$ requires C, 55·5; H, 3·2%).

6-Methylthio-2-acetonaphthone.—To an ice-cooled solution of methyl β-naphthyl sulphide (60 g.) and acetyl chloride (30 g.) in nitrobenzene (400 c.c.), finely powdered aluminium chloride (52 g.) was added in small portions with shaking; the deep red mixture was kept overnight at room temperature, then poured on ice, the nitrobenzene steam-distilled, and the residue taken up in benzene. The benzene solution was washed with aqueous sodium hydroxide, then with water, and dried (Na_2SO_4), the solvent removed, and the *ketone* vacuum-distilled, giving a product (60 g.), b. p. 222—225°/15 mm., leaflets, m. p. 120° (from ethanol), giving an orange-red colour with sulphuric acid (Found: C, 72·1; H, 5·5. $C_{13}H_{12}OS$ requires C, 72·2; H, 5·6%). The *semicarbazone* formed leaflets, m. p. 255°, from acetic acid (Found: C, 61·3; H,

5·8. $C_{14}H_{15}ON_3S$ requires C, 61·5; H, 5·6%); the *thiosemicarbazone* crystallised from ethanol as prisms, m. p. 201° (Found: C, 58·0; H, 5·3. $C_{14}H_{15}N_3S_2$ requires C, 58·1; H, 5·2%); the *oxime* formed needles, m. p. 163°, from ethanol (Found: C, 67·5; H, 5·8. $C_{13}H_{13}ONS$ requires C, 67·5; H, 5·6%).

TABLE 1. *α-Substituted β-(6-methylthio-2-naphthyl)acrylonitriles.*

α-Substituent [a]	M. p.	Formula	Found, %: C	Found, %: H	Reqd., %: C	Reqd., %: H
Ph	145°	$C_{20}H_{15}NS$	79·6	5·0	79·7	5·0
p-C_6H_4Me	158	$C_{21}H_{17}NS$	79·8	5·3	80·0	5·4
p-C_6H_4Cl	175	$C_{20}H_{14}NSCl$	71·2	4·0	71·5	4·2
p-C_6H_4Br	172	$C_{20}H_{14}NSBr$	63·1	3·8	63·2	3·7
p-C_6H_4I	169	$C_{20}H_{14}NSI$	56·0	3·2	56·2	3·3
p-MeO·C_6H_4	150	$C_{21}H_{17}ONS$	76·0	5·3	76·1	5·1
p-NO_2·C_6H_4 [b]	196	$C_{20}H_{14}O_2N_2S$	69·3	3·8	69·4	4·0
2-Thienyl [c]	142	$C_{18}H_{13}NS_2$	70·1	4·4	70·4	4·2
3-Thianaphthyl [d]	140	$C_{22}H_{15}NS_2$	73·6	4·4	73·9	4·2

[a] The first six substances formed, from ethanol–benzene, pale yellow needles, giving a violet colour with H_2SO_4. [b] Formed, from benzene, golden-yellow needles, giving a greenish-blue colour with H_2SO_4. [c] Golden-yellow needles from ethanol; violet colour with H_2SO_4. [d] Golden-yellow needles from ethanol; dark green colour with H_2SO_4.

6-Methylthio-2-naphthylacetic Acid.—6-Methylthio-2-acetonaphthone (10 g.), sulphur (3 g.), and morpholine (12 g.) were gently refluxed for 12 hours and the product heated for 2 hours with aqueous potassium hydroxide (charcoal). After filtration and acidification with hydrochloric acid, the solid *acid* crystallised from benzene as grey-tinged prisms, m. p. 159° (Found: C, 67·0; H, 5·2. $C_{13}H_{12}O_2S$ requires C, 67·2; H, 5·2%).

6-Ethyl-2-naphthyl Methyl Sulphide.—6-Methylthio-2-acetonaphthone (15 g.), reduced by hydrazine hydrate (15 g.) and potassium hydroxide (15 g.) in diethylene glycol (200 c.c.) in the usual way, yielded a *compound* (12·5 g.), b. p. 185°/15 mm., leaflets, m. p. 48° (from methanol) (Found: C, 77·2; H, 7·1. $C_{13}H_{14}S$ requires C, 77·2; H, 6·9%); the picrate had m. p. 101° (from ethanol).

6-Methylthio-2-naphthylamine.—An ice-cooled suspension of 6-methylthio-2-acetonaphthone oxime (20 g.) in ether (200 c.c.) was shaken with phosphorus pentachloride (20 g.) for 5 minutes, and the mixture poured on ice; the precipitated *2-acetamido-6-methylthionaphthalene* formed needles, m. p. 149°, from benzene (Found: C, 67·3; H, 5·8. $C_{13}H_{13}ONS$ requires C, 67·5; H, 5·6%). *6-Methylthio-2-naphthylamine*, obtained by heating this compound (11 g.) with hydrochloric acid (150 g.) for 2 hours and basification of the resulting hydrochloride (needles, m. p. *ca.* 212°), formed grey-tinged prisms, m. p. 117°, from methanol (Found: C, 69·5; H, 6·0. $C_{11}H_{11}NS$ requires C, 69·8; H, 5·8%).

Derivatives from 2-ω-Bromo-6-methylthioacetonaphthone.—A cooled solution of 6-methylthio-2-acetonaphthone (10 g.) in chloroform was treated with bromine (2·5 c.c.) in the usual way; the ω-bromo-ketone (5 g.) formed needles, m. p. 102°, from ethanol, which were not further purified; this compound, heated with *o*-phenylenediamine in ethanol, yielded *2-(6-methylthio-2-naphthyl)quinoxaline*, yellowish prisms m. p. 179° (from benzene–ethanol) (Found: C, 75·1; H, 4·7. $C_{19}H_{14}N_2S$ requires C, 75·5; H, 4·6%). The ω-bromo-ketone (1 g.) and α-picoline (0·3 g.) in ethanol (15 c.c.) were heated at 50—60° for 30 minutes; after cooling, ether was added to precipitate a picolinium compound, which was collected and treated with boiling 10% aqueous sodium hydrogen carbonate; the *2-(6-methylthio-2-naphthyl)pyrrocoline* formed crystallised as sublimable (>240°) prisms, m. p. 276°, from xylene (Found: C, 78·8; H, 5·1. $C_{19}H_{15}NS$ requires C, 78·9; H, 5·2%). A similar reaction with 2 : 4-lutidine gave *7-methyl-2-(6-methylthio-2-naphthyl)pyrrocoline*, leaflets, m. p. 293° (from toluene) (Found: C, 79·2; H, 5·8. $C_{20}H_{17}NS$ requires C, 79·2; H, 5·6%). *2-(6-Methylthio-2-naphthyl)glyoxalino*[1 : 2-α]*pyridine*, prepared by briefly refluxing a solution of the ω-bromo-ketone (1 g.) and 2-aminopyridine (0·3 g.) in ethanol (15 c.c.), and basification, crystallised as grey-tinged prisms, m. p. 189°, from methanol (Found: N, 9·8. $C_{18}H_{14}N_2S$ requires N, 9·7%).

2-(6-Methylthio-2-naphthyl)indole.—6-Methylthio-2-acetonaphthone phenylhydrazone (3 g.) was cautiously heated with finely powdered fused zinc chloride (3 g.) until a violent reaction set in; after cooling, the *indole* was taken up in toluene, washed with aqueous acetic acid, and recrystallised from toluene, giving grey-tinged prisms, m. p. 251°, giving a red colour with sulphuric acid (Found: C, 78·6; H, 5·0. $C_{19}H_{15}NS$ requires C, 78·9; H, 5·2%); its picrate formed violet-brown needles, m. p. 198°, from benzene.

6-*Methylthio-2-propionaphthone.*—To a solution of methyl β-naphthyl sulphide (50 g.) and propionic anhydride (40 g.) in nitrobenzene (400 c.c.), aluminium chloride (80 g.) was added in small portions, and the mixture kept overnight at room temperature; after the usual treatment, a *ketone* was obtained (52 g.), b. p. 232—235°/13 mm., leaflets, m. p. 100° (from ethanol), giving an orange-red colour with sulphuric acid (Found: C, 73·0; H, 6·2. $C_{14}H_{14}OS$ requires C, 73·0; H, 6·1%). The *semicarbazone* formed prisms, m. p. 217° (Found: N, 14·3. $C_{15}H_{17}ON_3S$ requires N, 14·6%), and the *thiosemicarbazone* pale yellow needles, m. p. 180° (Found: C, 59·6; H, 5·6. $C_{15}H_{17}N_3S_2$ requires C, 59·4; H, 5·6%), both from ethanol.

3-*Methyl*-2-(6-*methylthio*-2-*naphthyl*)*indole.*—A solution of the phenylhydrazone (3 g.) of the foregoing ketone in acetic acid saturated with hydrogen chloride (15 c.c.) was boiled for 2 minutes, and the product poured into water, taken up in benzene, and purified by vacuum-distillation; the *indole* (2 g.) crystallised from ethanol as colourless prisms, m. p. 146°, giving a red colour with sulphuric acid (Found: C, 79·0; H, 5·8. $C_{20}H_{17}NS$ requires C, 79·2; H, 5·6%); the picrate formed silky brown-violet needles, m. p. 162°, from ethanol.

β-(6-*Methylthio*-2-*naphthoyl*)*propionic Acid.*—To an ice-cooled solution of methyl β-naphthyl sulphide (55 g.) and succinic anhydride (34·7 g.) in nitrobenzene (400 c.c.), aluminium chloride (95 g.) was added in small portions, and the mixture kept overnight at room temperature; after decomposition with water and steam-distillation of the nitrobenzene, the *keto-acid* (68 g.) was purified through its sodium salt, and crystallised, as needles, m. p. 171°, from benzene (Found: C, 65·5; H, 5·2. $C_{15}H_{14}O_3S$ requires C, 65·7; H, 5·1%).

TABLE 2*a*. *Substituted* 2-(6-*methylthio*-2-*naphthyl*)*quinolines.*[a]

Substituents (in quinoline rings)	M. p.	Formula	Found, %: C	Found, %: H	Reqd., %: C	Reqd., %: H
(None)[b]	182°	$C_{20}H_{15}NS$	79·9	5·3	79·7	5·0
4-Carboxy	252	$C_{21}H_{15}O_2NS$	73·0	4·4	73·0	4·3
6-Methyl[c]	183	$C_{21}H_{17}NS$	79·8	5·7	80·0	5·4
4-Carboxy-6-methyl	242	$C_{22}H_{17}O_2NS$	73·4	4·6	73·5	4·7
6-Bromo-4-carboxy	276	$C_{21}H_{14}O_2NSBr$	59·2	3·3	59·4	3·3
4-Carboxy-6-chloro	270	$C_{21}H_{14}O_2NSCl$	66·3	3·5	66·3	3·7
3-Methyl[d]	138	$C_{21}H_{17}NS$	79·7	5·7	80·0	5·4
4-Carboxy-3-methyl	286	$C_{22}H_{17}O_2NS$	73·4	4·9	73·5	4·7
6-Bromo-3-methyl[e]	185	$C_{21}H_{16}NSBr$	64·2	4·0	64·0	4·1
6-Bromo-4-carboxy-3-methyl	310	$C_{22}H_{16}O_2NSBr$	60·2	3·5	60·3	3·7
3 : 6-Dimethyl	143	$C_{22}H_{19}NS$	80·1	6·0	80·2	5·8
4-Carboxy-3 : 6-dimethyl	302	$C_{23}H_{19}O_2NS$	73·7	5·0	74·0	5·1
6-Chloro-3-methyl	162	$C_{21}H_{16}NSCl$	72·3	4·8	72·1	4·6
4-Carboxy-6-chloro-3-methyl	316	$C_{22}H_{16}O_2NSCl$	66·9	4·3	67·1	4·1

[a] The cinchoninic acids formed pale yellow prisms from ethanol–toluene; the quinolines formed colourless needles from ethanol. [b] Picrate, orange-yellow prisms, m. p. 208° (decomp.), from toluene. [c] Orange-yellow picrate, m. p. 203°. [d] Orange-yellow picrate, m. p. 198°. [e] Orange-yellow picrate, m. p. 195°.

TABLE 2*b*. 2-*Substituted* 7-*methylthio*-1-*azaphenanthrene*-4-*carboxylic acids.*[a]

2-Substituent	M. p.	Formula	Found, %: C	Found, %: H	Reqd., % C	Reqd., % H
2′-Thienyl	306°	$C_{19}H_{13}O_2NS_2$	64·8	3·4	65·0	3·7
Phenyl	314	$C_{21}H_{15}O_2NS$	73·1	4·5	73·0	4·3
p-Methoxyphenyl	322	$C_{22}H_{17}O_3NS$	70·1	4·3	70·4	4·5
5′-Acenaphthyl	305	$C_{27}H_{19}O_2NS$	77·2	4·4	77·0	4·5
3′-Pyrenyl	310	$C_{31}H_{19}O_2NS$	79·0	4·3	79·3	4·1
9′-Phenanthryl	303	$C_{29}H_{19}O_2NS$	78·3	4·0	78·2	4·3
9′-Ethyl-3′-carbazolyl	306	$C_{29}H_{22}O_2N_2S$	75·0	4·9	75·3	4·8
p-Dimethylaminophenyl	325	$C_{23}H_{20}O_2N_2S$	71·0	5·5	71·1	5·2
p-Chlorophenyl	296	$C_{21}H_{14}O_2NSCl$	6·66	3·9	66·4	3·7
3′ : 4′-Methylenedioxyphenyl	346	$C_{22}H_{15}O_4NS$	67·6	4·2	67·9	3·9
α-Naphthyl	314	$C_{25}H_{17}O_2NS$	75·8	4·5	75·9	4·3
2′-Furyl	309	$C_{19}H_{13}O_3NS$	67·7	4·0	68·1	3·9
3′ : 4′-Dichlorophenyl	307	$C_{21}H_{13}O_2NSCl_2$	60·6	3·2	60·9	3·1
2′ : 4′-Dichlorophenyl	301	$C_{21}H_{13}O_2NSCl_2$	61·0	3·3	60·9	3·1
5′-Chloro-2′-thienyl	300	$C_{19}H_{12}O_2NS_2Cl$	58·8	3·0	59·1	3·1
2′-Methoxy-1′-naphthyl	305	$C_{26}H_{19}O_3NS$	73·3	4·8	73·4	4·5
2′-Methylthio-1′-naphthyl	304	$C_{26}H_{19}O_2NS_2$	70·4	4·1	70·7	4·3

[a] Purified by crystallisation from acetic acid or through their sodium salts. All yellow or orange-yellow needles, melting with decarboxylation.

TABLE 3. *4-Keto-2-thiazolinylhydrazones.*[a]

	M. p.	Formula	Found, %: C	Found, %: H	Reqd., %: C	Reqd., %: H
Of 2-methylthio-1-naphthaldehyde.						
4-Keto-2-thiazolinylhydrazone	263°	$C_{15}H_{13}ON_3S_2$	57·0	4·3	57·1	4·1
5-Ethyl-4-keto-2-thiazolinylhydrazone	240	$C_{17}H_{17}ON_3S_2$	59·3	5·1	59·5	5·0
5-*n*-Tetradecyl-4-keto-2-thiazolinylhydrazone	153	$C_{29}H_{41}ON_3S_2$	68·3	8·2	68·1	8·0
5-*n*-Hexadecyl-4-keto-2-thiazolinylhydrazone	131	$C_{31}H_{45}ON_3S_2$	68·8	8·1	69·0	8·3
Of 6-methylthio-2-acetonaphthone.						
4-Keto-2-thiazolinylhydrazone	228	$C_{16}H_{15}ON_3S_2$	58·1	4·7	58·4	4·6
5-Ethyl-4-keto-2-thiazolinylhydrazone	182	$C_{18}H_{19}ON_3S_2$	60·3	5·5	60·5	5·3
5-*n*-Tetradecyl-4-keto-2-thiazolinylhydrazone	111	$C_{30}H_{43}ON_3S_2$	68·3	8·0	68·6	8·2
5-*n*-Hexadecyl-4-keto-2-thiazolinylhydrazone	95	$C_{32}H_{47}ON_3S_2$	69·0	8·5	69·4	8·5

[a] Prepared by refluxing of a mixture of the thiosemicarbazone and chloroacetic acid or an α-bromo-acid in ethanol, and recrystallisation of the precipitate from ethanol or acetic acid.

γ-(*6-Methylthio-2-naphthyl*)*butyric Acid.*—The foregoing acid (65 g.), 85% hydrazine hydrate (45 g.), and potassium hydroxide (45 g.) in diethylene glycol (400 c.c.) were refluxed for 6 hours with removal of water; after dilution with water and acidification with hydrochloric acid, the *acid* was taken up in benzene and purified by distillation at *ca.* 260°/2 mm.; it formed colourless needles (44 g.), m. p. 109°, from *cyclo*hexane (Found: C, 69·1; H, 6·5. $C_{15}H_{16}O_2S$ requires C, 69·2; H, 6·2%).

Preparation of Substituted Acrylonitriles.—An equimolecular mixture of 2-methylthio-1-naphthaldehyde and the appropriate arylacetonitrile in ethanol was shaken with some drops of a 20% aqueous solution of potassium hydroxide; the precipitated *acrylonitrile* was collected, washed, and crystallised from the appropriate solvent; in the case of 4-nitrophenylacetonitrile, piperidine was used as catalyst.

6-Ethyl-2-methylthio-1(?)-acetonaphthone.—6-Ethyl-2-naphthyl methyl sulphide (12 g.) was acetylated with acetyl chloride (5 g.) and aluminium chloride (9 g.) in nitrobenzene (100 c.c.) in the usual way; the *ketone* obtained (8 g.) had b. p. 220—224°/15 mm., and crystallised as yellowish needles, m. p. 67° (from *cyclo*hexane), giving a blood-red colour with sulphuric acid (Found: C, 73·5; H, 6·6. $C_{15}H_{16}OS$ requires C, 73·8; H, 6·6%); it gave a positive Pfitzinger reaction with isatin, and a pale yellow cinchoninic acid, m. p. 185°.

Tests showed that *in vitro*, as in previous instances (Buu-Hoï and Hoán, *J.*, 1951, 1834), the thiosemicarbazones mentioned above were fairly tuberculostatic, in contrast with the corresponding 4-keto-2-thiazolinylhydrazones.

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