664. *The Preparation of Some New Substituted Naphthylamines and Naphthidines.*

By R. Belcher, S. J. Lyle, and W. I. Stephen.

The preparation of some new 1-substituted 2-*n*- and 2-*iso*-propyl naphthalenes is described.

The Fries and Lohmann oxidation of 2-methyl-1-naphthylamine to 3 : 3′-dimethylnaphthidine is applied to the oxidation of a number of 2-substituted 1-naphthylamines and is shown to be a general reaction for the preparation of 3 : 3′-disubstituted naphthidines. A mechanism is suggested for the reaction and some limitations are noted. A few naphthidines not obtainable by this reaction are prepared by other methods.

Naphthidine (I; R = H) is usually obtained by reducing 1 : 1′-azonaphthalene with stannous chloride in hydrochloric acid [1] or by oxidation of 1-naphthylamine with ferric oxide in 88% sulphuric acid.[2] 3 : 3′-Dimethylnaphthidine (I; R = Me) has been prepared by oxidation of 2-methyl-1-naphthylamine with ferric oxide in 66% sulphuric acid.[3] Both naphthidines prepared by these methods are heavily contaminated with, and difficult to free from, metal salts.

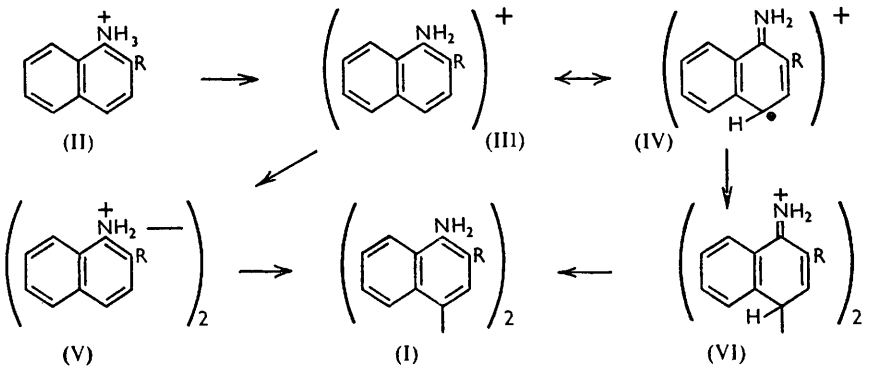
In view of the disadvantages associated with the above methods, Fries and Lohmann's method [4] has been investigated and shown to be general for the preparation of 3 : 3′-disubstituted naphthidines (I) from 2-substituted 1-naphthylamines. Fries and Lohmann found that treatment of 2-methyl-1-naphthylamine sulphate in hot acetic acid with a few drops of perhydrol resulted in a vigorous reaction, with deposition of a salt of the naphthidine (II; R = Me). They observed that 2-methyl-1-naphthylamine did not itself give the naphthidine and that 1-naphthylamine did not give naphthidine. It has now been found that sulphates of 2-ethyl-, 2-propyl-, 2-*iso*propyl-, 2-methoxy-, and 2-phenyl-1-naphthylamine react under the conditions described by Fries and Lohmann to give the corresponding naphthidine. With 2-chloro-, 2-bromo-, 2-hydroxy-, 2-nitro-, or 2-sulpho-1-naphthylamine, the corresponding naphthidine was not formed.

1-Naphthylamine, unless substituted in the 2-position, shows little inclination towards reaction. Substitution of benzoyl peroxide for perhydrol in the preparation of 3 : 3′-dimethylnaphthidine is not so efficient in the Fries and Lohmann reaction. Addition of water (5—10%) or sulphuric acid (1—2%) does not impair the yield of the naphthidine provided that the solubility of the naphthylamine salt is not affected. Reaction does not

[1] Cohen and Oesper, *J. Ind. Eng. Chem.* (Anal. Ed.), 1936, **8**, 306.
[2] Sah and Yuin, *Rec. Trav. chim.*, 1939, **58**, 751.
[3] Fierz-David, Blangey, and Dübendorfer, *Helv. Chim. Acta*, 1946, **29**, 1661.
[4] Fries and Lohmann, *Ber.*, 1921, **54**, 2912.

take place with *N*-acetyl derivatives of reactive naphthylamines even on prolonged boiling in acetic acid with perhydrol. It is also probably significant that 2 : 2′-dimethyl-1 : 1′-azonaphthalene cannot be prepared by Cohen and Oesper's method [1] and that Fierz-David and Mannhart [5] were unable to prepare this compound by reducing 2-methyl-1-nitronaphthalene with zinc dust in alkaline solution.

Possible Reaction Mechanisms.—The course of this reaction in some ways appears to be similar to that of the oxidation of diphenylamine to *NN*-diphenylbenzidine. In the



absence of acids, diphenylamine is oxidised to tetraphenylhydrazine [6] which is known to dissociate into the free radical $Ph_2N\cdot$, and which also undergoes the benzidine rearrangement. However, under conditions in which the hydrazine is dissociated, the benzidine change does not take place.[7] Oxidation with dichromate of diphenylamine in acetic acid containing a little sulphuric acid gives *NN*′-diphenylbenzidine in 20% yield, but *N*-acetylation prevents this reaction. Oxidation in 25% sulphuric acid to diphenylbenzidine-violet gives diphenylbenzidine in 60% yield by reduction.[8] From this evidence it would seem that oxidation of the naphthylamine salt (II) could give rise to the radical (III) by a mechanism similar to that suggested by Saunders and Watson [9] for the oxidation of *NNN′N′*-tetramethylbenzidine. Since the benzidine rearrangement is an intramolecular reaction [10] having specific hydrogen-ion catalysis with second-order dependence on hydrogen ions,[11] dimerisation of (III) could give rise directly to the protonated activation complex (V), which rearranges with loss of two hydrogen ions to (VII). However, by analogy with the oxidation of naphthols to dinaphthyldiols in alkaline solution [12] and oxidation of tertiary amines such as dimethylaniline, the radical (III) in the mesomeric form (IV) could dimerise to the intermediate (VI), which rearranges to the naphthidine (I). As yet, there is not sufficient evidence to distinguish between these two mechanisms.

Oxidation of 1-Naphthylamines with Other Oxidants.—Naphthidines, like benzidines, give intense colours on oxidation in neutral or acid solution. 1-Naphthylamines will, on oxidation in strong acid solution, give the same colour reactions as the corresponding naphthidines, suggesting that the naphthylamine is first oxidised to the naphthidine (I). 1-Aminonaphthalene-2-sulphonic acid can only be oxidised to the colour characteristic of the naphthidine by powerful oxidants (*e.g.*, Ce^{IV}). This would suggest that hydrogen peroxide is too weak to convert this naphthylamine into the naphthidine in the Fries and Lohmann reaction. 3 : 3′-Dinitronaphthidine (see below) cannot be oxidised with any

[5] Fierz-David and Mannhart, *Helv. Chim. Acta*, 1937, **20**, 1031.
[6] Chattaway and Ingle, *J.*, 1895, **67**, 1090.
[7] Wieland and Gambarjan, *Ber.*, 1906, **39**, 1503.
[8] Marqueyrol and Muraour, *Bull. Soc. chim.*, 1914, **15**, 186.
[9] Saunders and Watson, *Biochem. J.*, 1950, **46**, 629.
[10] Ingold, " Structure and Mechanism in Organic Chemistry," Bell, London, 1953, pp. 631—637.
[11] Hammond and Shine, *J. Amer. Chem. Soc.*, 1950, **72**, 220.
[12] Waters in H. Gilman (Ed.), " Organic Chemistry," Wiley, 1953, Vol. IV, p. 1216.

oxidant, so that it is hardly surprising that the Fries and Lohmann reaction fails with 2-nitro-1-naphthylamine.

Preparation of Naphthylamines.—The 2-substituted 1-naphthylamines are generally prepared by nitration of 2-substituted naphthalenes, followed by reduction to the amines. 2-Ethyl-1-naphthylamine was prepared by this route following the method described by Levy.[13] 2-Ethylnaphthalene is more conveniently prepared by reducing methyl 2-naphthyl-ketone by Huang-Minlon's method [14] rather than by Sah's use [15] of the Clemmensen procedure. Similarly, 2-*n*-propyl-1-naphthylamine was synthesised from ethyl 2-naphthyl ketone, made by Buu-Hoï and Caigniant's method. Oxidation of the product in strong mineral acid gave the purple-red colour associated with the lower homologues and the corresponding naphthidines, which supported the structure assigned; further evidence was provided by hydrolysis of the *N*-acetyl derivative to the known 2-*n*-propyl-1-naphthol.[17] 2-*iso*Propyl-1-naphthylamine was prepared similarly. Two independent syntheses of 2-*iso*propylnaphthalene have been examined, but neither gave very satisfactory yields, in agreement with the findings of Fieser and Chang.[18] The more convenient Friedel–Crafts synthesis described by Haworth *et al.*[19] is preferred to Bergmann and Weizmann's method [20] which probably gives a purer product, but polymerisation of the 2-2′-naphthyl-propene during the " dehydration " of 1-methyl-1-2′-naphthylethanol is difficult to prevent. The required mononitro-compound is isolated from the lower-boiling fractions of the nitration products of 2-*iso*propylnaphthalene. 2-*iso*Propyl-1-naphthylamine gives on oxidation in strong acid solution the characteristic purple-red colour associated with the other 2-alkyl-1-naphthylamines described. 2-Phenyl-1-naphthylamine was prepared according to Hey and Lawton.[21]

The naphthylamines described above are dissolved in ether and their sulphates are precipitated by addition of a solution of sulphuric acid in ether. These amine salts are converted into the corresponding naphthidines in 25—40% yields by the Fries and Lohmann reaction.

Other Naphthidines.—Hodgson and Habeshaw [22] reported the synthesis of 3 : 3′-dinitronaphthidine by nitrating 4 : 4′-diacetamido-1 : 1′-dinaphthyl. We have been unable to hydrolyse the nitrated diacetamido-compound either under the conditions described by these authors or by extending the time of hydrolysis. Deacetylation proceeds smoothly, however, in equal volumes of 10N-hydrochloric acid and ethanol. Reduction of the dinitronaphthidine to the diaminonaphthidine is readily effected with sodium dithionite. The diaminonaphthidine is very unstable to light and oxidising agents but it condenses readily with benzil (2 mols.), thus proving the compound to be 3 : 3′-diaminonaphthidine. Naphthidine-3 : 3′-disulphonic acid is prepared by reducing 1 : 1′-azonaphthalene-2 : 2′-disulphonic acid, synthesised by Cumming and Muir's method,[23] with stannous chloride in hydrochloric acid solution. The naphthidinedisulphonic acid differs from 1-naphthylamine-2-sulphonic acid used in its preparation in having a higher decomposition point and giving an *S*-benzylthiuronium derivative having a considerably lower m. p.

Experimental

M. p.s above 100° have been corrected.

Fries and Lohmann Reaction: *General Procedure.*—The naphthylamine salt (5 g.) is dissolved in sufficient warm acetic acid to prevent crystallisation when the mixture is cooled to 25—30°. The mixture is heated to boiling point, the source of heat removed, and hydrogen peroxide

[13] Levy, *Compt. rend.*, 1932, **195**, 801.
[14] Huang-Minlon, *J. Amer. Chem. Soc.*, 1946, **68**, 2487.
[15] Sah, *Rec. Trav. chim.*, 1940, **59**, 1021.
[16] Buu-Hoï and Caigniant, *Bull. Soc. chim.*, 1945, **12**, 307.
[17] Stroughton, *J. Amer. Chem. Soc.*, 1935, **57**, 202.
[18] Fieser and Chang, *ibid.*, 1942, **64**, 2050.
[19] Haworth, Letsky, and Mavin, *J.*, 1932, 1784.
[20] Bergmann and Weizmann, *J. Org. Chem.*, 1944, **9**, 352.
[21] Hey and Lawton, *J.*, 1940, 374.
[22] Hodgson and Habeshaw, *J.*, 1947, 1573.
[23] Cumming and Muir, *J. Royal Tech. Coll. Glasgow*, 1937, **4**, 63.

(5—10 drops, 30% w/v) added immediately. When the mixture is cooled the crude naphthidine salt separates, is filtered off, and washed with acetic acid (5 ml.), the wash solution being collected with the main filtrate. The liquid is then treated with hydrogen peroxide by the same cycle of operations, the precipitate is collected and treatment of the filtrate continued until precipitation ceases. The precipitates are combined and washed well with water.

2-*Ethylnaphthalene*.—Methyl 2-naphthyl ketone (51 g.), 80% (w/w) hydrazine hydrate (30 g.), sodium hydroxide (36 g.), and diethylene glycol (300 c.c.) were heated under reflux for 1 hr. Water and excess of hydrazine (*ca.* 30 c.c.) were removed by distillation until the temperature rose to 190—200° and the mixture was then refluxed for 4 hr. more, then cooled and diluted with water to 750 c.c. The distillate and the refluxed mixture were combined and extracted with ether (150-c.c. portions) until the extract no longer showed a blue fluorescence. The extract was dried, the ether removed, and the residue distilled in the presence of sodium. The fraction (43 g.), b. p. 127·5—128·5°/18 mm., was collected. It gave a picrate, m. p. 77°.

3 : 3′-*Diethylnaphthidine*.—The crude naphthidine salt, obtained by the Fries and Lohmann reaction, was stirred for 15 min. in 10% sodium hydroxide (100 c.c.). The base was filtered off and washed free from alkali. It was dissolved in ethanol (25 c.c.), treated with activated carbon, and filtered hot. The filtrate was heated to boiling and water was added slowly until a definite turbidity persisted. On cooling, 3 : 3′-diethylnaphthidine monohydrate (1 g.) separated in red-violet needles, m. p. 110—116°. A pure, colourless sample was obtained by dehydration under reduced pressure at 70—80° and recrystallisation from ligroin. The pure anhydrous *base* melted at 103° (sealed capillary) (Found: C, 84·7; H, 7·3; N, 8·2. $C_{24}H_{24}N_2$ requires C, 84·6; H, 7·1; N, 8·2%).

2-n-*Propylnaphthalene*.—The method was that used in the preparation of the lower homologue, starting with ethyl 2-naphthyl ketone (55·2 g.). The fraction (42 g.), b. p. 133·5—135·5°/12 mm., was collected. It gave a picrate, m. p. 90°.

1-*Nitro*-2-n-*propylnaphthalene*.—2-*n*-Propylnaphthalene (85·1 g.) in acetic acid (125 c.c.) was treated with nitric acid (40 g., *d* 1·5) dropwise, the mixture being stirred and kept below 10°. It was allowed to reach room temperature and remain there for 2 hr. before being warmed gradually (3 hr.) to 80°, with rapid stirring throughout. The mixture was poured into water (1 l.) and extracted with ether. The extract was washed with 10% sodium carbonate solution, then water, and finally dried. The products (106 g.), after removal of the ether, were fractionated (Vigreux column, 25 cm. long). The fractions, b. p. 178—182°/18 mm. and 183—185°/18 mm., yielded a solid on cooling (−15°) and seeding, if necessary. (Pure crystals of 1-*nitro*-2-n-*propylnaphthalene* were first obtained by chromatographic separation of the nitrated oil on alumina.) A third fraction, b. p. 186—190°/18 mm., gave the solid, heavily contaminated with an oil. Two recrystallisations of the solid from ligroin (b. p. 40—60°) gave the pure compound (19 g.), m. p. 31° (Found: C, 72·3; H, 6·1; N, 6·3. $C_{13}H_{13}O_2N$ requires C, 71·5; H, 6·1; N, 6·5%).

2-n-*Propyl*-1-*naphthylamine*.—1-Nitro-2-*n*-propylnaphthalene (18·5 g.) in boiling 50% acetic acid (225 ml.) was treated gradually with iron powder (18·5 g.) and refluxed for 4 hr. 10N-Hydrochloric acid (100 c.c.) was added to the cooled reaction mixture which was then left overnight at 0°. The amine hydrochloride was filtered off and distilled in steam, first from 4N-hydrochloric acid (300 c.c.) to remove unchanged nitro-compound and then from alkaline solution. The amine was extracted into ether, and converted into 2-n-*propyl*-1-*naphthylammonium hydrogen sulphate* with 10% sulphuric acid in ether (Found: C, 55·0; H, 5·9; N, 5·1; S, 11·4. $C_{13}H_{17}O_4NS$ requires C, 55·1; H, 6·1; N, 5·0; S, 11·3%). The free base melted at 8—9°. The *acetyl derivative*, from pyridine with acetyl chloride, had m. p. 152° (Found: C, 79·2; H, 7·4; N, 6·3. $C_{15}H_{17}ON$ requires C, 79·3; H, 7·5; N, 6·2%).

2-n-*Propyl*-1-*naphthol*.—Two thick-walled hard-glass tubes were each charged with *N*-acetyl-2-*n*-propyl-1-naphthylamine (1·25 g.) and sulphuric acid (2·5 g., in 40 c.c. of water); the tubes were sealed and heated at 210° for 7 hr. The brown oil was extracted into chloroform and the chloroform solution was repeatedly extracted with 2N-sodium hydroxide. The combined alkaline extracts were acidified and extracted with ether. The ether solution was washed free from acid and dried, and the ether removed. The residue was distilled under reduced pressure and the solid brown distillate was recrystallised twice from ligroin; it formed needles (0·5 g.), m. p. and mixed m. p. 49—50°.

The *toluene*-p-*sulphonate* had m. p. and mixed m. p. 86° (Found: C, 70·7; H, 5·9; S, 9·4. $C_{20}H_{20}O_3S$ requires C, 70·6; H, 5·9; S, 9·4%).

3 : 3′-*Di*-n-*propylnaphthidine*.—The crude free base (1·1 g.) was obtained by stirring a suspension of the naphthidine salt, prepared by the Fries and Lohmann reaction, in 10% sodium hydroxide solution (100 c.c.) at 40—50° for 30 min. The base could not be purified by recrystallisation, but the NN′-*diacetyl derivative* (1 g.), m. p. 348°, was prepared from the crude base (1·1 g.) and acetyl chloride in pyridine, and this was readily purified by 3 recrystallisations from acetic acid (charcoal) (Found: C, 79·5; H, 7·2; N, 6·4. $C_{30}H_{32}O_2N_2$ requires C, 79·6; H, 7·1; N, 6·2%).

The diacetyl derivative (1·5 g.) was hydrolysed by a refluxing mixture of 10N-hydrochloric acid (250 c.c.) and ethanol (250 c.c.) for 60 hr. The *naphthidine dihydrochloride* (1·4 g.) was filtered off from the cooled solution (Found: C, 71·2; H, 6·9; Cl, 16·1. $C_{26}H_{30}N_2Cl_2$ requires C, 70·8; H, 6·9; Cl, 16·1%). The *base*, liberated by grinding the dihydrochloride with aqueous ammonia, was recrystallised from ligroin, forming white silky needles, m. p. 100° (Found: C, 84·7; H, 7·6; N, 7·8. $C_{26}H_{28}N_2$ requires C, 84·8; H, 7·7; N, 7·6%).

1-*Nitro*-2-iso*propylnaphthalene*.—By the method used for the isolation of the 2-*n*-propyl isomer, 2-*iso*propylnaphthalene (85 g.) yielded 1-*nitro*-2-iso*propylnaphthalene* (6 g.), m. p. 52° (Found: C, 72·2; H, 6·0; N, 6·6%).

2-iso*Propyl*-1-*naphthylamine*.—(*a*) 1-Nitro-2-*iso*propylnaphthalene (7·5 g.) in 50% acetic acid (95 c.c.) was reduced to the amine with iron powder (7·5 g.) in the same way as the *n*-propyl isomer. Steam distillation gave a solid which recrystallised in tablets, m. p. 70°, from ligroin (90—95% yield) (Found: C, 84·0; H, 8·0; N, 7·7%). *Acetyl derivative*, m. p. 187° (Found: C, 78·9; H, 7·3; N, 6·1%).

(*b*) After nitration of 2-*iso*propylnaphthalene (0·5 mol.), the fraction, b. p. 182—190°/18 mm. (50 g.), was treated in 50% acetic acid (600 c.c.) with iron powder (50 g.) in the same way as the pure nitro-compound. Steam-distillation from acid gave an oil which solidified when seeded with the pure amine and yielded 2-*iso*propyl-1-naphthylamine (10 g.), m. p. 70°, after 3 recrystallisations from ligroin.

3 : 3′-*Di*iso*propylnaphthidine*.—The naphthylamine salt (5 g.) readily yielded this naphthidine by the Fries and Lohmann reaction. The base was obtained by suspending the naphthidine salt in ethanol (100 c.c.), and adding 20% sodium hydroxide (20 c.c.). The mixture was boiled for 10 min., cooled, and filtered, and the solid (0·7 g.) was washed free from alkali. It recrystallised from ligroin in small cubes, m. p. 260° (Found: C, 84·6; H, 7·6; N, 7·4%).

3 : 3′-*Dimethoxynaphthidine*.—The crude naphthidine salt was obtained by the Fries and Lohmann reaction. The free base, obtained from a suspension of the salt in 10% sodium hydroxide, was first partially purified by dissolving it in ethanol, treating the solution once or twice with activated carbon, and precipitating the base by making the boiling filtrate turbid with water and cooling; the yield was 0·3—0·5 g. Recrystallisation from ligroin (charcoal) gave the pure *naphthidine* in pale yellow flakes, m. p. 218° (Found: C, 76·8; H, 5·6; N, 8·2. $C_{22}H_{20}O_2N_2$ requires C, 76·7; H, 5·8; N, 8·1%).

3 : 3′-*Diphenylnaphthidine*.—2-Phenyl-1-naphthylamine sulphate (5 g.) dissolved in acetic acid (50 c.c.) gave the corresponding naphthidine salt by the Fries and Lohmann reaction. The latter salt was very difficultly soluble in water and the free base was best obtained by warming the salt in ethanol (100 c.c.) and aqueous 20% sodium hydroxide (20 c.c.) until dissolution was complete. The solution was then filtered, and the amine precipitated with water. The precipitate was washed free from alkali on the filter and dissolved in ethanol (charcoal). After filtration, the filtrate was made turbid at the b. p. with water; the purified *naphthidine* (1·5 g.) separated on cooling as a greyish-purple solid; after recrystallisation from ligroin it had m. p. 219° (Found: C, 87·9; H, 5·4; N, 6·3. $C_{32}H_{24}N_2$ requires C, 88·0; H, 5·5; N, 6·4%).

3 : 3′-*Dinitronaphthidine*.—Finely powdered 4 : 4′-diacetamido-3 : 3′-dinitro-1 : 1′-dinaphthyl (2 g.) was refluxed with ethanol (75 c.c.) and 10N-hydrochloric acid (75 c.c.) for 48 hr. The initially pale yellow suspension gradually assumed a deep orange colour. The mixture was poured into water (500 c.c.), and the precipitate was filtered off, washed well with water, and dried. It was dissolved in the minimum quantity of boiling pyridine, and the hot solution filtered and made permanently turbid at the b. p. with water. The *naphthidine* (1·6 g.) formed bronze leaflets having a metallic lustre, m. p. 360° (Found: C, 64·0; H, 3·8; N, 14·8. $C_{20}H_{14}O_4N_4$ requires C, 64·2; H, 3·8; N, 15·0%).

3 : 3′-*Diaminonaphthidine*.—Sodium dithionite (4 g.) was added to 3 : 3′-dinitronaphthidine (0·5 g.) in ethanol (100 c.c.) and water (25 c.c.); the mixture was refluxed for 1 hr., solvent

(75 ml.) was then distilled off, and the residual suspension poured into water (300 c.c.). The white solid (0·4 g.) was washed with water and dried. The amine formed a faintly yellow, fluffy solid (from ethanol) which had no definite m. p. and rapidly darkened in air and light.

The *diquinoxaline derivative* was prepared by dissolving 3 : 3′-diaminonaphthidine (0·2 g.) in the minimum amount of boiling ethanol and adding a solution of benzil (0·27 g.) in ethanol. The mixture was refluxed for 30 min., cooled, and filtered, and the solid benzil condensate was washed with aqueous ethanol. It recrystallised from pyridine–ethanol as pale yellow flakes, m. p. 362—363° (Found: C, 87·1; H, 4·7; N, 8·6. $C_{48}H_{30}N_4$ requires C, 87·0; H, 4·6; N, 8·4%). It dissolved in concentrated sulphuric acid to give an intense red colour.

Naphthidine-3 : 3′-disulphonic Acid.—1 : 1′-Azonaphthalene-2 : 2′-disulphonic acid (2·5 g.) was dissolved in 5N-hydrochloric acid (150 c.c.) and treated dropwise with a 20% solution of stannous chloride in 10N-hydrochloric acid, until the hot solution became colourless (*ca.* 5 min.). A white precipitate separated and boiling was continued for 30 min. The mixture was cooled, and the solid filtered off. It was dissolved in aqueous ammonia and the solution boiled for 5 min. and filtered. The filtrate was acidified and the precipitate recrystallised from boiling water forming white lustrous leaflets (*ca.* 2 g.). The naphthidine was very hygroscopic and gradually decomposed above 300° (Found: C, 53·8; H, 3·7; N, 6·3; S, 14·4. $C_{20}H_{16}O_6N_2S_2$ requires C, 54·0; H, 3·6; N, 6·3; S, 14·4%).

The S-*benzylthiuronium derivatives* were prepared as follows: (*a*) The 1-naphthylamine-2-sulphonic acid derivative was precipitated from neutral solution with *S*-benzylthiuronium chloride; it formed large white leaflets, m. p. 184°, from aqueous ethanol (Found: C, 55·5; H, 4·8. $C_{18}H_{19}O_3N_3S_2$ requires C, 55·5; H, 4·9%). (*b*) The naphthidine-3 : 3′-disulphonic acid derivative, prepared similarly, was a pale tan powder, m. p. 144°, from aqueous ethanol (Found: C, 55·2; H, 4·8. $C_{36}H_{36}O_6N_6S_4$ requires C, 55·6; H, 4·7%).

One of us (S. J. L.) thanks Messrs. J. Lyons and Co. for the award of a Fellowship.

CHEMISTRY DEPARTMENT,
THE UNIVERSITY, BIRMINGHAM, 15. [*Received, March 3rd,* 1958.]