65. *The Unsaturation and Tautomeric Mobility of Heterocyclic Compounds. Part XI. α- and β-Naphthoxazole and 5-Bromobenzoxazole Derivatives. The Ultra-violet Absorption Spectra of Some Tautomeric Selenazoles.*

By R. D. Desai, R. F. Hunter, and A. Rahman Khan Khalidi.

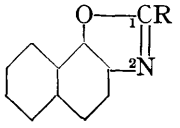
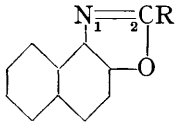
The α- and β-naphthoxazoles containing prototropic triad systems exhibit a close analogy to their thiazole analogues in their behaviour towards methylating agents. 1-Amino-α-naphthoxazole and its β-analogue react exclusively in the amino-aromatic form with methyl iodide, yielding iminomethyldihydro-derivatives. The phenyl group in anilinonaphthoxazoles, however, enables the nitrogen atom to which it is attached to compete with the ring nitrogen atom during methylation. The hydroxy- and thiol-naphthoxazoles also resemble their benzoxazole analogues on methylation under the usual conditions.

The orientation of the 5-bromo-derivatives obtained by bromination of 1-hydroxybenzoxazole and 1-thiolbenzoxazole follows from their rational syntheses, and their methylation gives rise to the expected *N*- and *S*-methyl derivatives.

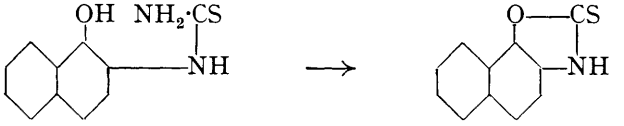
The ultra-violet absorption spectrum of 1-hydroxybenzselenazole in methyl alcohol is almost identical with that of the *N*-methyl ether, showing that the covalent form of the molecule has the ketodihydro-structure. In aqueous sodium hydroxide, however, there is a drop in the first maximum between 2800 and 2900 A., and a shift of the curve towards the region of longer wave-length. The curve of 1-thiolbenzselenazole in methyl alcohol also indicates that this molecule has the thiodihydro-structure. In aqueous

sodium hydroxide, there is a slight shift towards the region of shorter wave-length, and an appreciable drop in the first maximum connected with the ionisation of the hydrogen atom of the triad system.

As might be anticipated on the basis of the theory of sextuple valency group stability, α- and β-naphthoxazoles (I and II) containing prototropic triad systems exhibit a striking similarity to their thiazole analogues in their behaviour towards alkylating agents (compare Desai, Hunter, and Khalidi, J., 1934, 1186).

(I.)   (II.)

1-*Amino*-α-*naphthoxazole* (I, R = NH_2) was synthesised from 1-*hydroxy*-2-*naphthylthiourea* by treatment with freshly precipitated mercuric oxide in alcohol, but in somewhat poor yield, as the greater portion of the material underwent oxazole ring formation of quite a different type, leading to the production of 1-thiol-α-naphthoxazole. Since there is every reason to suppose that thioureas possess the thioamide structure in the covalent form (Hendrick, *J. Amer. Chem. Soc.*, 1928, **50**, 2455; compare Hunter and Jones, J., 1930, 2194), this reaction is readily explicable on the view that the proximity of the hydroxyl and the amino-group permits facile elimination of ammonia with the production of the thiolnaphthoxazole:



On methylation with methyl iodide, 1-amino-α-naphthoxazole reacted apparently exclusively in the amino-aromatic form (III, X = NH), yielding 1-*imino*-2-*methyl*-1 : 2-*dihydro*-α-*naphthoxazole* (V, R = H), unaccompanied by any detectable amount of 1-*methylamino*-α-*naphthoxazole* (VI, R = H) (compare Hunter and Jones, J., 1930, 941), which was synthesised for comparison from 1-thiol-α-naphthoxazole and methylamine.

(III.) $C_{10}H_6\langle^{O}_{N}\rangle C\cdot X[H]$ ⇌ $C_{10}H_6\langle^{O}_{N[H]}\rangle C{:}X$ (IV.)

(V.) $C_{10}H_6\langle^{O}_{NMe}\rangle C{:}NR$ $C_{10}H_6\langle^{O}_{N}\rangle C\cdot NMeR$ (VI.)

The phenyl group of the anilino-substituent in 1-anilino-α-naphthoxazole (III ⇌ IV, X = NPh), however, enables the nitrogen atom to which it is attached to compete with the ring nitrogen atom during methylation, leading to the production of 1-*phenylmethylamino*-α-*naphthoxazole* (VI, R = Ph) in substantial amount alongside the 1-*phenylimino*-2-*methyl*-1 : 2-*dihydro*-isomer (V, R = Ph) which constitutes the bulk of the methylation product. This result falls into line with the behaviour of the corresponding thiazole derivative, since a repetition of the methylation of 1-anilino-α-naphthathiazole (Chowdhury, Desai, and Hunter, *J. Indian Chem. Soc.*, 1933, **10**, 637) has shown that 1-phenylmethylamino-α-naphthathiazole is produced to the extent of about 12% (unpublished results).

1-*Hydroxy*-α-*naphthoxazole* was synthesised by condensation of ethyl chloroformate and 2-amino-1-naphthol. It was also prepared by the action of carbonyl chloride on the aminonaphthol, and by condensation of the latter with urethane. On methylation in alkaline medium, it gave 1-*keto*-2-*methyl*-1 : 2-*dihydro*-α-*naphthoxazole* (V, with O in place of NR).

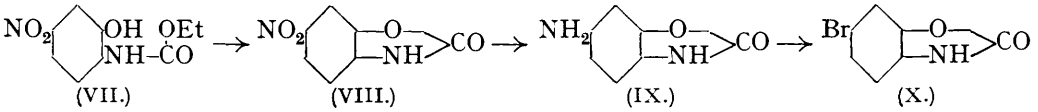
2-*Amino*-β-*naphthoxazole* (II, R = NH_2), synthesised from 2-*hydroxy*-1-*naphthylthiourea*, behaved similarly to the α-derivative and to its thiazole analogue (Desai, Hunter, and Kureishy, J., 1936, 1668) and gave 2-*imino*-1-*methyl*-1 : 2-*dihydro*-β-*naphthoxazole*

on methylation. 2-Anilino-β-naphthoxazole gave rise to a mixture of *2-phenylimino-1-methyl-1 : 2-dihydro-β-naphthoxazole* and *2-phenylmethylamino-β-naphthoxazole* on methylation, in which the former predominated to the extent of about 75%.

2-Hydroxy-β-naphthoxazole, which was synthesised from 1-amino-2-naphthol by all three methods, underwent methylation on the nuclear nitrogen atom under the usual conditions.

On methylation with methyl iodide in methyl-alcoholic sodium methoxide solution and also on treatment with methyl sulphate in the presence of aqueous potassium hydroxide, 2-thiol-β-naphthoxazole gave solely the S-*methyl* ether. No evidence was obtained of the presence of *2-thio-1-methyl-1 : 2-dihydro-β-naphthoxazole*, which was synthesised from 2-keto-1-methyl-1 : 2-dihydro-β-naphthoxazole and phosphorus pentasulphide.

The constitution of the bromo-substitution derivative previously obtained from 1-hydroxybenzoxazole (Desai, Hunter, and Khalidi, *loc. cit.*) has now been established by its identity with *5-bromo-1-hydroxybenzoxazole* (X), synthesised from 5-nitro-2-aminophenol by cyclisation of the *ester* (VII), reduction of the *5-nitro*-derivative (VIII), and replacement of the amino-group in the *base* (IX) by bromine.



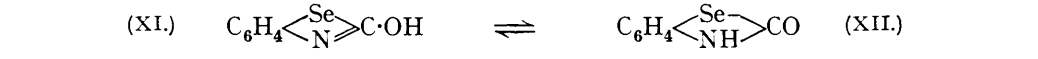
(VII.) (VIII.) (IX.) (X.)

As might be anticipated, methylation of 5-bromo-1-hydroxybenzoxazole in alkaline medium gave the N-*methyl* ether, whose constitution follows from its preparation by bromination of 1-keto-2-methyl-1 : 2-dihydrobenzoxazole (compare Hunter, J., 1930, 125).

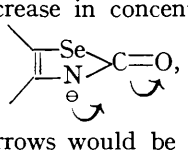
The orientation of the bromo-substitution derivative of 1-thiolbenzoxazole as the *5-bromo*-derivative was accomplished by a similar synthesis from *5-nitro-1-thiolbenzoxazole*, obtained from 5-nitro-2-aminophenol and carbon disulphide. The methylation of 5-bromo-1-thiolbenzoxazole gave the expected S-*methyl* ether, which was also obtained by direct bromination of 1-methylthiolbenzoxazole. No evidence of the formation of an isomeric methyl ether was obtained (compare Chiragh Hasan and Hunter, J., 1936, 1672).

The Absorption Spectra of Selenazole Derivatives.

An examination of the ultra-violet absorption spectra of the selenazoles previously studied (Chiragh Hasan and Hunter, J., 1935, 1766) affords interesting confirmation of their striking similarity to thiazole analogues. For instance, the curve of 1-hydroxybenzselenazole (XI $\rightleftharpoons$ XII) in methyl alcohol is almost identical with that of 1-keto-2-methyl-1 : 2-dihydrobenzselenazole (Fig. 1), showing that the covalent form of the molecule has the ketodihydro-structure (XII).



(XI.) (XII.)

The drop in the first maximum of the hydroxybenzselenazole between 2800 and 2900 A., which is characteristic of the carbonyl group, in aqueous sodium hydroxide may be attributed to the decrease in concentration of absorbing molecules consequent on the production of the ion  , in which some distribution of the negative charge in the sense of the arrows would be anticipated. The shift of the curve towards the region of longer wave-length also indicates deformation of the type observed in the case of 1-hydroxy-5-methylbenzthiazole (Hunter and Parken, J., 1935, 1755).

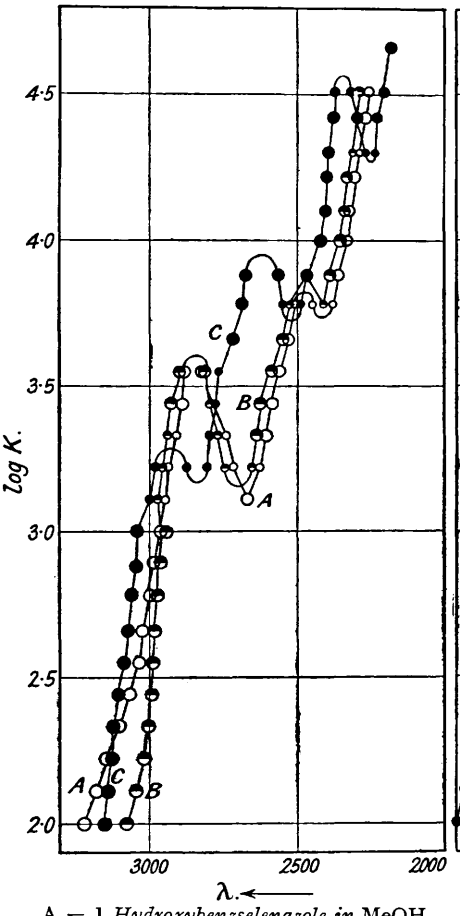
The curve of 1-thiolbenzselenazole (XI $\rightleftharpoons$ XII, with S in place of O) was almost identical with that of 1-thio-2-methyl-1 : 2-dihydrobenzselenazole (Fig. 2) (compare Chiragh Hasan and Hunter, J., 1936, 1672).

In aqueous sodium hydroxide solution, 1-thiolbenzselenazole gave a curve belonging to the same family, but slightly shifted towards the region of shorter wave-length, and

exhibiting an appreciable drop in the first maximum due to ionisation of the hydrogen atom of the triad system.

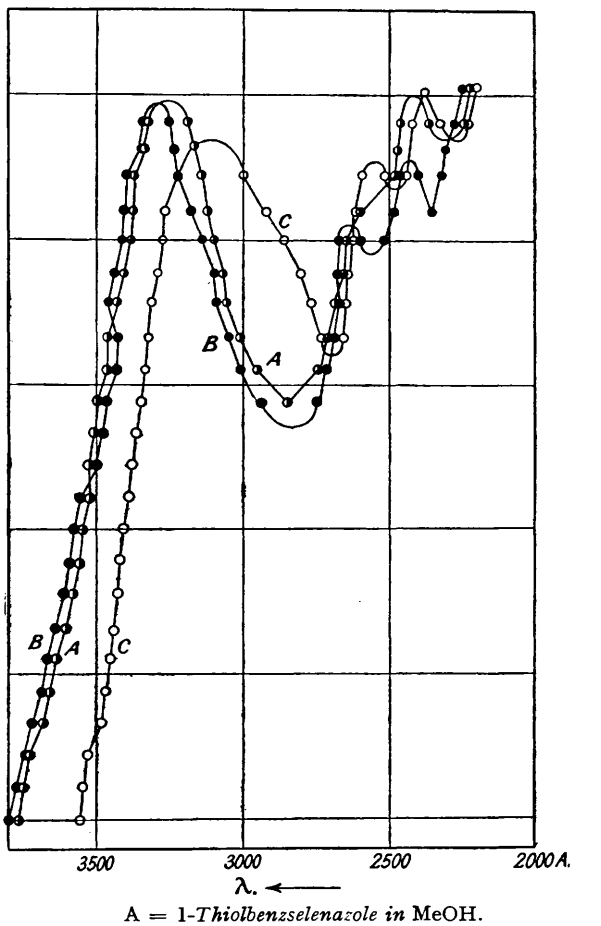
Both in the thiazoles and in the selenazoles, the shift in absorption curves of the

FIG. 1.



A = 1-*Hydroxybenzselenazole in* MeOH.
B = 1-*Keto*-2-*methyl*-1 : 2-*dihydrobenzselenazole in* MeOH.
C = 1-*Hydroxybenzselenazole in* NaOH.

FIG. 2.



A = 1-*Thiolbenzselenazole in* MeOH.
B = 1-*Thio*-2-*methyl*-1 : 2-*dihydrobenzselenazole in* MeOH.
C = 1-*Thiolbenzselenazole in* NaOH.

1-hydroxy- and 1-thiol derivatives due to deformation in aqueous sodium hydroxide takes place in opposite directions.

EXPERIMENTAL.

The method of reducing 2-nitro-1-naphthol (Hodgson and Kilner, J., 1924, **125**, 807) to 2-amino-1-naphthol recommended by Fischer and Hamer (J., 1934, 963) proved unsatisfactory in our hands, and the following procedure was therefore adopted. A solution of 2-nitro-1-naphthol (10 g.) in slightly more than its equivalent of dilute aqueous sodium hydroxide (4 g. in 300 c.c. of water) was heated to boiling and the filtered solution was treated with sodium hyposulphite (50 g.) until the red colour disappeared; the aminophenol separated, on cooling, as a mass of colourless crystals, m. p. 150° (darkening at 130°). Since this compound is more stable in the form of its hydrochloride, the aminonaphthol was dissolved in warm 10% hydrochloric acid (250 c.c.), and the filtered solution was mixed with hydrochloric acid (150 c.c.) and kept, the hydrochloride separating in almost quantitative yield, m. p. 260°.

1-*Hydroxy*-2-*naphthylthiourea*.—A solution of the hydrochloride of the aminonaphthol (10 g.), potassium thiocyanate (10 g.), and concentrated hydrochloric acid (20 c.c.) in water

(100 c.c.) was heated on a water-bath for 10 hours. The residue obtained after removal of inorganic salts by extraction with hot water, and treatment with ethyl acetate, was recrystallised from alcohol, the *thiourea* being obtained in small needles (10 g.), m. p. 252° (Found: S, 14·7. $C_{11}H_{10}ON_2S$ requires S, 14·6%). This thiourea is very sensitive to air and turns black on keeping, although the m. p. remains unaffected.

1-*Amino-α-naphthoxazole.*—When a solution of 1-hydroxy-2-naphthylthiourea (10 g.) in alcohol (100 c.c.) was heated under reflux with freshly precipitated mercuric oxide (25 g.) for 18—20 hours, ammonia was evolved. The filtrate, after removal of mercuric sulphide, was evaporated to dryness, and the residue treated with 10% aqueous sodium hydroxide. The alkali-insoluble residue, when warmed with benzene, partly dissolved, yielding a solution which on filtration and concentration deposited the *aminonaphthoxazole* (1·5—2 g.) in needles, m. p. 195° after recrystallisation from alcohol (Found: C, 71·7; H, 4·25. $C_{11}H_8ON_2$ requires C, 71·7; H, 4·3%). The *acetyl* derivative, prepared by heating a solution of the base in acetic anhydride, separated from dilute alcohol in needles, m. p. 210° (Found: C, 69·1; H, 4·3. $C_{13}H_{10}O_2N_2$ requires C, 69·0; H, 4·4%).

The residue insoluble in benzene consisted of the mercury salt of 1-thiol-α-naphthoxazole, which decomposed at about 300°. The alkaline extract on acidification gave a precipitate which on recrystallisation furnished 1-thiol-α-naphthoxazole (3·5 g.), m. p. and mixed m. p. 262°.

Methylation.—A mixture of 1-amino-α-naphthoxazole (1·5 g.) and methyl iodide (3·2 c.c.) was heated in a sealed tube at 100° for 16 hours; the product was basified and extracted with chloroform. The sticky residue obtained by removal of chloroform was treated with methyl alcohol (5 c.c.), and the residue recrystallised from alcohol; 1-*imino*-2-*methyl*-1 : 2-*dihydro*-α-*naphthoxazole* was obtained in small needles, m. p. 154° (Found: C, 72·8; H, 5·1. $C_{12}H_{10}ON_2$ requires C, 72·7; H, 5·05%). A mixture of this with the isomeric 1-methylamino-derivative had m. p. 140°. The 1-*acetimido*-2-*methyl*-1 : 2-*dihydro*-derivative separated from dilute alcohol in needles, m. p. 133° (Found: C, 70·1; H, 5·0. $C_{14}H_{12}O_2N_2$ requires C, 70·0; H, 5·0%).

Synthesis of 1-*Methylamino-α-naphthoxazole.*—A mixture of 1-thiol-α-naphthoxazole (1 g.) and methylamine (4 c.c. of a 30% solution) was heated in a sealed tube at 100° for 12 hours, the product extracted with ether, and the extract washed with 10% aqueous sodium hydroxide. The residue obtained after removal of the ether was crystallised from dilute methyl alcohol; the 1-*methylamino*-base separated in needles, m. p. 160° (Found: C, 72·7; H, 4·95. $C_{12}H_{10}ON_2$ requires C, 72·7; H, 5·05%). The *acetyl* derivative of this crystallised from dilute alcohol in needles, m. p. 136° (Found: C, 70·2; H, 5·0 $C_{14}H_{12}O_2N_2$ requires C, 70·0; H, 5·0%).

1-*Anilino-α-naphthoxazole.*—This was prepared by heating 1-thiol-α-naphthoxazole with aniline at 200° for 8 hours. The product was recrystallised from benzene and converted into picrate, and the base liberated by warm dilute alkali solution. After recrystallisation from alcohol or benzene, it had m. p. 236° (Found: C, 78·5; H, 4·65. Calc. for $C_{17}H_{12}ON_2$: C, 78·5; H, 4·6%). The picrate separated from benzene in small yellow needles, m. p. 218—220° (Found: C, 56·6; H, 3·0 Calc. for $C_{17}H_{12}ON_2,C_6H_3O_7N_3$: C, 56·4; H, 3·1%). Jacobson (*Ber.*, 1889, **22**, 3242) recorded m. p. 232—233° and 213—214°, respectively.

Methylation.—The base (2 g.) was heated with methyl iodide (3 c.c.) at 100° for 18 hours, and the product basified and extracted with chloroform. The gum obtained was dissolved in benzene and heated under reflux with a solution of picric acid (1·3 g.) in the same solvent for an hour. The residue obtained on evaporation of benzene was treated with ethyl acetate (10 c.c.); the filtered extract deposited the *picrate* of 1-phenylimino-2-methyl-1 : 2-dihydro-α-naphthoxazole in small yellow needles, m. p. 188° (Found: C, 57·3; H, 3·3. $C_{18}H_{14}ON_2,C_6H_3O_7N_3$ requires C, 57·25; H, 3·4%). This constituted about 75% of the product. Recrystallisation of the residue (from the ethyl acetate extract) from benzene furnished the *picrate* of 1-phenylmethylamino-α-naphthoxazole in yellow needles, m. p. 208° (Found: C, 57·0; H, 3·3%), which were identified by mixed m. p. determination with the specimen described below.

Synthesis of 1-*Phenylmethylamino-α-naphthoxazole.*—A mixture of 1-thiol-α-naphthoxazole (1 g.) and methylaniline (1 g.) was heated in an oil-bath at 180—190° for 8 hours. The product was extracted with dilute hydrochloric acid and with dilute aqueous sodium hydroxide, and a solution of the residual gum in benzene was treated with the calculated quantity of picric acid; the picrate of the 1-phenylmethylamino-base was obtained in needles, m. p. 207—208°.

1-*Hydroxy-α-naphthoxazole.*—(i) *Condensation of* 2-*amino*-1-*naphthol with ethyl chloroformate.* A solution of 2-amino-1-naphthol hydrochloride (3 g.) in ethyl-alcoholic sodium ethoxide (0·7 g. of sodium and 45 c.c. of absolute alcohol) was cooled in ice during the gradual addition of chloroformic ester (2 g.), and the mixture was heated under reflux for 6 hours. The gummy

residue obtained by removal of alcohol was heated in an oil-bath at 180—190° for 3 hours, and the cyclised product extracted with aqueous sodium hydroxide (10%). The *1-hydroxy-α-naphthoxazole* recovered on acidification crystallised from alcohol in needles (2·2 g.), m. p. 218—220° (Found: C, 71·5; H, 3·8. $C_{11}H_7O_2N$ requires C, 71·35; H, 3·8%). The m. p. was not raised by further recrystallisation from benzene.

(ii) *Action of carbonyl chloride on 2-amino-1-naphthol.* A mixture of the hydrochloride of 2-amino-1-naphthol (2 g.), pyridine (30 c.c.), and a 12% solution of carbonyl chloride in toluene (10 c.c.) was vigorously shaken at intervals during 3 hours and thereafter kept for 24 hours. The residue obtained by removal of toluene and pyridine was extracted with 10% aqueous sodium hydroxide, and the hydroxynaphthoxazole (m. p. 208°) recovered by acidification. On recrystallisation from alcohol this was obtained in small needles, m. p. 220°, not depressed by the specimen already described. A residue, insoluble in hot aqueous alkali and in alcohol and acetone, crystallised from glacial acetic acid in black needles, m. p. 268°.

(iii) *Synthesis from 2-amino-1-naphthol and urethane.* An intimate mixture of the amino-naphthol (3·2 g.) and urethane (2 g.) was heated at 160° for 4 hours, ammonia being evolved. Extraction of the cooled melt with aqueous alkali furnished the hydroxynaphthoxazole, m. p. 220° after recrystallisation from alcohol and benzene.

Methylation. A solution of the hydroxy-derivative (1 g.) in warm chloroform was shaken with aqueous potassium hydroxide (33%, 10 c.c.) and methyl sulphate (6 c.c.). Destruction of the excess of methyl sulphate with alkali and extraction with chloroform gave *1-keto-2-methyl-1 : 2-dihydro-α-naphthoxazole*, which crystallised from dilute alcohol in small needles, m. p. 198° (Found: C, 72·3; H, 4·6. $C_{12}H_9O_2N$ requires C, 72·3; H, 4·5%). Attempts to bring about hydrolytic ring fission by boiling the ketomethyldihydro-derivative with concentrated hydrochloric acid and also by heating with this acid in a sealed tube at 180° proved unsuccessful. The oxazole ring underwent fission, however, on treatment with 50% sulphuric acid at 160° for 12 hours.

1-Amino-2-naphthol was most conveniently prepared by reduction of Orange II in alkaline solution with sodium hyposulphite, and purified by conversion into its hydrochloride, which crystallised in long needles, m. p. 250—252°.

2-Hydroxy-1-naphthylthiourea, prepared as in the case of the 1-hydroxy-2-naphthyl derivative, formed small needles, decomp. about 300° (Found: S, 14·9. $C_{11}H_{10}ON_2S$ requires S, 14·7%), which turned black on exposure to air.

2-Amino-β-naphthoxazole.—A solution of 2-hydroxy-1-naphthylthiourea (10 g.) in alcohol (80 c.c.) was treated with freshly precipitated mercuric oxide (20—25 g.), and the mixture heated under reflux for 24—28 hours. The product obtained by evaporation of the filtered solution was treated with warm aqueous sodium hydroxide, and the residue extracted with warm benzene. *2-Amino-β-naphthoxazole* separated in plates, m. p. 176° (Found: C, 71·9; H, 4·4. $C_{11}H_8ON_2$ requires C, 71·4; H, 4·4%). The benzene-insoluble residue consisted of the mercuric mercaptide, m. p. 276—278°. The *acetyl* derivative, obtained by acetylation of the amino-naphthoxazole with acetic anhydride, crystallised from dilute alcohol in small needles, m. p. 212° (Found: C, 69·2; H, 4·3. $C_{13}H_{10}O_2N_2$ requires C, 69·0; H, 4·4%).

The alkaline extract from the original crude product, on acidification, deposited 2-thiol-β-naphthoxazole, which was identified by m. p. and mixed m. p. determination.

Methylation. The product obtained by heating 2-amino-β-naphthoxazole (1·5 g.) with methyl iodide (3·2 c.c.) at 100° for 20 hours was basified and extracted with chloroform; *2-imino-1-methyl-1 : 2-dihydro-β-naphthoxazole* was then obtained, which crystallised from dilute alcohol in small needles, m. p. 148—150° (Found: C, 72·7; H, 5·0 $C_{12}H_{10}ON_2$ requires C, 72·7; H 5·05%). *2-Acetimido-1-methyl-1 : 2-dihydro-β-naphthoxazole* crystallised from dilute alcohol in needles, m. p. 132° (Found: C, 70·1; H, 5·0. $C_{14}H_{12}O_2N_2$ requires C, 70·0; H, 5·0%).

2-Methylamino-β-naphthoxazole, prepared by heating 2-thiol-β-naphthoxazole with excess of aqueous methylamine (30%) at 100° for 14 hours, crystallised from dilute methyl alcohol in long needles, m. p. 158° (Found: C, 72·8; H, 5·15. $C_{12}H_{10}ON_2$ requires C, 72·7; H, 5·05%). The *acetyl* derivative separated from dilute alcohol in needles, m. p. 140° (Found: C, 70·0; H, 5·0. $C_{14}H_{12}O_2N_2$ requires C, 70·0; H, 5·0%).

2-Anilino-β-naphthoxazole crystallised from dilute alcohol in small needles, m. p. 172° (Found: C, 78·6; H, 4·8. Calc. for $C_{17}H_{12}ON_2$: C, 78·5; H, 4·6%); the picrate formed yellow needles, m. p. 210—212° (Found: C, 56·4; H, 3·15. Calc. for $C_{17}H_{12}ON_2,C_6H_3O_7N_3$: C, 56·4; H, 3·1%). Jacobson (*Ber.*, 1888, **21**, 417) recorded m. p. 167—168° and 207—208°, respectively.

Methylation of 2-Anilino-β-naphthoxazole.—The gum isolated by chloroform extraction of the

product formed by the methylation of 2-anilino-β-naphthoxazole (2 g.) with methyl iodide (3·5 c.c.) at 100° for 24 hours was dissolved in acetone and converted into picrate. Crystallisation gave mixtures, and the product obtained by removal of acetone was therefore shaken with ethyl acetate. The filtrate deposited the *picrate* of 2-phenylimino-1-methyl-1 : 2-dihydro-β- naphthoxazole in small yellow needles, m. p. 174—176° (Found : C, 57·2; H, 3·4. $C_{18}H_{14}ON_2,C_6H_3O_7N_3$ requires C, 57·25; H, 3·4%). This constituted about 75% of the total picrate. The residue which was sparingly soluble in ethyl acetate crystallised from benzene in small yellow needles, m. p. 194—196°, and was identified as the *picrate* of 2-phenylmethylamino-β-naphthoxazole (Found : C, 57·4; H, 3·3%).

Synthesis of 2-Phenylmethylamino-β-naphthoxazole.—A mixture of 2-thiol-β-naphthoxazole (1 g.) and methylaniline (1 g.) was heated at 180° for 8 hours. The base was obtained as a gum; this furnished a picrate which crystallised in needles, m. p. 196°.

2-Hydroxy-β-naphthoxazole.—(i) *Condensation of 1-amino-2-naphthol with ethyl chloroformate.* The reaction was carried out as in the case of the α-naphthoxazole, the mixture being heated for 8 hours. The resinous product obtained by removal of alcohol was extracted with water and thereafter heated at 180—190° for 4 hours, and the *2-hydroxy-β-naphthoxazole* was extracted with aqueous alkali and recrystallised from dilute alcohol, forming small needles (2·4 g.), m. p. 208° (Found : C, 71·3; H, 3·7. $C_{11}H_7O_2N$ requires C, 71·4; H, 3·8%).

(ii) *Action of carbonyl chloride on 1-amino-2-naphthol.* The hydroxynaphthoxazole, m. p. 207—208°, was obtained in nearly 50% yield, accompanied by a substance, m. p. 250°, which was insoluble in aqueous alkali.

(iii) *Synthesis from 1-amino-2-naphthol and urethane.* An intimate mixture of the hydrochloride of the aminonaphthol (6 g.) and urethane (3 g.) was heated at 190° for 6 hours, and the hydroxynaphthoxazole (4·5 g., m. p. 280° after recrystallisation) recovered from the alkaline extract.

Methylation. A solution of the hydroxynaphthoxazole (1 g.) in chloroform (50 c.c.) was shaken with 30% aqueous potassium hydroxide (10 c.c.) and methyl sulphate (5 c.c.); the mixture was kept for 3 hours, warmed for 30 minutes, cooled, and kept overnight. *2-Keto-1-methyl-1 : 2-dihydro-β-naphthoxazole* crystallised from dilute methyl alcohol in needles, m. p. 188° (Found : C, 72·4; H, 4·55. $C_{12}H_9O_2N$ requires C, 72·4; H, 4·5%).

2-Thiol-β-naphthoxazole.—A mixture of the hydrochloride of 1-amino-2-naphthol (10 g.), carbon disulphide (20 c.c.), and potassium hydroxide (5 g.) in alcohol (100 c.c.) was heated under reflux for 12 hours, and an aqueous extract of the residue obtained by removal of alcohol and excess of carbon disulphide was acidified. On recrystallisation from dilute alcohol, the thiolnaphthoxazole was obtained in needles, m. p. 252°. Yield, 80%.

Methylation.—(i) Methyl iodide (1 c.c.) was gradually added to a solution of 2-thiol-β-naphthoxazole (1 g.) in methyl-alcoholic sodium methoxide (0·12 g. of sodium in 30 c.c. of absolute methyl alcohol); after 5 hours, the mixture was warmed for 20 minutes and kept overnight. The residue obtained after removal of methyl alcohol was extracted with water to remove sodium iodide and recrystallised from methyl alcohol, the *S-methyl* ether being obtained in long needles, m. p. 66—68° (Found : C, 66·6; H, 4·1; S, 14·9. $C_{12}H_9ONS$ requires C, 67·0; H, 4·2; S, 14·9%).

(ii) A solution of the thiolnaphthoxazole (1 g.) in chloroform (30 c.c.) was treated with 30% aqueous potassium hydroxide (10 c.c.) and thereafter with methyl sulphate (5 c.c.); the mixture was gently heated, kept overnight, and the excess of methyl sulphate destroyed with alkali. Extraction with chloroform furnished 2-methylthiol-β-naphthoxazole, which, after recrystallisation from methyl alcohol, had m. p. 66—68° alone and when mixed with the specimen already described.

2-Thio-1-methyl-1 : 2-dihydro-β-naphthoxazole.—An intimate mixture of 2-keto-1-methyl-1 : 2-dihydro-β-naphthoxazole (0·5 g.) and phosphorus pentasulphide (0·3 g.) was heated in an oil-bath at 170° for 8 hours, and the cooled melt was extracted with benzene. The *thiomethyldihydro*-derivative crystallised in small needles, m. p. 180° (Found : S, 14·9. $C_{12}H_9ONS$ requires S, 14·95%).

5-Bromobenzoxazoles.

5-Bromo-1-hydroxybenzoxazole.—*Synthesis from 5-nitro-2-aminophenol.* Ethyl chloroformate (2·2 g.) was gradually added to 5-nitro-2-aminophenol (10 g.) in alcoholic sodium ethoxide (1·5 g. of sodium and 80 c.c. of absolute alcohol), and the mixture heated under reflux for 6 hours. The residue obtained by removal of alcohol was extracted with water to remove sodium chloride and then recrystallised from boiling water, *4-nitro-2-hydroxyphenylurethane*

being obtained in needles, m. p. 174° (Found: C, 47·7; H, 4·3. $C_9H_{10}O_5N_2$ requires C, 47·8; H, 4·4%). On dry distillation, this ester (which explodes on overheating) gave *5-nitro-1-hydroxybenzoxazole*, which crystallised from boiling water (containing a small amount of alcohol) in small lustrous needles, m. p. 244—246° (Found: C, 46·95; H, 2·3. $C_7H_4O_4N_2$ requires C, 46·7; H, 2·2%). Cyclisation was also effected by heating the nitrohydroxyphenylurethane at 180° for 30 minutes; the nitrohydroxybenzoxazole was isolated by extraction with 10% aqueous sodium hydroxide. A hot filtered solution of the nitrobenzoxazole in 10% aqueous sodium hydroxide was gradually treated with powdered sodium hyposulphite until the red colour disappeared. On cooling, *5-amino-1-hydroxybenzoxazole* separated as a mass of colourless crystals, which were washed with cold water and thereafter recrystallised from dilute alcohol; m. p. 204° (Found: C, 56·1; H, 3·85. $C_7H_6O_2N_2$ requires C, 56·0; H, 4·0%). The *acetyl* derivative, obtained by heating a solution of the base in acetic anhydride, crystallised from dilute alcohol in needles, m. p. 234° (Found: C, 56·3; H, 4·05. $C_9H_8O_3N_2$ requires C, 56·2; H, 4·2%). A mixture of copper sulphate (1·5 g.), sodium bromide (3 g.), copper turnings (1 g.), water (40 c.c.), and concentrated sulphuric acid (4 g.) was boiled under reflux until it was almost completely decolorised; 5-amino-1-hydroxybenzoxazole (1·5 g.) was then added to the mixture, which was cooled to 0° by addition of ice and gradually treated with a solution of sodium nitrite (1 g.) in cold water. The mixture was kept overnight and the precipitated *5-bromo-1-hydroxybenzoxazole* was washed with water and recrystallised from dilute alcohol, separating in needles (1·3 g.), m. p. 188—190° alone and when mixed with a specimen obtained by bromination of 1-hydroxybenzoxazole (Found: Br, 37·4. Calc. for $C_7H_4O_2NBr$: Br, 37·4%).

An attempt to hydrolyse 5-bromo-1-hydroxybenzoxazole with 25% aqueous sodium hydroxide proved unsuccessful, but on heating with concentrated hydrochloric acid under reflux for 14 hours the oxazole ring underwent fission. The basified and filtered solution gave on acidification with dilute hydrochloric acid the hydrochloride of 5-bromo-*o*-aminophenol, which crystallised from dilute alcohol in small needles, m. p. 290° (decomp.).

Methylation. A solution of the hydroxy-derivative (1 g.) in chloroform (15 c.c.) and 30% aqueous potassium hydroxide (5 c.c.) were treated with methyl sulphate (5 c.c.), kept for 4 hours, and gently warmed for 20 minutes. *5-Bromo-1-keto-2-methyl-1 : 2-dihydrobenzoxazole*, isolated by chloroform, crystallised from dilute alcohol in long needles, m. p. 150° (Found: Br, 35·1. $C_8H_6O_2NBr$ requires Br, 35·1%).

Bromination of 1-Keto-2-methyl-1 : 2-dihydrobenzoxazole.—A solution of the keto-derivative (1 g.) in chloroform (20 c.c.) was treated with bromine (1 g. in 5 c.c. of chloroform), and the mixture kept for 4 hours and then warmed. The product obtained by removal of chloroform was treated with sulphurous acid and recrystallised from alcohol, 5-bromo-1-keto-2-methyl-1 : 2-dihydrobenzoxazole being obtained, m. p. 149—150° alone and when mixed with the specimen already described.

5-Bromo-1-thiolbenzoxazole.—Synthesis from 5-nitro-o-aminophenol. 5-Nitro-1-thiolbenzoxazole was prepared by heating a mixture of 5-nitro-*o*-aminophenol (10 g.), carbon disulphide (30 c.c.), and potassium hydroxide (10 g.) in alcohol (40 c.c.) under reflux for 10 hours. The residue obtained by removal of alcohol and the excess of carbon disulphide was dissolved in water, and the filtered solution acidified, 5-nitro-1-thiolbenzoxazole being obtained, which on recrystallisation from dilute alcohol formed short needles, m. p. 216—218° (Found: S, 16·3. $C_7H_4O_3N_2S$ requires S, 16·3%). *5-Amino-1-thiolbenzoxazole* was obtained by treating a warm solution of the 5-nitro-compound (2 g.) in aqueous sodium hydroxide (1 g. in 30 c.c. of water) with sodium hyposulphite (3 g.) until the red colour was completely destroyed; the straw-coloured needles which separated on cooling had m. p. 228° after recrystallisation from dilute alcohol (Found: S, 19·3. $C_7H_6ON_2S$ requires S, 19·3%). *5-Bromo-1-thiolbenzoxazole*, prepared from diazotised 5-amino-1-thiolbenzoxazole, separated from dilute alcohol in long needles, m. p. 198—200° alone and when mixed with a specimen prepared by bromination of 1-thiolbenzoxazole (Found: Br, 34·7. Calc. for C_7H_4ONBrS: Br, 34·8%).

Methylation. (i) Methyl iodide (1 c.c.) was added to a solution of 5-bromo-1-thiolbenzoxazole (1·5 g.) in methyl-alcoholic sodium methoxide (0·2 g. of sodium and 30 c.c. of absolute methyl alcohol) and the mixture was kept for 6 hours, heated on a water-bath for 45 minutes, and left overnight. The residue obtained on evaporation of methyl alcohol was treated with water, and the product crystallised from dilute methyl alcohol, *5-bromo-1-methylthiobenzoxazole* being obtained in long needles, m. p. 148° (Found: Br. 32·8. C_8H_6ONBrS requires Br, 32·8%). (ii) A solution of 5-bromo-1-thiolbenzoxazole (1 g.) in chloroform (10 c.c.) and 30% aqueous potassium hydroxide (12 c.c.) was methylated with excess of methyl sulphate. The *S*-methyl ether so obtained proved identical with that already described.

***Bromination of** 1-Methylthiobenzoxazole.*—A solution of 1-methylthiobenzoxazole in chloroform (1 g. in 20 c.c.) was treated with bromine (1 g. in 5 c.c. of chloroform), and the mixture kept for some time. The residue obtained by removal of chloroform was treated with sulphurous acid and recrystallised from alcohol, 5-bromo-1-methylthiobenzoxazole being obtained, m. p. 148° alone and when mixed with a specimen obtained from methylation of 5-bromo-1-thiolbenzoxazole.

Absorption Spectra of Benzselenazole Derivatives (with ABDUL AZIZ FIRDAUS).

The measurements were made with a Carl Leiss spectrograph (type C), quartz absorption cells being used with a Wellington anti-screen plate, and a hydrogen tube which gave a constant source of light and enabled constant comparison spectra to be inserted between successive exposures with different cell thicknesses of solution. Juxtaposition was obtained by means of a Hartman diaphragm, and from the density matchpoints, molecular extinction coefficients followed.

An M/1000-solution of 1-hydroxybenzselenazole in absolute methyl alcohol was first examined and thereafter diluted to M/10,000 and then to M/100,000 with the same solvent. A similar procedure was followed with an M/1000-solution of 1-keto-2-methyl-1 : 2-dihydrobenzselenazole in methyl alcohol. An M/1000-solution of the hydroxyselenazole in N/100-aqueous sodium hydroxide was then examined and diluted with water first to M/10,000 and then to M/100,000. Similar experiments were carried out with 1-thiolbenzselenazole and 1-thio-2-methyl-1 : 2-dihydrobenzselenazole.

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