74. *Anhydro-compounds from Nitrogen-containing Derivatives of Thioglycollic Acid. Part II.* Glyoxaline and Benziminazole Compounds.*

By G. F. Duffin and J. D. Kendall.

(2-Benziminazolylthio)acetic acid (I; R = R′ = X = H) with acetic anhydride gives a thiazolidone (II) from which *mero*cyanine dyes have been prepared. 1-Substituted acids (I; R′ = X = H), like the corresponding quinoline compounds (Part I *), give stable anhydro-compounds which may be represented as (III) but which, unlike the quinoline anhydro-compounds, usually give products derived by attack of the reagent at two different points in the molecule. No anhydro-compounds corresponding to those derived from (2-quinolylthio)-propionic and -butyric acid could be obtained from the acids (I; R = Me or Et).

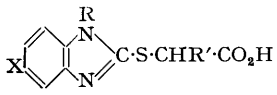
As mentioned in Part I,* dehydration of (2-benziminazolylthio)acetic acid (I; R = R′ = X = H) gives the thiazolidone (II) which possesses a very reactive methylene group (Kendall and Duffin, B.P. 634,951—2). Compounds of type (I; R = Me or Ph, X = H or NO_2), which may be prepared from the appropriate α-halogeno-acid and a 1-substituted benziminazole-2-thiol (V; R = Me or Ph, X = H or NO_2, Y = SH) by the methods of Everett [1] or Stephen and Wilson,[2] cannot undergo dehydration to a thiazolidone, but those in which R = H, like the corresponding (2-quinolylthio)acetic acids (Parts I), give anhydro-compounds of analogous structures (III). [Added, 19.9.55: After this paper had been submitted, publications appeared from Wilson Baker and Ollis [3] and Bieber [4] in

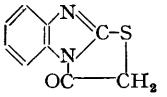
* Part I, *J.*, 1951, 734.

[1] Everett, *J.*, 1931, 3042.
[2] Stephen and Wilson, *J.*, 1928, 1420.
[3] Baker and Ollis, *Chem. and Ind.*, 1955, 910.
[4] Bieber, *ibid.*, p. 1055.

which new formulations were proposed for mesoionic structures. In accordance with that of the former, the compounds formulated as (III) would be represented by (*A*). The present authors cannot see how this helps to explain the reactions of their compounds, and it ignores the special character of intracyclic sulphur atoms which, as will be shown in later papers, have a decided effect on the properties of ring systems.]

That the acids (I) have the structure assigned to them and not that of the isomeric compounds (IV; R = Me or Ph, Z = $CHR'\cdot CO_2H$) is shown by the similarity of their ultraviolet absorptions in ethanol to that of the parent (I; R = R′ = X = H) and 1-methyl-2-methylthiobenziminazole (V; R = Me, X = H, Y = SMe) with maxima at 2850 and 2920 Å, and dissimilarity from that of 2 : 3-dihydro-1 : 3-dimethyl-2-thiobenziminazole (IV; R = Z = Me) which has a simple maximum at 3120 Å.


(I)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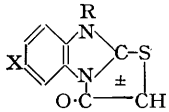
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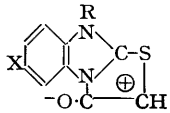
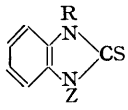
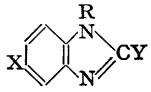
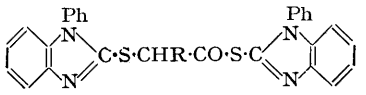

(*A*)

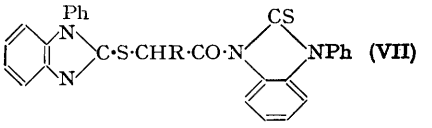
Like the corresponding quinoline derivatives the compounds (III) are stable, high-melting, and sparingly soluble in most organic solvents. Molecular-weight determinations were possible only on the anhydro-compound (III; R = Ph, X = H) and these indicated that the compound was unimolecular in camphor but was associated in acetic acid.

(IV) 

 (V)

The anhydro-compounds obtained from (I; R = Ph or Me, R′ = X = H) were studied in detail. Although stable to boiling water, the anhydro-compound (III; R = Ph, X = H) was rapidly reduced by zinc dust and ethanolic hydrochloric acid to the thiol (V; R = Ph, X = H, Y = SH). With ethanolic sulphuric acid, the compound (III; R = Ph, X = H) gave mainly an oil which could not be purified, together with some of the thiol (V; R = Ph, X = H, Y = SH). The oil reacted rapidly with aqueous alkali to give ethanol and the acid (I; R = Ph, R′ = H, X = H) and was presumed to be the ester (V; R = Ph, X = H, Y = $S\cdot CH_2\cdot CO_2Et$). Attempts to prepare the pure ester by unequivocal methods were, however, unsuccessful. With 50% aqueous sulphuric or hydrochloric acid, the anhydro-compound gave mainly the parent acid and a compound $C_{28}H_{20}ON_4S_2$. The latter was stable to acid but was hydrolysed by aqueous alkali to the thiol and the parent acid, which suggested that it had structure (VI or VII; R = H). With acetic anhydride it gave the 3-acetyl-2-thione (IV; R = Ph, Z = Ac) which had the

(VI) 

 (VII)

characteristic ultraviolet absorption in ethanol of a benziminazole-2-thione. The absorption of the compound $C_{28}H_{20}ON_4S_2$, however, included only the two maxima which are characteristic of the benziminazole ring and no maximum at 3120 Å, indicating that the compound had structure (VI; R = H).

With hot dilute nitric acid the anhydro-compound was rapidly oxidised to a mixture of 1-phenylbenziminazole (V; R = Ph, X = Y = H) and its 2-hydroxy-5-nitro-derivative

(V; R = Ph, X = NO_2, Y = OH), the latter being similarly obtained from the 5-nitro-anhydro-compound (III; R = Ph, X = NO_2). Under similar conditions the parent acid was unaffected whilst 2-hydroxy-1-phenylbenziminazole (V; R = Ph, X = H, Y = OH) gave the nitro-compound in high yield and 1-phenylbenziminazole-2-thiol gave 1-phenylbenziminazole only. It is suggested therefore that the compounds (V; R = Ph, X = H, Y = OH and SH) are the primary products of the action of dilute nitric acid on the anhydro-compound.

Aqueous-ethanolic sodium hydroxide or carbonate reacted with the anhydro-compound, giving equimolar proportions of 2-hydroxy-1-phenylbenziminazole and 1-phenylbenziminazole-2-thiol, which recrystallised as a eutectic.

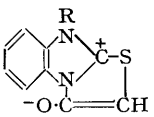
With excess of boiling benzylamine, the anhydro-compound gave the thiol and 2-benzylamino-1-phenylbenziminazole (V; R = Ph, X = H, Y = $NH{\cdot}CH_2Ph$), the latter also being obtained in high yield, under similar conditions, from the parent acid.

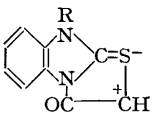
Corresponding products were obtained from the anhydro-compound (III; R = Me, X = H) by similar reactions, except that hydrolysis with aqueous sulphuric acid gave *only* the parent acid (I; R = Me, R′ = X = H), whilst ethanolic sodium hydroxide gave *only* the thiol (V; R = Me, X = H, Y = SH).

Unlike the quinoline derivatives the α-(benziminazolylthio)-propionic and -butyric acid (I; R = Me or Ph, R′ = Me or Et, X = H) did not give anhydro-compounds which could be isolated. With boiling acetic anhydride 3-acetyl-2-thiones (IV; R = Me or Ph, Z = Ac) were obtained, whilst solutions of the acids in cold pyridine and acetic anhydride developed a transitory yellow colour, suggestive of anhydro-compound formation, which was followed by an exothermic reaction, during which 0·5 mol. of carbon dioxide was evolved. A pure product, $C_{30}H_{24}ON_4S_2$, was, however, isolated from only one acid (I; R = Ph, R′ = Et, X = H) and, it is suggested, is the thiol-ester (VI; R = Et) because of its similarity in its chemical properties and ultraviolet absorption to the parent (VI; R = H).

An anhydro-compound was also prepared from (1-methyl-2-glyoxalinylthio)acetic acid. Like the corresponding benziminazole derivatives, this anhydro-compound, although colourless, had an ultraviolet absorption maximum not present in the parent acid. Molecular-weight determinations in water and acetic acid indicate that the anhydro-compound is bimolecular in these solvents.

The differences in chemical reactions of anhydro-(2-benziminazolylthio)acetic acids from those of the analogous quinoline compounds suggest certain differences in the contributions of individual dipolar forms of the two types of anhydro-compounds. Ease of attack by nucleophilic reagents on the compound (III; R = Ph, X = H) at position 2 of the benziminazole and at position 5 of the thiazole ring indicates powerful contributions from the forms (VIII and IX; R = Ph) whilst acid hydrolysis is favoured by a contribution from forms (X) and (XI). It will be noted that the sulphur atom in (IX) bears a negative charge and has a valency shell expanded to ten electrons. The formation of compounds


(VIII)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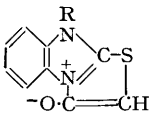
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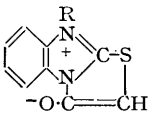
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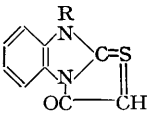
(XII)

(VI; R = H or Et) may result from the association of two molecules of the corresponding anhydro-compounds, indicated by molecular-weight determinations.

Like the quinoline analogues,[5] anhydro-(1-phenyl-2-benziminazolylthio)acetic acid in solution shows changes in the position of its longer-wavelength absorption maximum with changes in solvent polarity. It is, however, unlikely that this is due to a powerful contribution from form (XII) as the anhydro-compound shows no maximum indicative of a 2 : 3-dihydrobenziminazole-2-thione, but has the two maxima which are characteristic of the benziminazole ring.

[5] Knott, *J.*, 1955, 940.

Experimental

Absorption maxima were determined in ethanol.

Benziminazolo(2′ : 1′-2 : 3)*thiazolid*-4-*one* (II).—(2-Benziminazolylthio)acetic acid [1] (10 g.), pyridine (15 c.c.), and acetic anhydride (10 c.c.) were heated for 10 min. on a steam-bath. On cooling, a solid separated which, on recrystallisation from ethanol, gave the thiazolidone as pale yellow needles, m. p. 181° (5·8 g., 64%) (Found: N, 14·8; S, 16·7. Calc. for $C_9H_6ON_2S$: N, 14·7; S, 16·8%), $\lambda_{max.}$ 2380 (ε 18,900), 2820 (ε 10,300) and 2910 Å (ε 8900).

5-*Ethoxymethylenebenziminazolo*(2′ : 1′-2 : 3)*thiazolid*-4-*one*.—Benziminazolo(2′ : 1′-2 : 3)thiazolid-4-one (9·5 g.), ethyl orthoformate (12 c.c.), and acetic anhydride (15 c.c.) were boiled under reflux for 20 min. and evaporated *in vacuo* to leave a solid. Recrystallisation from ethanol gave the *ethoxymethylene compound* as yellow plates, m. p. 167—169° (5·6 g., 46%) (Found: C, 58·3; H, 3·8. $C_{12}H_{10}O_2N_2S$ requires C, 58·5; H, 4·05%).

5-(2 : 3-*Dihydro*-3-*methyl*-2-*benzothiazolylidenebenziminazolo*(2′ : 1′-2 : 3)*thiazolid*-4-*one*.—Benziminazolo(2′ : 1′-2 : 3)thiazolid-4-one (0·475 g.), 2-methylthiobenzothiazole methiodide (0·81 g.), ethanol (25 c.c.), and triethylamine (0·5 c.c.) were boiled for 10 min. Pale yellow crystals separated. Recrystallisation from dioxan gave the *compound* as pale yellow needles, m. p. 330° (0·68 g., 80%) (Found: N, 12·2; S, 19·0. $C_{17}H_{11}ON_3S_2$ requires N, 12·4; S, 19·0%).

The following were obtained similarly: 5-[2-(3-*Ethyl*-2 : 3-*dihydro*-2-*benzothiazolylidene*)-*ethylidene*]*benziminazolo*(2′ : 1′-2 : 3)*thiazolid*-4-*one* [from (II) and 2-2′-acetanilidovinylbenzothiazole ethiodide] from dioxan as red needles, m. p. 290° (64%) (Found: N, 10·9; S, 17·1. $C_{20}H_{15}ON_3S_2$ requires N, 11·1; S, 17·0%). The same compound was obtained (56%) from 5-ethoxymethylenebenziminazolo(2′ : 1′-2 : 3)thiazolid-4-one and 2-methylbenzthiazole ethiodide. The 5-[2-(2 : 3-*dihydro*-3-*methyl*-2-*benzoxazolylidene*)*ethylidene*] *analogue* [from (II) and 2-2′-ethylthiovinylbenzoxazole metho-*p*-toluenesulphonate] from dioxan as orange needles, m. p. 318° (60%) (Found: N, 12·0; S, 8·9. $C_{19}H_{13}O_2N_3S$ requires N, 12·15; S, 9·2%). The 5-[2-(1 : 3 : 3-*trimethyl*-2-*indolinylidene*)*ethylidene*] *analogue* [from (II) and 2-2′-acetanilidovinyl-3 : 3-dimethylindolenine methiodide] as orange needles (from methanol), m. p. 252° (42%) (Found: N, 11·4; S, 8·6. $C_{22}H_{19}ON_3S$ requires N, 11·3; S, 8·6%). The 5-[2-(1 : 4-*dihydro*-1-*methyl*-4-*quinolinylidene*)*ethylidene*] *analogue* [from (II) and 4-2′-ethylvinylquinoline methiodide] as dark blue plates (from methanol), m. p. 295° (57%) (Found: N, 11·7; S, 9·1. $C_{21}H_{15}ON_3S$ requires N, 11·8; S, 8·95%). The 5-[2-(1 : 2-*dihydro*-1-*methyl*-2-*quinolinylidene*)*ethylidene*] *analogue* [from (II) and 2-2′-ethylthiovinylquinoline methiodide] as dark red microscopic needles (from ethanol), m. p. 339° (67%) (Found: N, 11·95; S, 8·75. $C_{21}H_{15}ON_3S$ requires N, 11·8; S, 8·95%). The 5-*benzylidene*, pale yellow plates (from benzene), m. p. 219° (25%) (Found: N, 10·2. $C_{16}H_{10}ON_2S$ requires N, 10·1%), and the 5-p-*dimethylaminobenzylidene analogue*, orange needles (from ethanol), m. p. 269° (45%) (Found: N, 13·1. $C_{18}H_{15}ON_3S$ requires N, 13·1%).

2-*Hydroxy*-1-*phenylbenziminazole*.—2-Aminodiphenylamine (9·2 g.) and sodium cyanate (3·25 g.) in boiling ethanol (50 c.c.) and 10N-hydrochloric acid (5 c.c.) was boiled for 2 hr., water (200 c.c.) was added, and the precipitated solid was recrystallised from aqueous ethanol, to give 2-*ureidodiphenylamine* as colourless plates, m. p. 157° (6·1 g., 53%) (Found: C, 68·5; H, 5·5. $C_{13}H_{13}ON_3$ requires C, 68·7; H, 5·7%). The urea (5 g.) was heated for 1 hr. at 160°, ammonia being evolved. The solid which was obtained recrystallised from ethanol to give 2-*hydroxy*-1-*phenylbenziminazole* as colourless plates, m. p. 204° (2·8 g., 50%) (Found: C, 74·15; H, 4·45; N, 13·1. $C_{13}H_{10}ON_2$ requires C, 74·25; H, 4·7; N, 13·3%).

2-*Hydroxy*-1-*methylbenziminazole*.—By a similar process N-*methyl*-o-*ureidoaniline* (?) was prepared from *N*-methyl-*o*-phenylenediamine and was obtained from aqueous ethanol as plates, m. p. 180° (52%) (Found: C, 58·3; H, 6·7. $C_8H_{11}ON_3$ requires C, 58·2; H, 6·65%). Heating converted it into 2-hydroxy-1-methylbenziminazole, plates (from water), m. p. 188° (70%) (Found: C, 65·0; H, 5·3. Calc. for $C_8H_8ON_2$: C, 64·9; H, 5·4%), identical with the compound prepared from *N*-methyl-*o*-phenylenediamine and carbonyl chloride.[6]

1-*Methylbenziminazole*-2-*thiol*.—*N*-Methyl-*o*-nitroaniline (56·8 g.) was dissolved in ethanol (150 c.c.) and 20% aqueous sodium hydroxide (31·5 c.c.), and zinc dust (100 g.) added in portions during 20 min. The mixture was boiled until it became colourless, then filtered hot, and the solid washed with ethanol. Carbon disulphide (48 c.c.) was added to the filtrate and the solution boiled for 4 hr. The solid which separated on cooling recrystallised from ethanol, to give 1-*methylbenziminazole*-2-*thiol* as colourless needles, m. p. 195° (50 g., 83%) (Found: C, 58·4; H,

[6] Pinnow and Sämann, *Ber.*, 1899, **32**, 2190.

4·9; N, 17·2. $C_8H_8N_2S$ requires C, 58·55; H, 4·9; N, 17·5%). Benziminazole-2-thiol (87%) and 1-*phenylbenziminazole-2-thiol*, colourless needles, m. p. 194° (70%), from ethanol (Found: C, 68·65; H, 4·40; N, 12·4. $C_{13}H_{10}N_2S$ requires C, 69·0; H, 4·45; N, 12·4%), were obtained similarly from carbon disulphide with *o*-phenylenediamine and 2-aminodiphenylamine respectively.

1-*Methyl-2-methylthiobenziminazole.*—1-Methylbenziminazole-2-thiol (8·2 g.) in N-sodium hydroxide (50 c.c.) was shaken with methyl iodide (3·2 c.c.) for 1 hr., then extracted with chloroform (3 × 50 c.c.). The chloroform was removed and the residue was distilled, to give 1-*methyl-2-methylthiobenziminazole* as colourless plates, m. p. 56°, b. p. 112—115°/0·8 mm. (6·5 g., 73%) (Found: N, 15·7; S, 18·0. $C_9H_{10}N_2S$ requires N, 15·7; S, 18·0%), $\lambda_{max.}$ 2530 (ε 6500), 2850 (ε 13,600), and 2920 Å (ε 14,200).

1 : 3-*Dimethyl-2-methylthiobenziminazolium iodide* was obtained as colourless needles (from ethanol), m. p. 152° (Found: I, 39·7. $C_{10}H_{13}N_2SI$ requires I, 39·7%), from the above compound by 2 hours' heating with methyl iodide.

2 : 3-*Dihydro*-1 : 3-*dimethyl-2-thiobenziminazole.*—The above methiodide (1·5 g.) and pyridine (5 c.c.) were boiled under reflux for 2 hr. The solution was poured into water, and the precipitated solid was recrystallised from ethanol, to give the *thione* as colourless needles, m. p. 153—154° (0·5 g., 63%) (Found: N, 15·55; S, 18·0. $C_9H_{10}N_2S$ requires N, 15·7; S, 18·0%), $\lambda_{max.}$ 2540 (ε 18,100) and 3090 Å (ε 29,500).

1-*Methyl-5-nitrobenziminazole-2-thiol.*—2-Methylamino-5-nitroaniline (28 g.), potassium hydroxide (9·8 g.), 80% ethanol (600 c.c.), and carbon disulphide (28 c.c.) were boiled under reflux for 20 hr. After dilution with water (1 l.), the ethanol was removed by distillation and the hot residue added to N-hydrochloric acid (280 c.c.). This precipitated a solid which was recrystallized from acetic acid to give 1-*methyl-5-nitrobenziminazole-2-thiol* as yellow needles, m. p. 304—305° (decomp.) (30·2 g., 93%) (Found: C, 45·6; H, 3·4. $C_8H_7O_2N_3S$ requires C, 45·8; H, 3·35%).

5-*Nitro*-1-*phenylbenziminazole-2-thiol* was obtained by a similar process from ethanol as yellow needles, m. p. 282° (69%) (Found: C, 57·4; H, 3·3. $C_{13}H_9O_2N_3S$ requires C, 57·5; H, 3·3%).

(1-*Methyl-2-glyoxalinylthio*)*acetic Acid.*—1-Methylglyoxaline-2-thiol (5·7 g.), chloroacetic acid (4·8 g.), and water (20 ml.) were boiled under reflux for 1 hr. N-Sodium hydroxide (50 ml.) was added, the solution evaporated to dryness, and the residue extracted with chloroform (4 × 25 ml.). The chloroform was removed to give an oily *acid* which rapidly solidified and recrystallised from benzene–chloroform as colourless needles, m. p. 85° (7·1 g., 89%) (Found: S, 18·7. $C_6H_8O_2N_2S$ requires S, 18·6%), $\lambda_{max.}$ 2550 Å (20,600).

(2-*Benziminazolylthio*)*acetic Acids* (I).—The following exemplifies the procedure: 1-Methylbenziminazole-2-thiol (16·4 g.) in 10% aqueous sodium hydroxide (40 c.c.), and chloroacetic acid (9·5 g.) in 10% aqueous sodium hydroxide (40 c.c.), were heated together for 2 hr. on the steam-bath. The hot solution was filtered and acidified with concentrated hydrochloric acid (10 c.c.), and the precipitated (1-*methyl-2-benziminazolylthio*)*acetic acid* recrystallised from aqueous ethanol as colourless needles, m. p. 190° (16·5 g., 75%) (Found: C, 53·95; H, 4·2. $C_{10}H_{10}O_2N_2S$ requires C, 54·05; H, 4·5%), $\lambda_{max.}$ 2830 (ε 13,400) and 2910 Å (ε 13,900).

Analogous *products* are tabulated.

(2-*Benziminazolylthio*)*acetic acids* (I).

				Yield	Found (%)			Required (%)	
R	R′	X	M. p.	(%)	C	H	Formula	C	H
H [e]	H	H	211° [a]	67	52·0	3·8	Everett [1]		
Ph	H	H	176 [a]	60	62·9	4·45 [c]	$C_{15}H_{12}O_2N_2S$	63·4	4·25
Ph [f]	Me	H	97 [a]	39	61·45	5·0	$C_{16}H_{14}O_2N_2S$	61·50	4·8
Ph	Et	H	87 [a]	32	[d]		$C_{17}H_{16}O_2N_2S$	—	—
Ph	H	NO_2	234—235 [b]	67	54·6	3·6	$C_{15}H_{11}O_4N_3S$	54·7	3·65
Me	H	NO_2	235 [b]	30	44·85	3·1	$C_{10}H_9O_4N_3S$	45·0	3·35

[a] Colourless needles from ethanol. [b] Yellow needles from acetic acid. [c] Found: N, 9·85; S, 11·05. Required: N, 9·85; S, 11·25%. [d] Found: S, 9·65. Required: S, 9·55%. [e] $\lambda_{max.}$ 2480 (ε 6200), 2830 (ε 13,000) and 2910 Å (ε 12,900). [f] $\lambda_{max.}$ 2850 (ε 12,200) and 2930 Å (ε 12,500).

α-(1-*Methyl-2-benziminazolylthio*)*butyric Acid.*—α-Bromobutyric acid (9·3 g.) and 1-methylbenziminazole-2-thiol (9·2 g.) were boiled in water (50 c.c.) for 6 hr. After cooling, 40% aqueous

sodium hydroxide (5·5 c.c.) was added to precipitate crystals, which, recrystallised from aqueous ethanol, gave the *acid* as colourless needles, m. p. 132° (7·9 g., 48%) (Found: S, 12·6. $C_{12}H_{12}O_2N_2S$ requires S, 12·7%).

α-(1-*Methyl*-2-*benziminazolylthio*)*propionic acid* was obtained by a similar process as colourless needles (from water), m. p. 131° (61%) (Found: S, 13·5. $C_{11}H_{10}O_2N_2S$ requires S, 13·6%).

Anhydro-compound from (1-*Methyl*-2-*glyoxalinylthio*)*acetic Acid.*—The acid (6·0 g.), pyridine (18·0 ml.), and acetic anhydride (6·0 ml.) were warmed on a steam-bath for 5 min. Solid rapidly separated and, after cooling, was filtered off, washed with ether, and recrystallised from water, to give the pure *anhydro-compound* as colourless needles, m. p. 201° (4·25 g., 80%) [Found: C, 46·8; H, 3·8; S, 20·4; *M* (ebullioscopic in H_2O), 249, (in AcOH), 294. $C_6H_6ON_2S$ requires C, 46·7; H, 3·9; S, 20·7%; *M*, 154], $\lambda_{max.}$ in EtOH 2380 (ε 3400) and 3340 (ε 9900), in C_6H_6 3350 (ε 10,900) and in aqueous pyridine (1 : 1) 3370 Å (ε 36,700).

Anhydro-compound from (1-*Methyl*-2-*benziminazolylthio*)*acetic Acid.*—The acid (5 g.) was dissolved in warm pyridine (15 c.c.), and acetic anhydride (15 c.c.) was added, crystals being precipitated. After 15 min., the *anhydro-compound* was filtered off, washed with acetone, and dried, to give pale yellow needles, m. p. 255° (3·6 g., 78%), insoluble in all the usual solvents (Found: C, 59·05; H, 4·15; N, 13·85; S, 15·15. $C_{10}H_8ON_2S$ requires C, 58·8; H, 3·95; N, 13·7; S, 15·7%).

Anhydro-compound from (1-*Phenyl*-2-*benziminazolylthio*)*acetic Acid.*—The *anhydro-compound* was obtained (*a*) by a similar process to that above, as pale yellow needles (from a large volume of xylene), m. p. 222° (44%), or (*b*) (64%) by boiling the acid with twice its weight of acetic anhydride [Found: C, 67·6; H, 3·9; N, 10·0; S, 11·7; *M* (Rast), 269, (ebullioscopic in AcOH), 1200 ± 100. $C_{15}H_{10}ON_2S$ requires C, 67·65; H, 3·8; N, 10·5; S, 12·0%; *M*, 266], $\lambda_{max.}$ in EtOH 2550 (ε 12,000), 2860 (ε 7900), 2930 (ε 7800), and 3500 (ε 9700), in dioxan 2700 (ε 11,500), 2870 (ε 7500), 2940 (ε 7500), and 3600 (ε 7500), in C_6H_6 2880 (ε 8100), 2950 (ε 8200), and 3655 (ε 6950), and in aqueous pyridine (1 : 1) 2920 (ε 6850) and 3520 Å (ε 10,500). By similar reactions *anhydro*-(1-*methyl*-5-*nitro*-2-*benziminazolylthio*)*acetic acid* as orange needles, m. p. 238° (decomp.) (81%) (Found: C, 48·1; H, 2·9. $C_{10}H_7O_3N_3S$ requires C, 48·3; H, 2·8%), and *anhydro*-(5-*nitro*-1-*phenyl*-2-*benziminazolylthio*)*acetic acid* as yellow needles, m. p. 221° (62%) (Found: C, 57·75; H, 2·8. $C_{15}H_9O_3N_3S$ requires C, 57·8; H, 2·9%), were also prepared.

Action of Aqueous Sulphuric Acid on Anhydro-compound from (1-*Phenyl*-2-*benziminazolylthio*)*acetic Acid.*—The anhydro-compound (5·0 g.) was heated at 100° with 50% aqueous sulphuric acid (20 c.c.), the solid dissolving with evolution of carbon dioxide. Water (100 c.c.) was added, the mixture extracted with benzene (2 × 100 c.c.), and the benzene solution extracted successively with (*a*) 2N-sodium carbonate which gave, on acidification, (1-phenyl-2-benziminazolylthio)acetic acid (0·87 g., 18%), and (*b*) N-sodium hydroxide, from which 1-phenylbenziminazole-2-thiol (0·03 g.) was obtained. Removal of benzene gave a sticky solid which crystallised (2·6 g., 56%) on addition of ethanol. Recrystallisation from benzene–ethanol gave 1-*phenyl*-2-*benziminazolyl* α-(1-*phenyl*-2-*benziminazolylthio*)*thiolacetate* (VI; R = H) as colourless plates which became pink in air, m. p. 176° (2·1 g.) (Found: C, 68·7; H, 4·15; N, 10·8; S, 12·8. $C_{28}H_{20}ON_4S_2$ requires C, 68·4; H, 4·05; N, 11·4; S, 12·95%), $\lambda_{max.}$ 2500 (ε 24,800), 2850 (ε 21,800), and 2920 Å (ε 21,500). The compound (2·0 g.), when boiled for 1 hr. with 10% ethanolic sodium hydroxide, gave 1-phenylbenziminazole-2-thiol (0·7 g., 76%) and (1-phenyl-2-benziminazolylthio)acetic acid (1·0 g., 86%).

Under similar conditions, the anhydro-compounds from (1-methyl- and 5-nitro-1-phenyl-2-benziminazolylthio)acetic acid gave the parent acids only, in yields of 87% and 92% respectively.

Action of Nitric Acid on Anhydro-compound from (1-*Phenyl*-2-*benziminazolylthio*)*acetic Acid.*—The anhydro-compound (2·5 g.), water (80 c.c.), and nitric acid (*d* 1·41; 10 c.c.) were boiled under reflux for 1 hr. Nitrous fumes were evolved, and the resulting solution was cooled to give a crystalline precipitate which was filtered off. Recrystallisation from aqueous ethanol gave 2-*hydroxy*-5-*nitro*-1-*phenylbenziminazole* as pale yellow plates, m. p. 239—240° (1·2 g., 47%) (Found: C, 60·95; H, 3·6. $C_{13}H_9O_3N_3$ requires C, 61·2; H, 3·55%), identical with the compound obtained (45%) similarly from anhydro-(5-nitro-1-phenyl-2-benziminazolylthio)-acetic acid. The original acid filtrate was basified, to give an oil which gave 1-*phenylbenziminazole picrate* as yellow plates (from ethanol), m. p. 182° (1·6 g., 41%) (Found: N, 16·4. $C_{13}H_{10}N_2,C_6H_3O_7N_3$ requires N, 16·55%), identical with the picrate obtained from 1-phenylbenziminazole.[7]

By a similar process the anhydro-compound from (1-methyl-2-benziminazolylthio)acetic acid

[7] Phillips, *J.*, 1929, 2823.

gave 1-methylbenziminazole picrate, m. p. and mixed m. p. 244° (28%), and 2-hydroxy-1-methyl-5-nitrobenziminazole as yellow needles (from acetic acid), m. p. 302° (31%) (Found : C, 49·6; H, 3·7. Calc. for $C_8H_7O_3N_3$: C, 49·7; H, 3·65%), identical with the compound described by Romburgh and Huyser [8] and that obtained (40%) from anhydro-(1-methyl-5-nitro-2-benziminazolylthio)acetic acid and dilute nitric acid.

By similar reactions with dilute nitric acid, (*a*) 1-phenylbenziminazole-2-thiol gave 1-phenylbenziminazole as picrate (80%), (*b*) 2-hydroxy-1-phenylbenziminazole gave 2-hydroxy-5-nitro-1-phenylbenziminazole (63%), and (*c*) (1-phenyl-2-benziminazolylthio)acetic acid was recovered (83%).

Action of Alkali on the Anhydro-compound from (1-*Phenyl*-2-*benziminazolylthio*)*acetic Acid.*—The anhydro-compound (2·5 g.) was boiled for 1 hr. with 40% aqueous sodium hydroxide (10 c.c.) and ethanol (20 c.c.). Water (200 c.c.) was added, the ethanol removed, and the solution saturated with carbon dioxide to precipitate a solid which recrystallised from aqueous ethanol as colourless needles, m. p. 161° (1·8 g., 88%) [Found : C, 71·85; H, 4·95; N, 13·55; S, 7·4; *M* (Rast), 228. Calc. for $C_{13}H_{10}N_2S + C_{13}H_{10}ON_2$: C, 71·55; H, 4·65; N, 12·85; S, 7·35%; *M* (average of hydroxy- and mercapto-compounds), 218]. This substance was identical with the equimolar eutectic from 2-hydroxy-1-phenylbenziminazole and 1-phenylbenziminazole-2-thiol either by dissolution in alkali and reprecipitation with acid, or by recrystallisation from aqueous ethanol or benzene–light petroleum. The eutectic mixture was also obtained (81%) together with the parent acid (3%) by the prolonged action of boiling 10% aqueous sodium carbonate on the anhydro-compound.

By a similar process, anhydro-(1-methyl-2-benziminazolylthio)acetic acid gave 1-methylbenziminazole-2-thiol only (68%).

Reduction of Anhydro-compound from (1-*Phenyl*-2-*benziminazolylthio*)*acetic Acid.*—Granulated zinc (5·0 g.) was added to the anhydro-compound (5·0 g.), ethanol (50 c.c.), and concentrated hydrochloric acid (20 c.c.). A vigorous reaction took place with evolution of hydrogen sulphide, methanethiol, and carbon dioxide. The solution obtained was diluted with water to give 1-phenylbenziminazole-2-thiol (3·1 g., 75%).

Action of Benzylamine on the Anhydro-compound from (1-*Phenyl*-2-*benziminazolylthio*)*acetic Acid.*—The anhydro-compound (5·5 g.) and benzylamine (10 g.) were boiled under reflux for 1 hr. The solid dissolved, and hydrogen sulphide was evolved. The yellow solution, diluted with water (100 c.c.), gave an oil which was dissolved in ether and extracted with 2% aqueous sodium hydroxide. Acidification of the alkaline extracts gave benziminazole-2-thiol (2·2 g., 47%), whilst evaporation of the ether gave a brown solid (2·5 g., 45%) which, recrystallised from ethanol, gave 2-*benzylamino*-1-*phenylbenziminazole*, colourless needles, m. p. 145° (1·49 g., 25%) (Found : C, 80·35; H, 5·75; N, 13·9. $C_{20}H_{17}N_3$ requires C, 80·3; H, 5·7; N, 14·0%). Benzylamine, with the parent acid under similar conditions, gave 2-benzylamino-1-phenylbenziminazole (77%), but 1-phenylbenziminazole-2-thiol was recovered (88%) after 2 hours' boiling with excess of benzylamine.

Action of Acetic Anhydride on α-(1-*Phenyl*-2-*benziminazolylthio*)*butyric Acid.*—The acid (2·0 g.) and acetic anhydride (10 c.c.) were boiled for 1 hr. under reflux. The anhydride was removed *in vacuo* and the residue was recrystallised from acetone, to give 3-*acetyl*-2 : 3-*dihydro*-1-*phenyl*-2-*thiobenziminazole* as colourless needles, m. p. 191° (0·7 g., 41%) (Found : C, 67·15; H, 4·5; S, 11·75; N, 10·1. $C_{15}H_{12}ON_2S$ requires C, 67·2; H, 4·5; S, 11·95; N, 10·4%), $\lambda_{max.}$ 3120 Å (ε 20,800). The same compound was obtained (78% and 50%) from acetic anhydride and 1-phenylbenziminazole-2-thiol or α-(1-phenyl-2-benziminazolylthio)propionic acid respectively. 3-*Acetyl*-2 : 3-*dihydro*-1-*methyl*-2-*thiobenziminazole* was obtained (72%, 15%, and 28%) similarly from acetic anhydride and 1-methylbenziminazole-2-thiol, α-(1-methyl-2-benziminazolylthio)propionic acid, or α-(1-methyl-2-benziminazolylthio)butyric acid. It recrystallised from acetone as colourless needles, m. p. 144° (Found : C, 58·0; H, 4·8; S, 15·6. $C_{10}H_{10}ON_2S$ requires C, 58·1; H, 4·85; S, 15·5%), $\lambda_{max.}$ 2410 (ε 17,100) and 3100 Å (ε 21,500).

Action of Acetic Anhydride and Pyridine on α-(1-*Phenyl*-2-*benziminazolylthio*)*butyric Acid.*—The acid (5·0 g.) was dissolved in pyridine (6 c.c.), and acetic anhydride (5 c.c.) added, affording a yellow solution. Carbon dioxide was slowly evolved (170 c.c.) whilst the temperature rose to 41·5° and the colour gradually disappeared. The solution was cooled, to give colourless crystals (3·07 g., m. p. 145°) which gave 1-*phenyl*-2-*benziminazolyl* α-(1-*phenyl*-2-*benziminazolylthio*)*thiolbutyrate* (VI; R = Et) from benzene–light petroleum as colourless plates, m. p. 147° [Found :

[8] Romburgh and Huyser, *Verslag. k. Akad. Wetenschap. Amsterdam, Afd. Natuurk.*, 1926, **35**, 665. *Chem. Abs.*, 1927, **21**, 382.

C, 69·1; H, 4·45; S, 12·45; *M* (ebullioscopic in C_6H_6), 507. $C_{30}H_{24}ON_4S$ requires C, 69·2; H, 4·6; S, 12·3%; *M*, 520], $\lambda_{max.}$ 2420 (ε 22,000), 2850 (ε 19,400), and 2920 Å (ε 18,600). When boiled with 10% alcoholic sodium hydroxide (**5** c.c.) it (1 g.) gave α-(1-phenyl-2-benziminazolylthio)butyric acid (0·42 g., 70%), and 1-phenylbenziminazole-2-thiol (0·37 g., 85%); boiling acetic anhydride converted it into 3-acetyl-2 : 3-dihydro-1-phenyl-2-thiobenziminazole (68%).

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