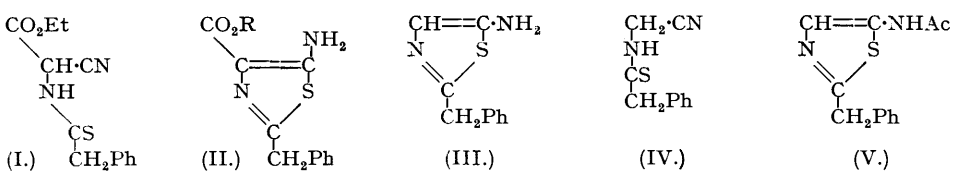
318. *Studies in the Azole Series. Part I. A Novel Route to 5-Aminothiazoles.*

By A. H. Cook, Sir Ian Heilbron, and A. L. Levy.

Dithiophenylacetic acid reacts with aminoacetonitrile or ethyl aminocyanoacetate to give 5-*amino*- and 5-*amino*-4-*carbethoxy*-2-*benzylthiazole*, (III) and (II; R = Et), respectively. The behaviour of these bases towards acylating agents, nitrous acid, and in the case of the first-mentioned towards diazonium salts, nitrating agents, etc., is described. This seems a general synthesis of the hitherto almost unknown class of 5-aminothiazoles, 5-*amino*-4-*phenyl*- and 5-*amino*-4-*carbethoxy-thiazole* being obtained analogously.

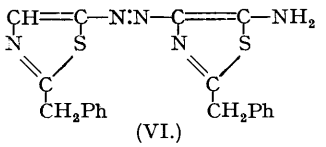
In connection with the study of penicillin (unpublished work) the reaction between sodium or methyl dithiophenylacetate and ethyl aminocyanoacetate was examined. The product was at first thought to be ethyl phenylthionacetamidocyanoacetate (I) but subsequent investigation showed that it was a base which could be better formulated as 5-*amino*-4-*carbethoxy*-2-*benzylthiazole* (II; R = Et). It formed a stable *hydrochloride* and on hydrolysis gave the corresponding *acid* (II; R = H). Hexoylation yielded 5-*hexoamido*-4-*carbethoxy*-2-*benzylthiazole* which still exhibited basic properties. Similarly, aminoacetonitrile and sodium dithiophenylacetate afforded an excellent yield of a base which by analogy is formulated as 5-*amino*-2-*benzylthiazole* (III). Its light absorption is compatible with this formulation and is



very similar to that of the corresponding 4-carbethoxy-compound above. It seems that *phenylthionacetamidoacetonitrile* (IV) occurs as an intermediate and cyclises on warming, for a small amount of an alkali-soluble isomeride was isolated from the crude aminothiazole. The isomeride passed into the aminothiazole on being kept with hydrogen chloride in organic solvents and appears therefore to be the acyclic thioamide. This facile formation of 5-aminothiazoles is

of interest as they have been so far almost unknown in the literature. Weidel and Niemilowicz (*Monatsh.*, 1895, **16**, 721) described some degradation products of uric acid which are possibly derivatives of 5-aminothiazole. The only other noteworthy reference is to a series of derivatives of 5-amino-2-thiocarboxyamidothiazole (" chrysean ") originating in the interaction of hydrocyanic acid and hydrogen sulphide (see Beilstein's " Handbuch ", Vol. 27, 334; Arnold and Scaife, *J.*, 1944, 103). Jensen and Hansen (*Dansk Tids. Farm.*, 1943, **17**, 189) and Ganapathi and Venkataraman (*Proc. Indian Acad. Sci.*, 1945, **22***A*, 343) have recently prepared some 5-aminothiazoles by orthodox reactions but the methods are not entirely satisfactory in scope and yield.

5-Amino-2-benzylthiazole formed a *hydrochloride* and on acetylation gave 5-*acetamido*-2-*benzylthiazole* (V) which had marked basic properties, and formed a *hydrochloride* and a *methiodide*; the latter clearly contained a " reactive " methylene group (in the adjacent benzyl substituent) and developed an intense cyanine-like colour on being heated with ethyl orthoformate under appropriate conditions. The 5-*acetylsulphanilamido*- and 5-*sulphanilamido*-compounds were also prepared. The sulphanilamide inhibited the growth of *Staph. aureus* at a limiting dilution of 1 : 50,000, but the inhibition was not complete, and even at 1 : 5000 abnormal agglutinated clumps of bacterial growth were observed. When (III) was treated with 1 mol. of nitrous acid there was some evolution of hydrogen sulphide and rapid appearance of a deep red-brown precipitate from which two *products* were isolated, $C_{20}H_{17}N_5S_2$ (A) and $C_{20}H_{17}ON_5S$ (B). The former formed brilliant crystals with a copper-like lustre and gave deep red solutions. The fact that (II) failed to behave similarly with nitrous acid supports structure (VI) rather than (VII) (cf. formation of aminoazobenzene). Formulation (VI), representing a diazonium salt coupling with a second molecule of amine in the 4-position, is perhaps novel to thiazole chemistry but strictly comparable with *ortho*-coupling of aromatic amines; it is supported by the fact that (V) couples with diazonium salts whereas (II) does not share this ability.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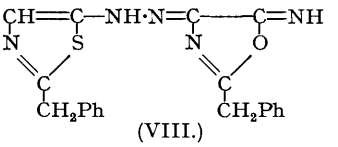
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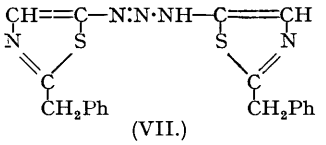
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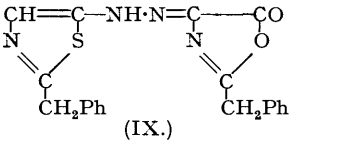
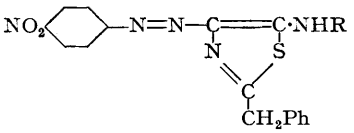
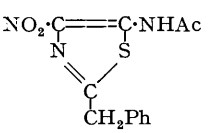

(IX.)

Product (B) formally contained a sulphur atom of (A) replaced by oxygen, but in view of its paler colour and altered light absorption it is tentatively formulated as the imino-compound (VIII). This formulation is in keeping with its behaviour on hydrolysis with cold dilute hydrochloric acid, which gave a compound $C_{20}H_{16}O_2N_4S$, obviously the oxazolone (IX).

It was mentioned above that (III) coupled with diazonium salts, and in illustration the orange-scarlet *azo*-compound (X; R = H) was prepared. The acetamido-compound (V) likewise coupled to give (X; R = Ac). Both azo-compounds were remarkable in giving intense violet colorations with caustic alkalis. When (V) was treated with nitrosyl chloride in acetic acid in an attempt to obtain the *N*-nitroso-derivative (" diazonium acetate ") the sole product isolated was a nitro-compound which, in view of the ready reactivity of the 4-position, is obviously 4-*nitro*-5-*acetamido*-2-*benzylthiazole* (XI). In this connection it may be noted that nitrous acid not infrequently acts as a nitrating agent (*e.g.*, Hodgson, *J.*, 1932, 1812). Compound (XI) was also produced by direct nitration of (IV) with a nitric–sulphuric acid mixture, and by treatment of its *nitrate* with sulphuric acid in acetic acid solution.


(X.)


(XI.)

Similar syntheses have been carried out by employing sodium dithioformate in place of dithiophenylacetate. As the reaction with aminoacetonitrile is complex, and in view of its special interest, it will form the subject of a separate communication. With ethyl aminocyano-

acetate reaction was facile, giving 5-*amino*-4-*carbethoxythiazole* identical with the product obtained by heating the analogous 2-mercaptothiazole (see following paper) with Raney nickel. In the same way α-aminobenzyl cyanide and sodium dithioformate afforded 5-*amino*-4-*phenylthiazole*, characterised as its *hydrochloride* and *acetyl* derivative, and likewise identified with the base obtained by desulphurising the analogous 2-mercaptothiazole.

It is noteworthy that all the ring-syntheses described here take place at room temperature, several of them in aqueous neutral solution.

Light-absorption data on the aminothiazole derivatives are recorded on p. 1598 in tabular form (cf. table in Part II).

Methyl ethylxanthate failed to exhibit the reactivity of the above dithio-acid derivatives towards α-amino-nitriles. On the other hand, it behaved as a " thioacylating " agent towards strong bases; *e.g.*, it gives with morpholine N-*monothiocarbethoxymorpholine*.

Experimental.

(*a*) Crude ethyl aminocyanoacetate (3 g.), prepared by reducing ethyl nitrosocyanoacetate with amalgamated aluminium, was allowed to stand with methyl dithiophenylacetate (4 g.). Heat and thiol were evolved spontaneously and after a few minutes the mixture set to a mass of yellow needles. Treatment with a small quantity of ether gave almost pure 5-*amino*-4-*carbethoxy*-2-*benzylthiazole* (II; R = Et) (3·6 g., a further 0·8 g. being recovered from the ethereal residues). It separated from ethanol in long colourless needles, m. p. 157° (Found: C, 59·8; H, 5·6; N, 10·9. $C_{13}H_{14}O_2N_2S$ requires C, 59·5; H, 5·4; N, 10·7%).

(*b*) Ethyl aminocyanoacetate (5 g.) was shaken overnight in ether (50 c.c.) with sodium dithiophenylacetate (1 equiv.) in water (20 c.c.). Evaporation of the dried ethereal solution gave the free base, 5-amino-4-carbethoxy-2-benzylthiazole, in poor yield, m. p. 156°. The thiazole (780 mg.) in dioxan (3 c.c.) and water (7 c.c.) was kept with 0·51N-sodium hydroxide (6 c.c.) overnight and then heated on the steam-bath for two hours. The filtrate was acidified with dilute hydrochloric acid, and the acid recrystallised from ethanol. 5-*Amino*-4-*carboxy*-2-*benzylthiazole* separated in irregular prisms, m. p. 169° with violent evolution of gas (on slow heating) (Found: C, 56·5; H, 4·6; N, 12·0. $C_{11}H_{10}O_2N_2S$ requires C, 56·4; H, 4·3; N, 12·0%). Small quantities of this acid were obtained as a by-product during the preparation of the ester *via* sodium dithiophenylacetate.

The ester-thiazole (II) (0·52 g.) suspended in ethanol (5 c.c.) was treated with hydrogen chloride at − 10°. After 12 hours at 20° the solution was evaporated in a vacuum, and the solid, m. p. 180°, washed with ether and crystallised from ethanol–ether. 5-*Amino*-4-*carbethoxy*-2-*benzylthiazole hydrochloride* separated in rectangular plates, m. p. 180° (Found: C, 52·3; 52·4; H, 5·5, 5·2; N, 9·7. $C_{13}H_{15}O_2N_2ClS$ requires C, 52·5; H, 5·1; N, 9·4%). The ester-thiazole (II) (1 g.), *n*-hexoyl chloride (0·7 g.), and pyridine (20 c.c.) were heated together at 80—90° for 2 hours, and the mixture evaporated in a vacuum. The residue was extracted with ether but the base remained oily on evaporation of solvent. Addition of ethereal hydrogen chloride gave a solid. 5-n-*Hexoamido*-4-*carbethoxy*-2-*benzylthiazole hydrochloride* crystallised from chloroform–light petroleum in clumps of feathery needles, m. p. 110°, which lost hydrogen chloride on heating to 56° in a vacuum and were dried at room temperature over phosphoric oxide (Found: C, 57·5; H, 6·7. $C_{19}H_{25}O_3N_2ClS$ requires C, 57·5; H, 6·3%).

Aminoacetonitrile sulphate (135 g.) in water (200 c.c.) was neutralised (brilliant-yellow) with potassium hydroxide (98 g.) in water (230 c.c.) in the cold. A neutral solution of potassium dithiophenylacetate (1 equiv.) in water (510 c.c.) was added with ether (1500 c.c.), the solution again brought to neutrality, and the whole shaken overnight. On separation of the ethereal layer and removal of solvent, the residual oil solidified (yield, 165 g., 98%). Crude 5-*amino*-2-*benzylthiazole* (III) crystallised from ether–light petroleum or chloroform–light petroleum to form colourless needles, m. p. 87° (130 g.), which darkened on exposure to light (Found: C, 63·5; H, 5·5; N, 14·5. $C_{10}H_{10}N_2S$ requires C, 63·2; H, 5·3; N, 14·7%). The crude product, m. p. 83° (1·0 g.), was stood for 3 days in a mixture of dioxan (5·0 c.c.) and water (8·0 c.c.), and the product (0·2 g.) which separated recrystallised from ethanol to give colourless needles, m. p. 161° (decomp.), of *phenylthionacetamidoacetonitrile* (IV) (Found: C, 63·0; H, 5·2; N, 14·8. $C_{10}H_{10}N_2S$ requires C, 63·2; H, 5·3; N, 14·7%). The compound was soluble in aqueous-alcoholic potash and was transformed by ethanolic hydrogen chloride into 5-amino-2-benzylthiazole hydrochloride, m. p. and mixed m. p. 195° (decomp.).

The base could be conveniently converted into its hydrochloride by several methods; *e.g.*, the base was covered with 3 vols. of warm ethanol and a little water and treated with a little ethanolic hydrogen chloride. This technique was only necessary when starting with the hydrochloride, which was insoluble in dry ethanol, but soluble in the wet solvent. The *hydrochloride* separated and could be recrystallised in the same manner, forming rectangular tablets, m. p. 194° (decomp.) (Found: C, 53·0; H, 4·9; N, 12·4. $C_{10}H_{11}N_2ClS$ requires C, 53·0; H, 4·9; N, 12·4%).

5-Amino-2-benzylthiazole (1 g.) was treated with acetic anhydride (1 c.c.). The mixture became very hot, and on being rubbed with light petroleum set to a mass of yellowish crystals (yield, 1·2 g.). 5-*Acetamido*-2-*benzylthiazole* (V) crystallised excellently from benzene, or a mixture of ethyl acetate, ethanol, or acetone with light petroleum, in square plates, m. p. 121° (Found: C, 61·8; H, 5·3; N, 11·7. $C_{12}H_{12}ON_2S$ requires C, 62·1; H, 5·2; N, 12·1%). It crystallised from water or aqueous solvents as a hydrate, m. p. 74—75°, in long hair-like needles.

The compound was set aside with cold ethanolic hydrogen chloride for 2 days. It passed into solution (4 hours) and 5-amino-2-benzylthiazole hydrochloride, m. p. 194° (decomp.), crystallised cleanly from the colourless solution in good yield. The acetyl compound (0·95 g.) in concentrated hydrochloric acid (5 c.c.) was cooled to − 10° and a little water added. The well-formed crystals were filtered off and

washed with a little acetone. *5-Acetamido-2-benzylthiazole hydrochloride* separated from ethanol–acetone in laths, m. p. 204—206°, which were very stable and did not discolour at 250° (Found : C, 53·7; H, 5·0; N, 10·5. $C_{12}H_{13}ON_2SCl$ requires C, 53·6; H, 4·9; N, 10·4%). The same compound was obtained by adding ethereal hydrogen chloride to a solution of the base in acetone. The acetyl compound (1 g.) was refluxed with methyl iodide (2 c.c.) in acetone (10 c.c.) for 30 minutes, and the quaternary salt filtered off. It was insoluble in hot acetone and sparingly soluble in cold water, but crystallised from acetic acid (needles), water (rectangular tablets), or spirit (laths); *5-acetamido-2-benzylthiazole methiodide* had m. p. 265° (Found : C, 41·9; H, 4·1; N, 7·4. $C_{13}H_{15}ON_2SI$ requires C, 41·7; H, 4·0; N, 7·5%). It gave intense blood-red colours with 1 : 3 : 3-trimethyl-2-methyleneindoline-ω-aldehyde or ethyl orthoformate in hot acetic anhydride–pyridine.

5-Amino-2-benzylthiazole (9·5 g.) in ice-cold ethanol (280 c.c.) was treated during 15 minutes with stirring with ice-cold N-sodium nitrite (50 c.c.) to which had been added 0·474N-hydrochloric acid (105 c.c., 1 equiv.). The solution became orange and deposited red-brown crystals; these increased as the solution was allowed to assume room temperature and were filtered off (yield, 11 g.) after 40 minutes; some evolution of hydrogen sulphide was noticed. The solid was extracted with boiling benzene (100 c.c.); the residue (3·5 g.) of bright orange-red powder (A) could be supplemented by a small quantity obtained from the alcoholic mother-liquor above. (A) was insoluble in water, ether, and light petroleum, slightly soluble in hot ethanol, acetone, chloroform, or ethyl acetate, readily soluble in hot acetic acid. It crystallised from acetic acid, nitrobenzene or much toluene in coppery, rectangular tablets or needles, m. p. 213° (Found : C, 61·2; H, 4·2; N, 17·4. $C_{20}H_{17}N_5S_2$ requires C, 61·4; H, 4·4; N, 17·9%), formulated as the *azo*-compound (VI). Light absorption (chloroform) : λ max. = 281, 291, 306 mμ, $E^{1\%}_{1\,cm.}$ = 230; 453 mμ, $E^{1\%}_{1\,cm.}$ = 660. It was insoluble in sodium hydrogen carbonate solution, apparently slowly changed by hot aqueous sodium hydroxide, gave a brown hydrochloride when its chloroform solution was treated with ethanolic hydrogen chloride, and gave a deep red solution in concentrated sulphuric acid. The benzene mother-liquors (above) were chromatographed on alumina; material (B), obtained from a sharp brown band on developing with benzene–ethanol (1 : 1), recrystallised from chloroform–light petroleum in pale yellow rectangular plates, m. p. 139° (Found : C, 64·2; H, 4·7; N, 18·4. $C_{20}H_{17}ON_5S$ requires C, 64·0; H, 4·6; N, 18·6%); in a later preparation the chromatography could be omitted. (B) is perhaps best formulated as the *imino*-derivative (VIII); it was insoluble in cold water, aqueous sodium hydrogen carbonate, and sodium hydroxide, but was changed by warm dilute mineral acid. Light absorption (ethanol) : λ max. = 265, 322 mμ, $E^{1\%}_{1\,cm.}$ = 200, 250. The imino-derivative was dissolved in warm methanol and diluted with warm 2N-hydrochloric acid. On cooling, the *oxazolone* derivative (IX) separated, filling the tube with crystals, m. p. 116°, which recrystallised from methanol in platelets, m. p. 114—116° (Found : C, 62·4; H, 4·6; N, 13·9. $C_{20}H_{16}O_2N_4S$,MeOH requires C, 61·8; H, 4·9; N, 13·7%). Heating at 100° in a vacuum raises the m. p. to 202—205°. Light absorption (ethanol) : λ max. = 301 mμ, $E^{1\%}_{1\,cm.}$ = 290.

5-Amino-2-benzylthiazole (1 g.) in ethanol (30 c.c.) containing potassium acetate was treated with a diazonium salt solution prepared with *p*-nitroaniline (0·7 g.) in excess of 8% hydrochloric acid. The vessel was immediately filled with a highly crystalline scarlet precipitate of the azo-dye (2·3 g., m. p. 140°). It crystallised fairly well from ethanol, *iso*propanol, *tert.*-butanol, or chloroform–ether; it also crystallised from acetic acid but was partly transformed into green crystals, though the nature of this change is obscure. *5-Amino-4-p-nitrobenzeneazo-2-benzylthiazole* (X; R = H) crystallised best from toluene containing a little nitrobenzene and then formed rust-brown needles, m. p. 158° on rather rapid heating (Found : C, 56·8; H, 3·6; N, 20·3. $C_{16}H_{13}O_2N_5S$ requires C, 56·6; H, 3·9; N, 20·6%); it gave an intense purple solution with alkali.

Diazotised *p*-nitroaniline was coupled similarly with 5-acetamido-2-benzylthiazole. Coupling was slower and the colour (orange) less intense than with the aminothiazole. The dye was moderately soluble in ether or ethanol, easily soluble in the cold in chloroform, ethyl acetate or acetone. *5-Acetamido-4-p-nitrobenzeneazo-2-benzylthiazole* (X; R = Ac) crystallised from aqueous acetone or benzene in laths, m. p. 175—176° (Found : C, 57·2; H, 4·1; N, 18·0. $C_{18}H_{15}O_3N_5S$ requires C, 56·7; H, 4·0; N, 18·4%); it also gave a magnificent purple colour with sodium hydroxide.

5-Amino-2-benzylthiazole (1·9 g.) and acetylsulphanilyl chloride (2 g.) were kept together in pyridine (5 c.c.) overnight, and the solution poured into water. The oil soon crystallised (yield, 3·2 g.); *5-acetylsulphanilamido-2-benzylthiazole* crystallised from ethyl acetate containing a little ethanol, or from aqueous acetone, in needles, m. p. 189° (Found : C, 55·7; H, 4·4. $C_{16}H_{17}O_3N_3S_2$ requires C, 55·8; H, 4·4%). The acetylsulphanilamide (1·5 g.) was refluxed with 2N-hydrochloric acid (20 c.c.) for 0·5 hour. Filtration from a little gum and addition of concentrated aqueous sodium acetate gave *5-sulphanilamido-2-benzylthiazole* (1 g.), which crystallised from dilute ethanol in prismatic needles, m. p. 182° (Found : C, 55·4; H, 4·4; N, 11·8. $C_{10}H_{15}O_2N_3S_2$ requires C, 55·6; H, 4·3; N, 12·2%).

5-Acetamido-2-benzylthiazole (1·25 g.) in 0·5N-hydrochloric acid (10 c.c.) and dioxan to give a permanent solution was treated with N-sodium nitrite (10 c.c.) at 0°. After standing for one week the brownish needles were collected and recrystallised from aqueous methanol. This compound was *5-acetamido-2-benzylthiazole nitrate* and was obtained from the base and nitric acid in alcohol; it separated in colourless needles, m. p. 111° (decomp.) (Found : C, 48·9; H, 4·3; N, 14·2. $C_{12}H_{13}O_4N_3S$ requires C, 48·8; H, 4·4; N, 14·2%). When it was dissolved in acetic acid containing concentrated sulphuric acid and the solution poured into water it was converted into *4-nitro-5-acetamido-2-benzylthiazole* (XI), which crystallised from ethanol in needles, m. p. 152° (Found : C, 52·5; H, 4·0; $C_{12}H_{11}O_3N_3S$ requires C, 52·0; H, 4·0%). 5-Acetamido-2-benzylthiazole (4 g.) in acetic anhydride (10 c.c.) and acetic acid (30 c.c.) containing fused sodium acetate (4 g.) and phosphoric oxide (0·5 g.) was cooled to 8°, and nitrosyl chloride in acetic acid added (0·5 hr.) until the red colour persisted. The mixture was allowed to stand at room temperature for 1 hour and was then poured into water (cf. France, Heilbron, and Hey, *J.*, 1940, 369). On standing, crystals separated, m. p. 135—140° raised to 152° on crystallisation from benzene and light petroleum (charcoal). 5-Acetamido-2-benzylthiazole (1·0 g.) was dissolved in acetic acid (10 c.c.) containing concentrated sulphuric acid (1 c.c.), and concentrated nitric acid (0·5 c.c.) added. After

30 hours at room temperature the mixture was poured into iced water, and the 4-nitrothiazole, m. p. 152°, collected. It was soluble in aqueous sodium hydroxide to give a red solution.

α-Aminobenzyl cyanide (1·3 g.) in ether (10 c.c.) was shaken with sodium dithioformate (1·0 g.) in water (10 c.c.) for 2 days. *5-Amino-4-phenylthiazole* (0·7 g.) separated in colourless needles, m. p. 135—136°, and was recrystallised from benzene; a further quantity of crude material (0·4 g.) was recovered from the ether [Found : C, 61·6; H, 4·6; *M* (Rast), 170. $C_9H_8N_2S$ requires C, 61·4; H, 4·6%; *M*, 176]. The substance coupled with diazotised aniline in methanol solution containing sodium acetate. Treatment of a warm benzene solution of the base with acetic anhydride and addition of light petroleum (b. p. 40—60°) gave *5-acetamido-4-phenylthiazole*, m. p. 147—148°, crystallising from benzene in sheaves of colourless needles (Found : C, 60·4; H, 4·7. $C_{11}H_{10}ON_2S$ requires C, 60·5; H, 4·6%). Solution of 5-amino-4-phenylthiazole in acetic acid and addition of a little ethanolic hydrogen chloride caused rapid separation of *5-amino-4-phenylthiazole hydrochloride* (Found : C, 51·1; H, 4·1. $C_9H_9N_2SCl$ requires C, 50·8; H, 4·2%). The compound crystallised from acetic acid in needles, m. p. 218° (decomp.), and gave a blue precipitate with sodium nitrite in aqueous solution.

Crude ethyl aminocyanoacetate (*ca.* 5 g.) in ether (100 c.c.) was shaken with sodium dithioformate (4 g.) in water (50 c.c.), and the product kept overnight at 0°. The crystals recrystallised from ethanol to give *5-amino-4-carbethoxythiazole* as prisms, m. p. 163·5° (Found : N, 16·3; S, 18·6. $C_6H_8O_2N_2S$ requires N, 16·3; S, 18·6%); the m. p. was undepressed by the product of desulphurisation of 5-amino-2-mercapto-4-carbethoxythiazole (Part II). The amine (0·5 g.) was boiled with acetic anhydride (0·5 c.c.) for 30 mins., and the solution poured on ice. *5-Acetamido-4-carbethoxythiazole* crystallised from water in long needles, m. p. 123° (Found : C, 44·7; H, 4·4; S, 15·0. $C_8H_{10}O_3N_2S$ requires C, 44·9; H, 4·7; S, 15·0%).

Methyl ethylxanthate (1·4 g.) and morpholine (0·9 g.) were mixed. Heat and methylthiol were evolved and crystals separated. *N-Monothiocarbethoxymorpholine* was precipitated completely by adding ethanol and water, and recrystallised from aqueous ethanol or light petroleum in long needles, m. p. 58—59° (Found : C, 48·2; H, 7·4; N, 8·4. $C_7H_{13}O_2NS$ requires C, 48·0; H, 7·4; N, 8·0%).

Light Absorption of Thiazoles, 

Substituent : 2.	4.	5.	Solvent.	$\lambda_{max.}$.	$E^{1\%}_{1\,cm.}$.
CH_2Ph	H	NH_2	EtOH	281	325
				290	300
CH_2Ph	CO_2Et	NH_2	,,	280	460
				290	390
H	CO_2Et	NH_2	,,	280	650
H	Ph	NH_2	,,	280	660
				290	630
CH_2Ph	H	NHAc	,,	272 (inflexion)	485
				278	535
CH_2Ph	NO_2	NHAc	$CHCl_3$	245	690
				350	370

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