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A New Mode of the Formation of the Meso-ionic Pyrido[2, 1-b]-3, 4-dihydro-4-oxothiazole: An Attempted Preparation of Pyrido[2, 1-b]-3, 5-dihydro-5-oxothiazole[1-3]

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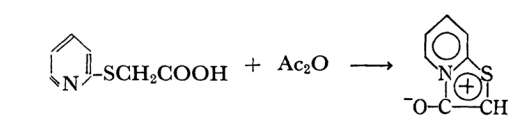
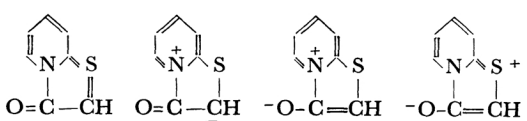
The acylation of 2-mercaptopyridine gives *S*-acyl derivatives, which, on treatment with chloroacetic acid, give the title compound.

The structure of the reaction product of (2-pyridylthio)acetic acid (I) and acetic anhydride was reinvestigated by Duffin and Kendall[4] and was shown to have a pyrido [2, 1-b]thiazole skeleton (II). This type of ring formation has since then been extended to many aza-heterocyclic systems with a mercapto group *ortho* to the ring nitrogen atom.[6-8]



I IIa



IIb IIc IId IIe

Duffin and Kendall first[5] classified this type of compound as meso-ionic, but later[6] they abandoned this idea in favor of the structure IIb, in which the participation of the sulfur d-orbitals gives rise to a wholly covalently-bonded structure. In our opinion, however, though the structure

1) Studies on Meso-ionic Compounds. Part XXIV. Part XXIII: M. Ohta and C. Shin, This Bulletin, **38**, 1816 (1965).

2) For a preliminary communication, see H. Kato, K. Tanaka and M. Ohta, This Bulletin, **35**, 1901 (1962).

3) In this communication, we will use the symbol which was officially adopted by The Chemical Society (London) for meso-ionic compounds.[4] This, however, does not necessarily mean that we consider these compounds to exist in strongly polarized forms, as is suggested by the symbol. For a more detailed discussion, see M. Ohta and H. Kato, *J. Chem. Soc. Japan, Pure Chem. Sect.* (*Nippon Kagaku Zasshi*), **86**, 661 (1965).

4) W. Baker, *Proc. Chem. Soc.*, **1959**, 75.

5) G. F. Duffin and J. D. Kendall, *J. Chem. Soc.*, **1951**, 734.

6) G. F. Duffin and J. D. Kendall, ibid., **1956**, 361.

7) M. Hashimoto and M. Ohta, This Bulletin, **33**, 1394 (1960).

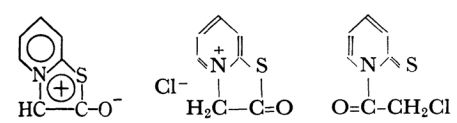
8) M. Ohta and K. Kishimoto, ibid., **34**, 1403 (1961).

IIb certainly would contribute to some degree to the resonance of this compound, other cannonical structures, such as IIc-e, would also be important participants in the resonance; therefore, we feel it more reasonable to assume the meso-ionic structure for this type of compound.

The present investigation was initiated with the idea of preparing a condensed ring system III, in which the positions of the CH and CO groups in the ring are reversed relative to the structure II. The preparation of such a ring system may be interesting because, for this ring system, no single satisfactory covalently-bonded structure can be devised, even if the sulfur d-orbitals are considered for the bonding. The preparation of such a ring system and comparison of its properties with those of the compound II would give a wealth of information concerning the evaluation of the degree of the contribution of the sulfur d-orbitals to the ring. Uncondensed ring system with the same arrangement of the atoms in the meso-ionic part of the ring as in III has been prepared by Lawson and others,[9] and has been found to be quite stable.

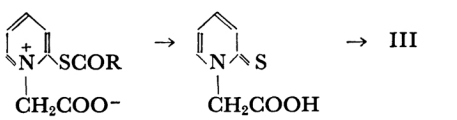
Results and Discussion

As a possible route toward a synthesis of III, we first tried the reaction of 2-mercaptopyridine with chloroacetyl chloride, anticipating the formation of an intermediate, IV. When this reaction was carried out in a dilute aqueous solution of sodium hydroxide, the reaction product was (2-pyridylthio)acetic acid (I). In order to avoid hydrolytic conditions, the same reaction in dry benzene was attempted; the crude reaction product was then treated immediately with acetic anhydride and sodium acetate. The reaction product isolated was compound II. From this result, it seems likely that the reaction first gave an *N*-acylated product (V), which then went through ring closure to give compound II.



III IV V

VI



9) A. Lawson and C. E. Searle, *J. Chem. Soc.*, **1957**, 1556; M. Ohta and C. Shin, This Bulletin, **38**, 704 (1965).

A similar reaction is reported by Goerdeler et al.,[10] who report that the acylation of thioamides with acyl chlorides gives *N*-acyl derivatives, or that the *S*-acyl derivatives first formed rearrange to give the *N*-acyl derivatives.

In order to secure the pyridine nitrogen atom as the only available position to an attack of chloroacetyl group, we tried to prepare III by the above-described series of reactions. 2-Acylthiopyridines (VI) were prepared by heating 2-mercaptopyridine with acetic anhydride, or by the treatment of sodium 2-pyridylmercaptide with acetyl or benzoyl chloride. Infrared absorptions of the acetylated compound at 1050, 652 and 768 cm^{-1} which have been assigned to a (C=O)S group,[11] the lack of absorptions of a non-aromatic double-bond system between 1600 and 1700 cm^{-1} (1620 and 1623 cm^{-1} have been reported for 2-thiopyridone and *N*-methyl-2-thiopyridone[12]); and a similar absorption pattern of the acetyl derivative to that of 2-methylthiopyridine[13] support the *S*-acetyl structure against the *N*-acetyl structure. Further, they are soluble in dilute hydrochloric acid, from which they can be recovered by rapid and careful neutralization. From this fact, it may be deduced that *S*-acylated 2-mercaptopyridines are not very sensitive to hydrolysis, but they are readily attacked by nucleophilic reagents; 2-acetylthiopyridine, for example, reacts rapidly at room temperature with aniline to form 2-mercaptopyridine and acetanilide. When 2-acetylthiopyridine was warmed with chloroacetic acid in benzene, an exothermic reaction took place to give a resinous product, the treatment of which with water or ethanol created a new precipitate which was identical with II. The same product, II, was formed by a similar reaction of 2-benzoylthiopyridine with chloroacetic acid. In this case, benzoic acid was also formed.

These results suggest a rapid reaction of 2-acylthiopyridines with chloroacetic acid to give (2-pyridylthio)acetyl acylates VIIa or chloride VIIb. To check this possibility, 2-acetylthiopyridine was warmed in benzene with ethyl chloroacetate. The reaction products were ethyl (2-pyridylthio)acetate (VIII) and acetyl chloride, the former being identified by conversion to (2-pyridylthio)acetic acid, and the latter, by conversion to acetanilide.

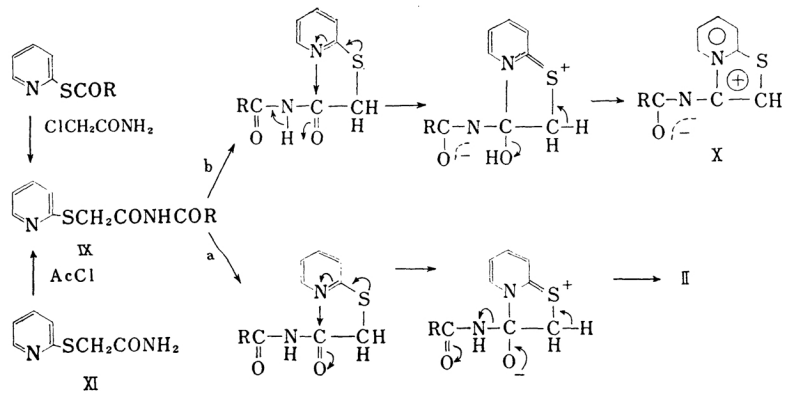
Of special interest would be the reaction of 2-acylthiopyridines with chloroacetamide, because,

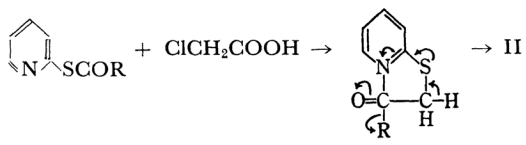
10) J. Goerdeler and K. Stadelbauer, *Chem. Ber.*, **98**, 1556 (1965), and the references cited therein.

11) R. Sasin, W. F. Aschley, J. W. Manning, Jr., A. Paolini, Jr., and G. S. Sasin, *J. Am. Oil Chemists Soc.*, **35**, 192 (1958).

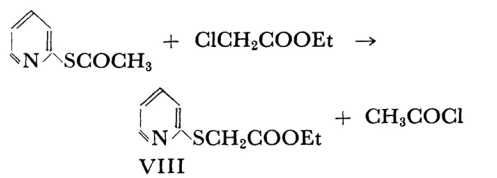
12) A. R. Katritzky, "Physical Methods in Heterocyclic Chemistry," Vol. II, Academic Press, New York (1963), p. 259.

13) E. Spinner, *J. Chem. Soc.*, **1960**, 1237; Compare the strongest infrared absorptions of 2-methylthiopyridine at 1584, 1456, 1415, 1126 and 753 cm^{-1} with 1578, 1450, 1420, 1110 and 768 cm^{-1} of 2-acetylthiopyridine.





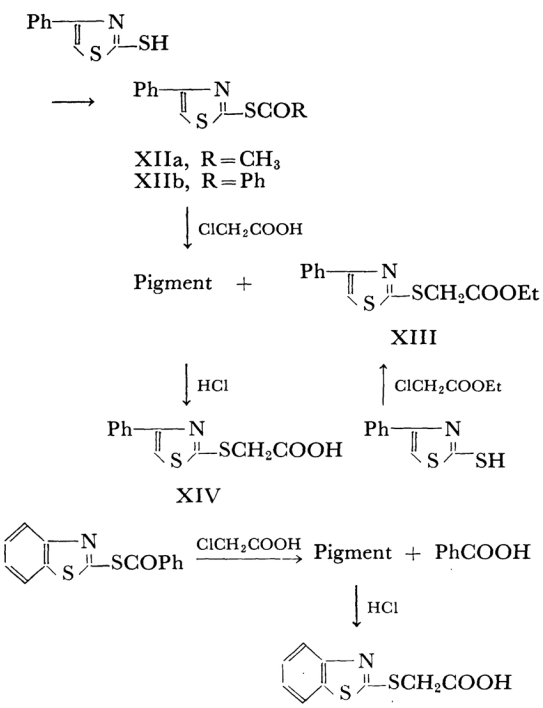
VIIa, R=$OCOCH_3$
VIIb, R=Cl



VIII

if a similar type of reaction takes place, it would give an *N*-acyl derivative IX, which would give either compound II by the removal of the acylimino group (route a) or a new meso-ionic compound, X, by dehydration (route b).[14] When 2-acetylthiopyridine was warmed in benzene with chloroacetamide, compound II was formed. The same compound, II, was formed from 2-benzoylthiopyridine. When (2-pyridylthio)acetamide (XI), prepared from 2-mercaptopyridine and chloroacetamide, was treated with acetyl chloride, the same compound, II, was again formed. It has been reported[5] that no reaction occurs upon the treatment of (2-quinolylthio)acetamide with acetic anhydride, though the corresponding anhydro base was formed when (2-quinolylthio)acetic acid was heated with acetic anhydride. This is probably due to an insufficient acylating power of an acid anhydride to give an *N*-acyl derivative, IX.

The foregoing reactions would, in principle, be the same as the reaction of (2-pyridylthio)-acetic acid with an equimolar amount of acyl chloride. This type of reaction was applied to 4-phenyl-2-mercaptothiazole and to 2-mercaptobenzothiazole. With the (thiazolylthio)acetic acids derived from these compounds, it has been reported[7] that the reaction with acetic anhydride always gives intractable red pigments of unknown structures instead of the corresponding meso-ionic rings. The treatment of 4-phenyl-2-mercaptothiazole with acetic anhydride gave the acetyl derivative (XIIa); this derivative, on being warmed with chloroacetic acid in benzene, gave the same pigment as that reported earlier[7] and a compound with the formula $C_{11}H_{11}ON_3S_2$ after recrystallization from ethanol. The latter compound gave a hydrazide with hydrazine hydrate and, on hydrolysis, gave (4-phenylthiazolyl-2-thio)acetic acid. The compound was identified as ethyl (4-phenylthiazolyl-2-thio)acetate (XIII) by comparison with a specimen which was prepared from 4-phenyl-2-mercaptothiazole and ethyl chloroacetate. The same amorphous pigment and benzoic acid were formed by the reaction of chloroacetic acid and 2-benzoylthio-4-phenylthiazole



14) The preparation of this ring system will be the subject of the following paper.

(XIIb), which had been prepared from 4-phenyl-2-mercaptothiazole and benzoyl chloride. The pigment gave (4-phenylthiazolyl-2-thio)acetic acid (XIV) by acid hydrolysis. The fact that an identical substance was formed from both the *S*-acetyl and *S*-benzoyl derivatives shows that these acyl groups are absent in the reaction product; the actual structure of this product, however, still remains to be elucidated. When 2-benzoylthiobenzothiazole was treated with chloroacetic acid in benzene, a red pigment, with a quantitative amount of benzoic acid, and a small amount of 2-mercaptobenzothiazole were formed. The pigment was identical with the reaction product of (2-benzothiazolylthio)acetic acid and acetic anhydride.[7] The red pigment gave a small amount of (2-benzothiazolylthio)acetic acid by acid hydrolysis.

Experimental

All melting points were determined on a micro hot stage and are corrected. All boiling points are uncorrected. The infrared spectra were taken on a Nippon Bunko Spectrophotometer, Model S, equipped with an NaCl prism on KBr tablets, unless otherwise stated.

The Reaction of 2-Mercaptopyridine and Chloroacetyl Chloride.—a) To a solution of 2 g. of 2-mercaptopyridine and 1.4 g. of sodium hydroxide in 50 ml. of water, 4 g. of chloroacetyl chloride was added in one portion with cooling and vigorous stirring. The stirring was continued until the excess chloroacetyl chloride had been decomposed. The crystals which separated out were collected and were recrystallized from ethanol to give 2.3 g. of yellow crystals with a green fluorescence, m. p. 130°C. Recrystallization from ethanol raised the m. p. to 136—137°C. This substance is soluble in 5% aqueous sodium bicarbonate. The melting point of this substance was undepressed on admixture with an authentic specimen of (2-pyridylthio)acetic acid (I).

b) An aqueous solution of 2 g. of 2-mercaptopyridine and 0.8 g. of sodium hydroxide was concentrated to dryness under reduced pressure. Benzene was added to the residue, and to this suspension was added 2.2 g. of chloroacetyl chloride in one portion with cooling and stirring. After thirty minutes, the dark green precipitate was collected and then warmed on a water bath for thirty minutes with a mixture of acetic acid, acetic anhydride and anhydrous sodium acetate. The mixture was concentrated under reduced pressure, the residue was treated with ice water, and the greenish yellow precipitate was collected and recrystallized from ethanol to give 0.5 g. of yellow silky needles, m. p. 189°C, undepressed on admixture with an authentic specimen of pyrido[2, 1-b]-3, 4-dihydro-4-oxothiazole (II).

Found: C, 55.24; H, 3.60; N, 9.23. Calcd. for C_7H_5ONS (II): C, 55.63; H, 3.34; N, 9.27%.

2-Acetylthiopyridine (VI, R=CH_3).—a) A mixture of 14 g. of 2-mercaptopyridine and 26 ml. of acetic anhydride was refluxed for one hour. The excess acetic anhydride and acetic acid were then distilled off under reduced pressure, and the residual oil was distilled to give 13 g. of a yellow liquid, boiling at 96—99°C/3.5 mmHg.

Found: C, 54.56; H, 4.86; N, 9.30. Calcd. for C_7H_7ONS: C, 54.90; H, 4.61; N, 9.15%.

This substance is soluble in dilute hydrochloric acid. IR (liquid film); strong absorptions at 1708, 1578, 1450, 1420, 1350, 1110, 1050, 991, 952 and 768 cm^{-1}.

b) An aqueous solution of 0.8 g. of sodium hydroxide and 2.2 g. of 2-mercaptopyridine was concentrated to dryness under reduced pressure. The residue was suspended on benzene, and to this suspension was added 2 ml. of acetyl chloride under stirring and cooling. After an hour, water was added to this suspension, and the solution was neutralized with sodium bicarbonate. The benzene layer was separated, and the aqueous layer was extracted with ether. The combined extracts were dried over sodium sulfate and distilled under reduced pressure to give 2 g. of the same substance as that prepared by the preceding procedure.

2-Benzoylthiopyridine (VI, R=C_6H_5).—An aqueous solution of 4.1 g. of sodium hydroxide and 11.6 g. of 2-mercaptopyridine was concentrated to dryness under reduced pressure. The residue was suspended on dry benzene, and 15 g. of benzoyl chloride was stirred into this suspension with cooling. The newly-formed precipitate was filtered off, and the filtrate was distilled under reduced pressure to give 7.3 g. of a colorless liquid boiling at 171.6—172°C/3 mmHg; this liquid soon solidified to white needles, m. p. 44—45°C. This substance is soluble in dilute hydrochloric acid.

Found: C, 66.67; H, 4.39; N, 6.48. Calcd. for $C_{12}H_9ONS$: C, 66.97; H, 4.22; N, 6.51%.

The Reaction of 2-Acetylthiopyridine with Aniline.—To a solution of 1 g. of 2-acetylthiopyridine in 10 ml. of benzene, 1 ml. of aniline was added with cooling by an ice bath. After thirty minutes, benzene was removed by distillation under reduced pressure. The residual oil solidified upon the addition of petroleum ether. It was then washed with 5% hydrochloric acid, and the residue (0.7 g., m. p. 115°C) was recrystallized from water to give 0.4 g. of colorless leaflets, m. p. 116°C, undepressed on admixture with an authentic specimen of acetanilide.

The hydrochloric acid washings were neutralized with sodium bicarbonate and were extracted with chloroform. The chloroform extracts were dried over magnesium sulfate and concentrated, and the residue was recrystallized from benzene to give 0.2 g. of yellow prisms, melting at 129—130°C, undepressed on admixture with an authentic specimen of 2-mercaptopyridine.

The Reaction of 2-Acetylthiopyridine and Chloroacetic Acid.—To a solution of 0.5 g. of 2-acetylthiopyridine in dry benzene, 0.31 g. of chloroacetic acid was added; then the mixture was slightly warmed on a water bath. An exothermic reaction took place, and an oily substance separated out. After five minutes, the benzene layer was decanted and, on the addition of ethanol, the oily substance solidified to give a yellowish-green powder. This powder was collected by filtration, suspended on water, and neutralized with sodium bicarbonate. The yellow suspension which resulted was collected and recrystallized from ethanol to give 0.3 g. of yellow silky needles, melting at 181—183°C,

undepressed on admixture with an authentic specimen of pyrido[2, 1-b]-3, 4-dihydro-4-oxothiazole.

Found: C, 55.24; H, 3.60; N, 9.23. Calcd. for C_7H_5ONS (II): C, 55.63; H, 3.34; N, 9.27%.

The Reaction of 2-Benzoylthiopyridine and Chloroacetic Acid.—To a solution of 0.5g. of 2-benzoylthiopyridine in 2 ml. of dry benzene, 0.22 g. of chloroacetic acid was added. The mixture was then warmed on a water bath for five minutes. When the oily substance which separated out was worked up by essentially the same procedure as that described above, 0.1 g. of yellow silky needles were obtained; the m. p. and mixed m. p. with II was 178—179°C.

The benzene mother liquor of the above experiment was extracted wtih an aqueous solution of sodium bicarbonate, and the aqueous extract was acidified with hydrochloric acid to give 0.1 g. of benzoic acid.

The Reaction of 2-Acetylthiopyridine and Ethyl Chloroacetate.—A solution of 1.53 g. of 2-benzoylthiopyridine and 1.23 g. of ethyl chloroacetate in 10 ml. of benzene was gently boiled on a water bath and the heating was so adjusted that a small but steady amount of a distillate came out through a short air condenser. The distillate, with a peculiar odor of acetyl chloride, was poured into a solution of 1 g. of aniline in 2 ml. of benzene. The crystals which separated out were collected and washed with a small amount of water to afford 0.75 g. of white crystals, m. p. 108—110°C. One crystallization from hot water gave pure acetanilide as colorless leaflets, m. p. 114°C, undepressed on admixture with an authentic specimen.

The reaction mixture of the above experiment was concentrated under reduced pressure, and the viscous oily residue which could not be crystallized was washed with 5% aqueous sodium bicarbonate and warmed with 10 ml. of 10% hydrochloric acid on a water bath for thirty minutes. The mixture was then concentrated under reduced pressure, and the residue was extracted with aqueous sodium bicarbonate. The extract was washed with benzene and was neutralized with hydrochloric acid to give 1.0 g. of yellow crystals melting at 133—134°C. One recrystallization from ethanol gave a pure sample of (2-pyridylthio)acetic acid, melting at 136°C, undepressed on admixture with an authentic specimen.

The Reaction of 2-Acetylthiopyridine with Chloroacetamide.—A solution of 1.5 g. of 2-acetylthiopyridine and 0.94 g. of chloroacetamide in 10 ml. of dry benzene was refluxed for thirty minutes on a water bath. The residue which separated out was collected, washed with ethanol and water, and neutralized with sodium bicarbonate. The green precipitate was recrystallized from benzene to give 0.35 g. of orange silky needles, melting at 181—183°C. The melting point of this substance was undepressed on admixture with an authentic specimen of II.

Found: N, 9.13. Calcd. for C_7H_5ONS: N, 9.27%.

The Reaction of 2-Benzoylthiopyridine with Chloroacetamide.—A solution of 2.15 g. of 2-benzoylthiopyridine and 0.94 g. of chloroacetamide in 5 ml. of benzene was refluxed on a water bath for one hour. The green precipitate which separated out was worked up by the procedure described in the above experiment, to give 0.1 g. of greenish yellow needles of II, m. p. 181—183°C, undepressed on admixture with an authentic specimen.

Found: N, 8.96. Calcd. for C_7H_5ONS: N, 9.27%.

(2-Pyridylthio)acetamide (XI).—To a solution of 1 g. of 2-mercaptopyridine and 0.36 g. of sodium hydroxide in 4 ml. of ethanol, 0.48 g. of chloroacetamide was added with cooling and stirring. The precipitate which separated out was filtered off, the filtrate was concentrated under reduced pressure, and the residue was recrystallized from benzene to give 1.5 g. of white leaflets, m. p. 80°C.

Found: C, 49.88; H, 4.88; N, 16.88. Calcd. for $C_7H_8ON_2S$: C, 50.00; H, 4.80; N, 16.66%.

The Reaction of (2-Pyridylthio)acetamide and Acetyl Chloride. — A solution of 0.9 g. of (2-pyridylthio)acetamide and 0.5 g. of acetyl chloride in 5 ml. of benzene was refluxed for one hour. The precipitate which separated out was collected, washed with aqueous sodium bicarbonate, and recrystallized from benzene to give 0.36 g. of greenish yellow needles, m. p. 181—183°C undepressed on admixture with an authentic specimen of II.

4-Phenyl-2-acetylthiothiazole (XIIa).—A mixture of 2 g. of 4-phenyl-2-mercaptothiazole and 4 ml. of acetic anhydride was refluxed for one hour, the resultant solution was concentrated under reduced pressure, and the residue was recrystallized from benzene to give 1.8 g. of white plates melting at 89°C (yield, 77%).

Found: C, 55.94; H, 4.06; N, 5.94. Calcd. for $C_{11}H_9ONS_2$: C, 56.17; H, 3.86; N, 5.96%.

The Reaction of 4-Phenyl-2-acetylthiothiazole with Chloroacetic Acid.—A mixture of 10 g. of 4-phenyl-2-acetylthiothiazole and 4.7 g. of chloroacetic acid in 20 ml. of benzene was warmed on a water bath for one hour. Ethanol was added to the mixture, and the red amorphous powder which separated out was collected and recrystallized from pyridine to give 5 g. of a red amorphous powder, m. p. 185°C.

Found: C, 56.37; H, 3.64; N, 6.16%.

The infrared spectrum of this substance was identical with that of the reaction product between (4-phenylthiazolyl-2-thio)acetic acid and acetic anhydride.[7]

The filtrate of the above experiment was concentrated under reduced pressure, and the residue was purified by column chromatography (alumina-benzene) and recrystallized from ethanol to give 3.6 g. of colorless prisms, m. p. 62°C, undepressed on admixture with ethyl (4-phenylthiazolyl-2-thio)acetate (XIII) prepared by the method described below.

Found: C, 55.74; H, 4.91; N, 4.91. Calcd. for $C_{13}H_{13}O_2NS$: C, 55.91; H, 4.70; N, 5.02%.

Hydrazide: white needles, m. p. 105—106°C, undepressed on admixture with a sample prepared by another route (see below).

Found: N, 15.97. Calcd. for $C_{11}H_{11}ON_3S_2$: N, 15.84%.

Ethyl (4-Phenylthiazolyl-2-thio)acetate (XIII).—To a solution of 5 g. of 4-phenyl-2-mercaptothiazole and 1.5 g. of potassium hydroxide in 50 ml. of ethanol, there was added 3.2 g. of ethyl chloroacetate with stirring and cooling. The precipitate was removed by filtration, the filtrate was concentrated, and the residue was recrystallized from ethanol to give 5.5 g. of white needles, m. p. 62—63°C.

Found: N, 15.97. Calcd. for $C_{13}H_{13}O_2NS_2$: N, 5.02%.

Hydrazide: white needles, m. p. 105—106°C.

4-Phenyl-2-benzoylthiothiazole (XIIb).—A mixture of 2 g. of 4-phenyl-2-mercaptothiazole and 3 ml. of benzoyl chloride was gently refluxed for one hour. After cooling, the crystals which separated out were collected and recrystallized from benzene to give 2.3 g. of pale yellow crystals, m. p. 95—96°C (yield, 81%).

Found: C, 64.89; H, 3.72; N, 4.48. Calcd. for $C_{16}H_{11}ONS_2$: C, 64.64; H, 3.72; N, 4.71%.

The Reaction of 4-Phenyl-2-benzoylthiothiazole with Chloroacetic Acid.—When 4-phenyl-2-benzoylthiothiazole was treated with chloroacetic acid under conditions similar to those in the case of 2-acetylthio derivative, the same red pigment (identical in infrared spectrum with that from 2-acetylthio derivative) was isolated. From the mother liquor of the reaction medium, a quantitative amount of benzoic acid was isolated.

The Acid Hydrolysis of the Red Pigment.—The red substance isolated from the preceding experiment (0.5 g.) was refluxed for one hour in 20 ml. of concentrated hydrochloric acid, and then the reaction mixture was concentrated under reduced pressure. The residue was extracted with aqueous sodium bicarbonate, and the extracts were acidified by the addition of hydrochloric acid. The crystals (0.2 g.) which separated out were recrystallized from ethanol to give white needles, m. p. 91—92°C, undepressed on admixture with an authentic specimen of (4-phenylthiazolyl-2-thio)acetic acid.[7]

The Reaction of 2-Benzoylthiobenzothiazole with Chloroacetic Acid.—A mixture of 10 g. of 2-benzoylthiobenzothiazole and 3.5 g. of chloroacetic acid in 20 ml. of benzene was warmed at 60°C for one and a half hours, and then the benzene was removed under reduced pressure. The red residue was washed with ether and ethanol, and then recrystallized from ethanol to give 4.6 g. of fine red needles, m. p. 234°C. The infrared spectrum of this substance was identical with that of the reaction product between (benzothiazolyl-2-thio)acetic acid and acetic anhydride.[7]

Found: C, 53.05; H, 2.56; N, 6.34%.

The ether washings of the above experiment were extracted with aqueous sodium bicarbonate, the extract was acidified with hydrochloric acid, and the crystals which separated out were collected and recrystallized from water to give 1.5 g. of benzoic acid as white leaflets melting at 122°C, undepressed on admixture with an authentic specimen of benzoic acid.

The ether layer separated from sodium bicarbonate washing was concentrated, and the residue was extracted with ethanol to give a small amount of an amorphous yellow powder melting at 179—180°C, undepressed on admixture with an authentic specimen of 2-mecrapto-benzothiazole.

Found: N, 8.70. Calcd. for $C_7H_5NS_2$: N, 8.38%.

The Acid Hydrolysis of the Red Pigment.—The red pigment obtained by the above-described experiment (0.5 g.) was refluxed in 10 ml. of concentrated hydrochloric acid for one hour, and then the mixture was concentrated under reduced pressure. The residue was extracted with aqueous sodium bicarbonate, the extract was acidified with hydrochloric acid, and the precipitate which separated out was recrystallized from ethanol to give 0.1 g. of (benzothiazolyl-2-thio)acetic acid, melting at 156°C, undepressed on admixture with an authentic specimen.

We wish to thank to The Kawakami Foundation for its partial financial support of this work.