Studies on Meso-ionic Compounds. XII[1]. Reaction between Acetic Anhydride and Azoles having Carboxymethylmercapto-group[*]

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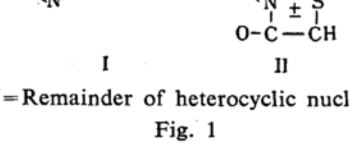
Duffin et al.[2,3] already reported that when a heterocyclic compound of the type I was subjected to the action of acetic anhydride, water was eliminated and a ring closure followed to give a meso-ionic compound of the type II.



I II

Y=Remainder of heterocyclic nucleus.

Fig. 1

The heterocyclic nuclei used by them were pyridine, quinoline, imidazole and benzimidazole.

In the present paper, this reaction is extended further to several kinds of azoles containing oxygen or sulfur (III–IX), and their behavior to acetic anhydride is investigated in detail.

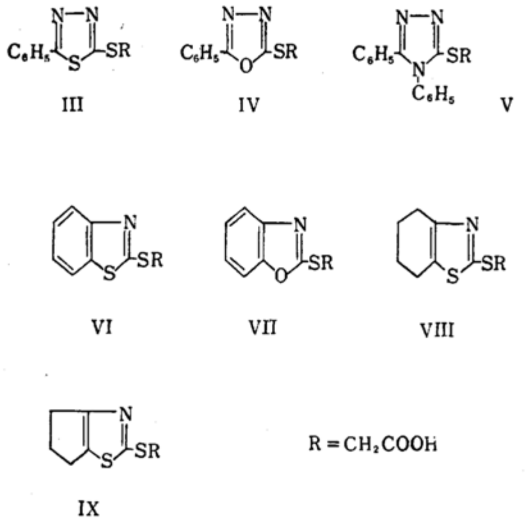


Fig. 2

Action of Acetic Anhydride on the Azoles.— 5-Phenyl-1, 3, 4-thiadiazolyl-2-thioglycollic acid (III) is sparingly soluble in acetic anhydride at room temperature, while being heated on a

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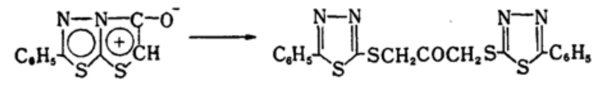
[1] Part XI. M. Masaki and M. Ohta, This Bulletin, 33, 1392 (1960).

[*] Presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April 2, 1959.

[2] G. F. Duffin and J. D. Kendall, *J. Chem. Soc.*, **1951**, 734.

[3] G. F. Duffin and J. D. Kendall. ibid., **1956**, 361.

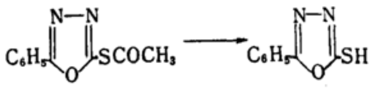
water bath, it dissolves in acetic anhydride and the solution quickly turns from yellow to dark red, and after 5 min. yellow crystals separate, which can be recrystallized unchanged from acetic anhydride. Elemental analysis indicates the compound to be an anhydro-compound of the structure X**, which is also supported by infrared analysis described below. When refluxed gently with 50% aqueous sulfuric acid or pyridine, the anhydro-compound X gives bis-5-phenyl-1, 3, 4-thiadiazolyl-2-thioacetone (XI).



X XI

Fig. 3

When 5-phenyl-1, 3, 4-oxadiazolyl-2-thioglycollic acid (IV) is boiled in acetic anhydride, no intense color develops, but 5-phenyl-1, 3, 4-oxadiazolyl-2-thioacetate (XII) is obtained. The product XII is hydrolyzed to 2-mercapto-5-phenyl-1, 3, 4-oxadiazole (XIII) with 10% aqueous sodium hydroxide.

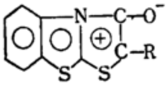


XII XIII

Fig. 4

Under similar conditions, 1, 5-diphenyl-1, 3, 4-triazolyl-2-thioglycollic acid (V) gives no pure reaction product.

When benzothiazolyl-2-thioglycollic acid (VI) is dissolved in acetic anhydride and the solution is warmed, it rapidly becomes dark red, and lustrous red-purple crystals separate. The compound is sparingly soluble in organic solvents and so difficult to burn that its elemental analysis corresponds to $C_{11}H_7O_2NS_2$ for the acetyl derivative of an anhydro-compound (XIVa; R=$COCH_3$) with a difference of 1% or so in the carbon content. However, the same colored crystals are obtained by the action of propionic anhydride instead of acetic anhydride on the acid VI, and consequently the assignment of the structure XIVa for the colored compound would not be correct.

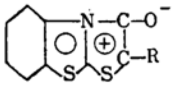


XIV

Fig. 5

On being treated with acetic anhydride, benzoxazolyl-2-thioglycollic acid (VII) gives only a yellow gummy material.

When cyclohexenothiazolyl-2-thioglycollic acid (VIII) is warmed in acetic anhydride, an orange color quickly develops which gradually changes to intense blue-violet, and black-violet crystals separate. The compound is as sparingly soluble in organic solvents and as difficult to burn as that obtained from the acid VI. Elemental analysis of the compound corresponds to $C_{11}H_{11}O_2NS_2$ with a difference of 1% or so in the carbon content. Although the formula $C_{11}H_{11}O_2NS_2$ suggests the structure of the acetyl derivateve of an anhydro-compound derived from the acid VIII (XVa; R=$COCH_3$), this structure should be excluded by the fact that the same compound is also obtained on treating with propionic anhydride.



XV

Fig. 6

The infrared spectra of the compounds $C_{11}H_7O_2NS_2$ and $C_{11}H_{11}O_2NS_2$ are similar to each other and show that there is great resemblance between structures of both compounds, and these structures are under investigation.

Action of Acetic Anhydride and Pyridine or Triethylamine on the Azoles.—When 5-phenyl-1, 3, 4-thiadiazolyl-2-thioglycollic acid (III) is added to a mixture of acetic anhydride and dry pyridine (volume ratio of 1 : 2), a yellow color immediately develops and the color changes to orange as the acid III dissolves. After several minutes yellow crystals separate, which are identical with the anhydro-compound X described above.

Under similar conditions, 5-phenyl-1, 3, 4-oxadiazolyl-2-thioglycollic acid (IV) affords 5-phenyl-1, 3, 4-oxadiazolyl-2-thioacetate (XII) which is obtained from IV by treating with acetic anhydride only, while 1, 5-diphenyl-1, 3, 4-triazolyl-2-thioglycollic acid (V) is recovered unchanged.

When benzothiazolyl-2-thioglycollic acid (VI) is added to acetic anhydride and dry pyridine (volume ratio of 1 : 2), the mixture immediately turns yellow as the acid VI dissolves, and the color finally becomes dark green. After a few minutes blue-green crystals separate, from which yellow needles are obtained by extraction with benzene. Elemental analysis shows

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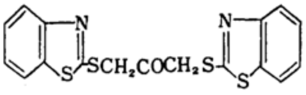
** The formulation adopted is that put forward by Baker and Ollis. W. Baker and W. D. Ollis, *Quart. Rev.*, 11, 15 (1957); W. Baker, *Proc. Chem. Soc.*, 1959, 75.

the compound to be an anhydro-compound of the structure (XIVb; R=H), which is also supported by infrared analysis described below.

Besides the anhydro-compound XIVb, the lustrous red-purple crystals are obtained from the benzene-insoluble portion in a considerable yield.

When the acid VI is dissolved in a mixture of acetic anhydride and triethylamine (volume ratio of 1 : 2), a yellow color develops and yellowish-brown crystals separate, which are recrystallized from benzene to yield the anhydro-compound XIVb.

On refluxing gently with pyridine the anhydro-compound XIVb affords bisbenzothiazolyl-2-thioacetone (XVI), which is identical with a specimen prepared from sym-dichloroacetone and 2-mercaptobenzothiazole. With hot 50% aqueous sulfuric acid the compound XIVb affords the compound XVI and the parent acid VI.



XVI

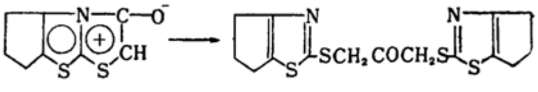
Fig. 7

When benzoxazolyl-2-thioglycollic acid (VII) is treated with acetic anhydride in pyridine or triethylamine, no anhydro-compound can be obtained but the starting material is recovered.

When cyclohexenothiazolyl-2-thioglycollic acid (VIII) is dissolved in a mixture of acetic anhydride and dry pyridine (volume ratio of 1 : 2), a deep yellow color quickly develops which gradually changes to blue-green, and light blue crystals separate. Extraction of the crystals with benzene gives benzene-soluble light green needles and the benzene-insoluble black-violet crystals. The former compound is also obtained exclusively on treating the acid VIII with acetic anhydride and triethylamine. Elemental analysis of the compound indicates that it is not an anhydro-compound of the structure (XVb; R=H), but a compound of the formula $C_{10}H_9ONS_2$.

With hot 50% aqueous sulfuric acid the compound $C_{10}H_9ONS_2$ is hydrated to the parent acid VIII, and with boiling pyridine it affords a compound of the formula $C_8H_{11}ONS_2$. The structures of both compounds $C_{10}H_9ONS_2$ and $C_8H_{11}ONS_2$ await further investigation.

When cyclopentenothiazolyl-2-thioglycollic acid (IX) is dissolved in a mixture of acetic anhydride and triethylamine (volume ratio of 1 : 2), deep yellow crystals immediately separate, which are shown to be an anhydro-compound of the structure XVII by elemental and infrared analyses. The compound XVII is hydrated to the parent acid IX with hot 50% aqueous sulfuric acid, and with boiling pyridine it affords monohydrate of biscyclopentenothiazolyl-2-thioacetone (XVIII).



XVII XVIII

Fig. 8

It seems very interesting that the behavior of the acid VIII to acetic anhydride and triethylamine differs greatly from that of the acid IX; nevertheless, the structures of two acids nearly the same. However, the question what factor of the acids can give rise to such a significant difference remains obscure.

The results presented in this paper speak for themselves. Several points deserve further comment, however.

In the first place, it is clear that the azoles free from sulfur in their nuclei; IV, V and VII give no intensely colored compounds like the compounds $C_{11}H_{11}O_2NS_2$ and $C_{11}H_9O_2NS_2$ on treating with acetic anhydride. Duffin et al., on the other hand, did not report that such a colored compound was obtained. Consequently, it is considered that the reaction center in formation of the colored compounds might be at the ring-sulfur of heterocycle.

It is also clear that the azoles containing sulfur in their nuclei; III, VI and IX can be subjected to two different types of reactions to give the colored compound and the anhydro-compound like X, XIVb and XVII, respectively.

The mechanism of formation of the anhydro-compounds is obscure, but in this case the reaction center seems to be at the ring-nitrogen of heterocycle.

Infrared Analyses of the Anhydro-compounds X, XIVb and XVII.—The infrared spectra of the anhydro-compounds, their parent acids and decomposition products were taken.

When the spectra of the anhydro-compounds are compared with those of their parent acids, three remarkable changes can be observed. Firstly, the disappearance of the band at 1720∼1708 cm^{-1} due to the C=O vibration of carboxylic group and the appearance of a band at 1645 cm^{-1}, which is probably due to the amide I band of tertiary amide. Secondly, the appearance of a new strong band near 1600 cm^{-1}, which disappears again in the spectrum of the decomposition product. Consequently, this band seems to be produced by formation of a meso-ionic ring, but the assignment of the band is still unknown. Lastly, the red shift of 35 cm^{-1} or so of the band at 1180± 10 cm^{-1}.

The three remarkable changes mentioned above can be also observed in the spectra of the anhydro-compound derived from (2-pyridylthio)acetic acid, whose structure has been confirmed synthetically.[2)]

Experimental

5-Phenyl-1, 3, 4-thiadiazolyl-2-thioglycollic Acid (III).—This acid was prepared by Sato's method[4)].

Anhydro-compound X from III. — (a) A solution of the acid III (5.0 g.) in acetic anhydride (100 ml.) was heated on a boiling water bath for 5 min., quickly turning from yellow to red. Yellow crystals which separated were filtered off and recrystallized from acetic anhydride to give the anhydro-compound as small yellow needles (1.9 g.), m. p. 231°C (decomp.).

Found: C, 51.54; H, 2.80; N, 11.71. Calcd. for $C_{10}H_6ON_2S_2$: C, 51·29; H, 2.58; N, 11.96%.

(b) III (1.0 g.) was dissolved with stirring at room temperature in a mixture of acetic anhydride (3 ml.) and dry pyridine (6 ml.). A yellow color immediately developed and the color changed to orange. After several minutes yellow crystals separated, which were filtered off after 0.5 hr., washed with water, and dried to give deep yellow crystals (0.6 g.), m. p. 229~230°C (decomp.). Recrystallization from acetic anhydride gave small yellow needles, m. p. 231°C (decomp.).

Found: N, 11.70. Calcd. for $C_{10}H_6ON_2S_2$: N, 11.96%.

Action of Aqueous Sulfuric Acid on the Anhydro-compound X.—X (1.0 g.) was refluxed gently with 50% aqueous sulfuric acid (10 ml.) for 10 min. The cooled solution was diluted with water (50 ml.) to give a crystalline precipitate which was filtered off and recrystallized from ethanol, affording small colorless needles of bis-5-phenyl-1,3,4-thiadiazolyl-2-thioacetone (XI) (0.69 g.), m. p. 148°C.

Found: C, 51.36; H, 3.42; N, 12.75; S, 29.06; mol. wt. (Rast), 455. Calcd. for $C_{19}H_{14}ON_4S_4$: C, 51.58; H, 3.17; N, 12.67; S, 28.96%; mol. wt., 442.

Action of Pyridine on X.—X (0.3 g.) was refluxed gently with pyridine (10 ml.) for 5 min. After cooling, the solution was diluted with water (50 ml.) to give a crystalline precipitate (0.24 g.), m. p. 146~147°C. Recrystallization from ethanol yielded small colorless needles, m. p. 148°C, undepressed by admixture with XI.

5-Phenyl-1, 3, 4-oxadiazolyl-2-thioglycollic Acid (IV).—A solution of chloroacetic acid (2.0 g.) and sodium carbonate (1.1 g.) in water (20 ml.) was added to a solution of crude 2-mercapto-5-phenyl-1,3,4-oxadiazole (3.0 g.) and potassium hydroxide (1.0 g.) in water (30 ml.). The solution was kept to stand at room temperature overnight, neutralized with dilute hydrochloric acid. The resulting precipitate was filtered off, dissolved in aqueous sodium bicarbonate to remove insoluble impurities and neutralized with dilute hydrochloric acid. After filtration and drying 5-phenyl-1,3,4-oxadiazolyl-2-thioglycollic acid was obtained (5.0 g.), m. p. 157~162°C. Recrystallization from hot water gave white needles, m. p. 168~169°C.

Found: N, 12.15. Calcd. for $C_{10}H_8O_3N_2S$: N, 12.86%.

Action of Acetic Anhydride on IV. — The acid IV (1.0 g.) and acetic anhydride (10 ml.) were boiled under reflux for 0.5 hr. The anhydride was evaporated under reduced pressure and the residue was recrystallized from ethanol to give 5-phenyl-1,3,4-oxadiazolyl-2-thioacetate (XII) as colorless needles (0.22 g.), m. p. 152.5~153°C.

Found: C, 54.33; H, 3.63; N, 12.74. Calcd. for $C_{10}H_8O_2N_2S$: C, 54.54; H, 3.64; N, 12.73%.

XII was dissolved in 10% aqueous sodium hydroxide and then neutralized with 10% aqueous sulfuric acid to give colorless needles, m. p. 217°C, undepressed by admixture with authentic 2-mercapto-5-phenyl-1,3,4-oxadiazole.

1, 5-Diphenyl-1, 3, 4-triazolyl-2-thioglycollic Acid (V).—This acid was prepared by Ueda's method[5)].

Action of Acetic Anhydride on V.—The acid V (0.5 g.) and acetic anhydride (10 ml.) were boiled under reflux for 0.5 hr., affording a yellow solution. On addition of water (100 ml.) the solution yielded a pale brown gummy material from which no pure compound could be isolated.

Benzothiazolyl-2-thioglycollic Acid (VI).—This acid was prepared by Ohta's method[6)].

Action of Acetic Anhydride on VI.—The acid VI (1.0 g.) was added to acetic anhydride (20 ml.) and warmed on a water bath. The solution rapidly became dark red and at the same time crystals separated, which were filtered off and washed with hot ethanol, giving lustrous red-purple crystals (0.57 g.), m. p. 297°C.

The anhydride filtrate was diluted with water (100 ml.) and washed with hot ethanol to give lustrous red-purple crystals (0.35 g.), m. p. 297°C. Total yield, 0.92 g.

Found: C, 51.80; H, 3.00; N, 5.85. Calcd. for $C_{11}H_7O_2NS_2$: C, 53.01; H, 2.81; N, 5.62%.

The above experiment was repeated but with propionic anhydride instead of acetic anhydride, the same product being obtained.

Benzoxazolyl-2-thioglycollic Acid (VII).—A solution of chloroacetic acid (1.9 g.) and sodium carbonate (1.06 g.) in water (20 ml.) was added to a solution of 2-mercaptobenzoxazole (3.0 g.) and sodium hydroxide (0.8 g.) in water (20 ml.). The solution was warmed on a water bath for 0.5 hr. and kept standing at room temperature overnight. After neutralization with dilute hydrochloric acid, the resulting precipitate was filtered off, washed with water and recrystallized from dilute ethanol to give colorless plates of VII (3.85 g.), m. p. 160~161°C.

Found: N, 6.27. Calcd. for $C_9H_7O_3NS \cdot H_2O$; N, 6.17%.

Action of Acetic Anhydride on VII.—The acid VII (1.0 g.) was refluxed gently with acetic anhydride (10 ml.) for 0.5 hr., affording a deep yellow

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[4)] T. Sato and M. Ohta, *J. Pharm. Soc. Japan*, **77**, 771 (1957).

[5)] H. Ueda, unpublished work.

[6)] H. Ohta and M. Ohta, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 700 (1957).

solution. The anhydride was evaporated under reduced pressure, the residue of violet gum extracted with ether and the extract evaporated to dryness to give yellowish gummy material which could not be purified.

Cyclohexenothiazolyl-2-thioglycollic Acid (VIII).—This acid was prepared by the same process as used for benzothiazolyl-2-thioglycollic acid (VI)[6]. Colorless lancets, m. p. 124~125°C. Yield, 80.4%.

Action of Acetic Anhydride on VIII.—The acid VIII (1.0 g.) was added to acetic anhydride (2 ml.) and warmed on a water bath. An orange color quickly developed which gradually changed to intense blue-violet, and black-violet crystals separated. The crystals were filtered off and washed with hot ethanol to give black-violet crystals (0.7 g.), m. p. 254.5~255°C (decomp.).

The anhydride filtrate was diluted with water (200 ml.), and the resulting precipitate was filtered off and washed with hot ethanol to give black-violet crystals (0.02 g.), m. p. 254.5~255°C (decomp.). Total yield, 0.76 g.

Found: C, 50.84; H, 4.35; N, 5.72. Calcd. for $C_{11}H_{11}O_2NS_2$: C, 52.17; H, 4.35; N, 5.53%.

The above experiment was repeated but with propionic anhydride instead of acetic anhydride, the same product being obtained.

Action of Acetic Anhydride and Pyridine on IV.—The acid IV (1.0 g.) was refluxed in a mixture of acetic anhydride (5 ml.) and dry pyridine (5 ml.) for 0.5 hr. and the solvent was removed in vacuo to give a black oil, which was solidified by addition of a small amount of ethanol. Recrystallization from ethanol gave XII as colorless needles (0.12 g.), m. p. 149~150°C, undepressed by admixture with authentic sample.

Action of Acetic Anhydride and Pyridine on V.—The acid V (0.5 g.) was refluxed in a mixture of acetic anhydride (3 ml.) and dry pyridine (6 ml.) for 5 min., the solvent removed in vacuo and the residue recrystallized from ethanol to give colorless needles, m. p. 238°C, undepressed by admixture with the acid V.

Found: N, 13.65. Calcd. for $C_{16}H_{13}O_2N_3S$: N, 13.50%.

Anhydro-compound XIVb from VI. — (a) The acid VI (1.0 g.) was dissolved with stirring at room temperature in a mixture of acetic anhydride (3 ml.) and dry pyridine (6 ml.). The solution immediately turned yellow and the color finally became dark green. After a few minutes crystals separated, which were filtered off, washed thoroughly with water, dried and then extracted with hot benzene. The extract was evaporated to dryness giving yellow crystals (0.3 g.), m. p. 209~212°C (decomp.). Recrystallization from benzene yielded the anhydro-compound as bright yellow leaflets, m. p. 215~216°C (decomp.).

Found: C, 51.94; H, 2.58; N, 6.89. Calcd. for $C_9H_5ONS_2$: C, 52.18; H, 2.43; N, 6.76%.

From the benzene-insoluble portion, the lustrous red-purple crystals were obtained (0.33 g.).

(b) VI (1.0 g.) was dissolved with stirring at room temperature in a mixture of acetic anhydride (3 ml.) and triethylamine (6 ml.), a yellow color quickly developing. After a few minutes yellowish brown crystals separated, which were filtered off, washed thoroughly with water, dried and extracted with hot benzene. The extract was evaporated to dryness to give yellow crystals (0.47 g.), m. p. 210~212°C (decomp.). Recrystallization from benzene yielded the anhydro-compound as bright yellow leaflets, m. p. 216~216.5°C (decomp.).

Found: N, 6.55. Calcd. for $C_9H_5ONS_2$: N, 6.76%.

Action of Pyridine on the Anhydro-compound XIVb.—XIVb (0.3 g.) was refluxed gently with pyridine (10 ml.) for 5 min. After cooling, the solution was diluted which water (50 ml.) to give a crystalline precipitate with was filtered off and recrystallized from ethanol, affording bisbenzothiazolyl-2-thioacetone (XVI) as colorless needles (0.18 g.), m. p. 127°C, undepressed by admixture with authentic sample.

Found: N, 7.36. Calcd. for $C_{17}H_{12}ON_2S_4$: N, 7.21%.

Bisbenzothiazolyl-2-thioacetone.—To a solution of 2-mercaptobenzothiazole (5.5 g.) in absolute ethanol (50 ml.) containing metallic sodium (0.8 g.) was added *sym*-dichloroacetone (2.0 g.). After 5 min. crystals separated at a time. The crystals were filtered off, washed with water and recrystallized twice from ethanol to give colorless needles (8.0 g.), m. p. 127°C.

Found: C, 52.83; H, 3.37; N, 7.18. Calcd. for $C_{17}H_{12}ON_2S_4$: C, 52.56; H, 3.09; N, 7.21%.

Action of Aqueous Sulfuric Acid on XIVb.—XIVb (0.3 g.) was refluxed gently with 50% aqueous sulfuric acid (10 ml.) for 10 min. and the cooled solution was diluted with water (50 ml.) to give a crystalline precipitate which was filtered off and recrystallized from ethanol, affording colorless needles (0.05 g.), m. p. 124°C, undepressed by admixture with authentic sample of XVI. Addition of water to the mother-liquor precipitated pale yellow prisms (0.06 g.), m. p. 157~158°C, undepressed by admixture with the acid VI.

Action of Acetic Anhydride and Pyridine on VII.—The acid VII (1.0 g.), acetic anhydride (1 ml.) and dry pyridine (3 ml.) were heated on a boiling water bath for 0.5 hr. and after cooling, the solution was concentrated under reduced pressure to give colorless leaflets (0.9 g.), m. p. 160~162°C, undepressed by admixture with the acid VII.

Action of Acetic Anhydride and Triethylamine on VII.—The acid VII (1.0 g.) was dissolved in a mixture of acetic anhydride (1 ml.) and triethylamine (3 ml.) and the solution kept to stand at room temperature for 3 hr. The solution was concentrated under reduced pressure to give an orange oily material, which rapidly solidified by addition of water. Colorless leaflets (0.91 g.), m. p. 163°C, undepressed by admixture with the acid VII.

Action of Acetic Anhydride and Pyridine on VIII.—The acid VIII (1.0 g.) was dissolved with stirring at room temperature in a mixture of acetic anhydride (3 ml.) and dry pyridine (6 ml.). A deep yellow color quickly developed which gradually changed to blue-green and light blue crystals separated. After 0.5 hr., the crystals were filtered off, washed thoroughly with water, dried and then extracted with hot benzene and the extract was evaporated to dryness to give light green needles (0.52 g.), m. p. 198~199°C (decomp.). Recrystallization from benzene gave m. p. 198~199°C (decomp.).

Found: C, 53.51; H, 4.60; N, 6.08. Calcd. for $C_{10}H_9ONS_2$: C, 53.81; H, 4.06; N, 6.28%.

From the benzene-insoluble portion, the black-violet crystals were obtained (0.17 g.).

Action of Acetic Anhydride and Triethylamine on VIII.—The acid VIII (1.0 g.) was dissolved with stirring at room temperature in a mixture of acetic anhydride (3 ml.) and triethylamine (6 ml.). Light brown crystals rapidly separated, which were filtered off, washed thoroughly with water, dried and extracted with hot benzene. The extract was evaporated to dryness to give light yellow crystals (0.68 g.), m. p. 197~199°C (decomp.). Recrystallization from benzene yielded light yellow needles, m. p. 198°C (decomp.).

Found: N, 6.26. Calcd. for $C_{10}H_9ONS_2$: N, 6.28%.

Action of Aqueous Sulfuric Acid on the Compound $C_{10}H_9ONS_2$.—The compound (0.5 g.) was refluxed gently with 50% aqueous sulfuric acid (12 ml.) for 0.5 hr. The cooled solution was diluted with water (50 ml.) and extracted with ether. The ether extract was evaporated and the residue recrystallized from ethanol to give colorless prisms, m. p. 125~126°C, undepressed with the acid VIII.

Found: N, 5.94. Calcd. for $C_9H_{11}O_2NS_2$: N, 6.11%.

Action of Pyridine on the Compound $C_{10}H_9ONS_2$.—The compound (1.0 g.) was refluxed gently with pyridine (20 ml.) for 20 min. After cooling, the solution was diluted with water (150 ml.) and colorless needles which separated were filtered off and dried. M. p. 94.5°C, 1.0 g. Recrystallization from dilute pyridine gave colorless silky needles, m p. 98.5~99.5°C.

Found: C, 47.60; H, 5.35; N, 6.86; S, 31.1. Calcd. for $C_8H_{11}ONS_2$: C, 47.76; H, 5.47; N, 6.97; S, 31.84%.

Cyclopentenothiazolyl-2-thioglycollic Acid (IX).—This acid was prepared by the same process as used for benzothiazolyl-2-thioglycollic acid (VI)[6]. Colorless needles, m. p. 126°C, yield, 45.6%.

Anhydro-compound XVII from IX.—The acid IX (1.0 g.) was dissolved with stirring at room temperature in a mixture of acetic anhydride (3 ml.) and triethylamine (6 ml.). After one minute crystals separated, which were filtered off, washed thoroughly with water and dried. M. p. 198~201°C, 0.67 g. Recrystallization from benzene gave the anhydro-compound as deep yellow crystals, m. p. 213.5~214°C (decomp.).

Found: C, 48.65; H, 3.97; N, 7.20. Calcd. for $C_8H_7ONS_2$: C, 48.74; H, 3.58; N, 7.11%.

Action of Aqueous Sulfuric Acid on the Anhydro-compound XVII.—XVII (0.5 g.) was dissolved in 50% aqueous sulfurid acid (12 ml.) and the resultant yellow solution refluxed gently for 10 min., the yellow color disappearing. The solution was diluted with water (150 ml.), neutralized with sodium carbonate, extracted with ether and the extract evaporated to give colorless needles (0.38 g.), m. p. 117°C. Recrystallization from dilute ethanol gave colorless needles, m. p. 124~126°C, undepressed by admixture with the acid IX.

Found: N, 6.41. Calcd. for $C_8H_9O_2NS_2$: N, 6.51%.

Action of Pyridine on XVII.—XVII (0.3 g.) was refluxed gently with pyridine (10 ml.) for 5 min. The solution was diluted with water (50 ml.) and a crystalline precipitate filtered off, washed with water and dried. M. p. 81.5°C, 0.27 g. Recrystallization from dilute ethanol afforded colorless silky needles, m. p. 81~82°C.

Found: C, 46.39; H, 4.83; N, 7.53. Calcd. for $C_{15}H_{16}ON_2S_4 \cdot H_2O$: C, 46.63; H, 4.66; N, 7.25%.

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