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Synthesis of 1,3-Thiazine Derivatives from 2-Iminocyclopentanedithiocarboxylic Acid[1)]

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Several new 3-substituted and 3,3-disubstituted-1,3,4,5,6,7-hexahydro-1-thioxocyclopenta[*d*]-[1,3]thiazines were obtained by the reactions of 2-iminocyclopentanedithiocarboxylic acid with some aldehydes and ketones. Some intermediate compounds in these reactions such as 2-amino-2-[2-(piperonylidenamino)-1-cyclopenten-1-yl]thiocarbonylthiocyclopentanedithiocarboxylic acid, 2-amino-2-[2-(vanillylidenamino)-1-cyclopenten-1-yl]thiocarbonylthiocyclopentanedithiocarboxylic acid, and 2-amino-2-[2-(4-methoxybenzylidenamino)-1-cyclopenten-1-yl]thiocarbonylthiocyclopentanedithiocarboxylic acid could be isolated.

Several new 1,3-thiazine derivatives were synthesized by the reactions of 2-iminocyclopentanedithiocarboxylic acid (I) with carbonyl compounds. Compound I was isolated as the intermediate during the course of synthesis of 1,3,4,5,6,7-hexahydro-1-thioxocyclopenta[*d*][1,3]thiazine-3-spirocyclopentane. The coupling reactions of I with ketones were partly reported.[2)]

The reactions in question were effected by acid or base, and 3-substituted and 3,3-disubstituted-1,3,4,5,6,7-hexahydro-1-thioxocyclopenta[*d*][1,3]-thiazines (III) were produced. Aliphatic and alicyclic ketones, in the presence of morpholine,[2)] easily reacted with I to give respective thiazine derivatives. However, aldehydes and acetophenone under the same conditions did not afford the expected products.

On treatment with sulfuric acid in place of morpholine, we have found that aldehydes such as piperonal, vanillin, anisaldehyde, acetaldehyde, salicylaldehyde, benzaldehyde, *o*-methoxy or *p*-hydroxybenzaldehyde and *p*-tolualdehyde as well as ketones such as acetophenone, methyl ethyl ketone and acetone reacted with I to afford the corresponding thiazine derivatives III. This paper deals with the results.

Evidence for the structures of IIIa—j was provided by comparison of their IR, UV and NMR spectra with those of known 1,2,5,6,7,8-hexahydro-4-thioxo-4*H*-3,1-benzo[*d*]thiazine-2-spirocyclohexane, 2-ethyl-2,4,5-trimethyl-2,3-dihydro-6-thioxo-6*H*-1,3-thiazine, and 3,3-dimethyl-1,3,4,5,6,7-hexahydro-1-thioxocyclopenta[*d*][1,3]thiazine.[2-4)] The doublet near δ 6.15 (J=4—6 Hz) was assigned to a C-3 proton, and thus structures

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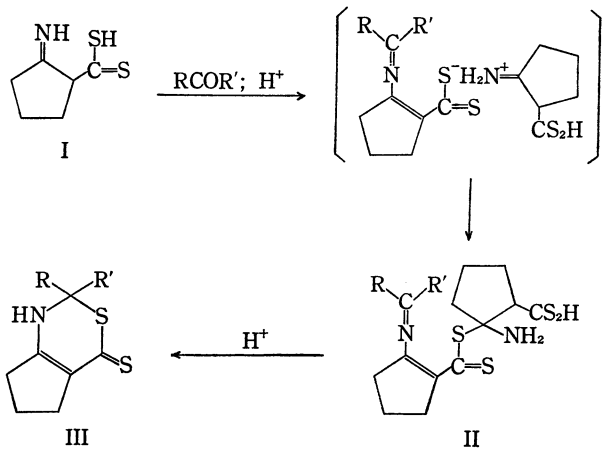
2) T. Takeshima, M. Yokoyama, T. Imamoto, M. Akano and H. Asaba, *J. Org. Chem.*, **34**, 730 (1969).



I

III

II

IIIa, R=H, R'=3,4(-OCH_2O-)C_6H_3
IIa, R=H, R'=3,4(-OCH_2O-)C_6H_3
IIIb, R=H, R'=3-CH_3O-4-HO-C_6H_3
IIb, R=H, R'=3-CH_3O-4-HO-C_6H_3
IIIc, R=H, R'=*p*-CH_3O-C_6H_4
IIc, R=H, R'=*p*-CH_3O-C_6H_4
IIId, R=H, R'=CH_3
IIIe, R=CH_3, R'=C_6H_5
IIIf, R=H, R'=*o*-HO-C_6H_4
IIIg, R=H, R'=C_6H_5
IIIh, R=H, R'=*o*-CH_3O-C_6H_4
IIIi, R=H, R'=*p*-HO-C_6H_4
IIIj, R=H, R'=*p*-CH_3-C_6H_4
IIIk, R=CH_3, R'=C_2H_5
IIIl, R=R'=CH_3

III were proposed as the corresponding thiazine structures.

It was shown that the reaction of methyl ethyl ketone with I was abortive.[2] However, the present experiment revealed that 3-ethyl-3-methyl-1,3,4,5,6,7 - hexahydro-1-thioxocyclopenta[*d*][1, 3]-thiazine IIIk, had a molecule of water of crystallization which was lost on heating at 138°C under reduced pressure and thus was of a different physical nature. Likewise, the thiazine derivatives IIIa and IIIj which were obtained by the reactions of I with piperonal and *p*-tolualdehyde, respectively, also had a molecule of water of crystallization which was lost on heating at 110°C under reduced pressure.

Under the acidic conditions, piperonal, vanillin and anisaldehyde gave respective intermediate compounds IIa, IIb and IIc at low temperature which changed to IIIa—b on treatment with sulfuric acid. Compound IIc was resistant to conversion into IIIc.

Structures IIa, IIb and IIc were assigned by spectral data (see Experimental).

Experimental

2-Amino-2-[2-(piperonylidenamino)-1 - cyclopenten-1-yl]thiocarbonylthiocyclopentanedithiocarboxylic acid (IIa). A solution of I (4.1 g), piperonal (4 g) and sulfuric acid (96%, 1 g) in 150 m*l* of methanol was allowed to stand for 5 min at room temperature. The yellow material was collected, washed with methanol and recrystallized from methanol-*N*,*N*-dimethylformamide. Yellow long plates (IIa): yield 4.6 g, 70%; mp 211—214°C with dec. (slow heating), 215—220°C with dec. (rapid heating); UV λ_{max}^{MeOH} 311, 397 mμ (log ε=4.04, 4.32); IR (KBr) 3380 (m, NH_2), 3296 (s, NH_2), 1609 (s, δ NH_2), 1600 (vs, C=N), 1500 (s, ring), 1486 (s, ring), 1475 cm^{-1} (m, ring); NMR (CF_3COOH) δ 9.00 (br, 1H, S$\underline{H}$), 7.08 (m, 4H, $C_6\underline{H}_3$ and C$\underline{H}$=N), 6.30 (s, 2H, OC$\underline{H}_2$O), 3.03 (m, 9H, C-1, 3,5,3',5' $\underline{H}_2$), 2.20(m, 4H, C-4,4'$\underline{H}_2$); NMR (CD_3-$SOCD_3$) δ 10.80 (br, *ca.* 2H, N$\underline{H}_2$), 9.00 (br, *ca.* 1H, S$\underline{H}$); Found: C, 53.56; H, 5.09; N, 6.18; S, 28.36%. Calcd for $C_{20}H_{22}N_2S_4O_2$: C, 53.30; H, 4.92; N, 6.22; S, 28.45%.

NMR absorptions of NH_2 and SH in CD_3SOCD_3 disappeared by addition of deuterium oxide.

Conversion of IIa into IIIa. A mixture of IIa (1 g), sulfuric acid (96%, 400 mg) and 50 m*l* of methanol was refluxed for *ca.* 1 hr until a clear solution was obtained. After cooling, a yellowish orange material was collected and recrystallized from *N*,*N*-dimethylformamide-water as yellowish orange long plates: mp 177—178°C, undepressed on admixture with an authentic specimen; yield 500 mg, 77%. IR and UV spectra of both specimens also were identical.

2-Amino-2- [2-(vanillylidenamino)-1-cyclopenten-1-yl]thiocarbonylthiocyclopentanedithiocarboxylic acid (IIb). To an ice-cold solution of I (4.7 g) and vanillin (5 g) in methanol (130 m*l*), sulfuric acid (96%, 2 g) was added and the solution was kept at 0°C for 5 min. The resulting yellow material was recrystallized from acetone-water. Yellow long plates (IIb): yield 5.2 g, 77%; mp 190—192°C with dec. (slow heat-

3) T. Takeshima, T. Hayashi, M. Muraoka and T. Matsuoka, *ibid.*, **32**, 980 (1967).

4) T. Takeshima, T. Imamoto, M. Yokoyama, K. Yamamoto and M. Akano, *ibid.*, **33**, 2877 (1968).

ing), 199—201°C with dec. (rapid heating); UV λ_{max}^{MeOH} 308, 397 mμ (log ε=4.13, 4.30); IR ($CHCl_3$) 3320 (m, NH_2), 3260 (m, NH_2), 1614 (s, δ NH_2), 1603 (vs, C=N), 1510 (m, ring), 1500 (m, ring), 1472 cm^{-1} (m, ring); NMR (CF_3COOH) δ 8.97 (br, 1H, SH), 7.30 (m, 4H, C_6H_3 and CH=N), 6.12 (s, 1H, OH), 4.04 (s, 3H, OCH_3), 3.08 (m, 9H, C-1,3,5,3′,5′ H_2), 2.23 (m, 4H, C-4,4′ H_2); NMR (CD_3SOCD_3) δ 10.86 (br, *ca.* 2H, NH_2), 8.97 (br, *ca.* 1H, SH); Found: C, 53.13; H, 5.49; N, 6.16; S, 28.53%. Calcd for $C_{20}H_{24}N_2S_4O_2$: C, 53.07; H, 5.35; N, 6.19; S, 28.32%.

Conversion of IIb into IIIb. A mixture of IIb (1 g), sulfuric acid (96%, 0.5 g), *N,N*-dimethylformamide (25 m*l*) and methanol (50 m*l*) was refluxed for 15 min and allowed to stand at room temperature for 2 hr and then was added water. The resulting material was recrystallized from *N,N*-dimethylformamide-water as orange prisms: yield 400 mg, 62%; mp 229—238°C with dec., undepressed by addition of an authentic specimen. UV and IR spectra of both specimens also were identical.

2 - Amino - 2 - [2-(4-methoxybenzylidenamino)-1-cyclopenten-1-yl]thiocarbonylthiocyclopentanedithiocarboxylic acid (IIc). To an ice-cold solution of I (2.5 g) and anisaldehyde (2.5 g) in methanol (100 m*l*), sulfuric acid (96%, 1 g) was added and kept at 0°C for 10 min. The reaction mixture was worked up as above. Yellow long plates (IIc): yield 3 g, 88%; mp 209—214°C with dec. (slow heating), 213—223°C with dec. (rapid heating); UV λ_{max}^{MeOH} 275, 392 mμ (log ε=4.15, 4.27); IR (KBr) 3389 (m, NH_2), 3294 (s, NH_2), 1607 (vs. C=N), 1510 (s, ring), 1450 cm^{-1} (s, ring); NMR (CF_3COOH) δ 9.50 (br, 1H, SH), 7.18 (m, 5H, C_6H_4 and CH=N), 4.03 (s, 3H, OCH_3), 3.07 (m, 9H, C-1,3,5,3′,5′ H_2), 2.27 (m, 4H, C-4,4′ H_2); NMR (CD_3SOCD_3) δ 10.81 (br, *ca.* 2H, NH_2), 8.97 (br, *ca.* 1H, SH); Found: C, 54.96; H, 5.70; N, 6.53; S, 29.14%. Calcd for $C_{20}H_{24}N_2S_4O$: C, 55.02; H, 5.54; N, 6.42; S, 29.36%.

3 - (3,4 - Methylenedioxyphenyl) - 1,3,4,5,6,7-hexahydro-1-thioxocyclopenta[*d*][1,3]thiazine(IIIa). A solution of I (2 g), piperonal (2 g) and sulfuric acid (96%, 1 g) in methanol (100 m*l*) was refluxed for 35 min. The resulting material was collected and recrystallized from *N,N*-dimethylformamide-water and dried at 110°C under reduced pressure for 1 day to give yellowish orange plates (IIIa): yield 3.6 g, 92%; mp 178—179°C; UV λ_{max}^{EtOH} 341, 408 mμ (log ε=4.00, 4.61); IR ($CHCl_3$) 3406 (s, NH), 1541 (s, conjd C=C), 1520 (s, ring), 1506 (vs, ring), 1446 cm^{-1} (s, ring); NMR (CF_3COOH) δ 9.42 (br, 1H, NH), 7.02 (m, 3H, C_6H_3), 6.14 (d, 1H, *J*=4 Hz, C-3 H), 6.07 (s, 2H, OCH_2O), 3.05 (m, 4H, C-5,7 H_2). 2.37 (m, 2H, C-6 H_2); Found: C, 57.86; H, 4.46; N, 4.79; S. 22.08%. Calcd for $C_{14}H_{13}NS_2O_2$: C, 57.71; H, 4.50; N, 4.81; S, 21.99%.

3-(3-Methoxy-4-hydroxyphenyl)-1,3,4,5,6,7-hexahydro-1-thioxocyclopenta[*d*][1,3]thiazine (IIIb). A solution of I (2.5 g), vanillin (2.5 g) and sulfuric acid (96%, 1 g) in methanol (60 m*l*) was refluxed for 1 hr. The resulting material was worked up as above. Light lustrous orange prisms (IIIb): yield 4.1 g, 89%; mp 229—239°C with dec. (slow heating), 237—250°C with dec. (rapid heating); UV λ_{max}^{EtOH} 340, 408 mμ (log ε=3.93, 4.32); IR ($CHCl_3$) 3365 (s, NH), 1560 (s, conjd C=C), 1505 (vs. ring), 1444 cm^{-1} (m, ring); NMR (CF_3COOH) δ 9.50 (br, 1H, NH), 7.12 (m, 3H, C_6H_3), 6.15 (d, *J*=4 Hz, C-3 H), 3.97 (s, 3H, OCH_3), 3.00 (m, 4H, C-5,7 H_2), 2.36 (m, 2H, C-6 H_2); NMR (CD_3SOCD_3) δ 9.60 (s, 1H, OH), 9.37 (br, 1H, NH); Found: C, 57.31; H, 5.09; N, 4.80; S, 21.60%. Calcd for $C_{14}H_{15}NS_2O_2$: C, 57.32; H, 5.16; N, 4.78; S, 21.85 %.

3 - (4 - Methoxyphenyl) - 1,3,4,5,6,7 - hexahydro-1-thioxocyclopenta[*d*][1,3]thiazine (IIIc). To a hot solution of I (2.5 g) and anisaldehyde (2.5 g) in methanol (100 m*l*), was added sulfuric acid (96%, 1 g) and refluxed for 30 min. The resulting mixture was worked up as above. Red long prisms (IIIc): yield 3.5 g, 81%; mp 179—180°C; UV λ_{max}^{EtOH} 341, 408 mμ (log ε=3.70, 4.08): IR ($CHCl_3$) 3410 (s, NH), 1545 (s, conjd C=C), 1515 cm^{-1} (vs. ring): NMR (CF_3COOH) δ 9.39 (br, 1H, NH), 7.34 (q, 4H, C_6H_4), 6.17 (d, 1H, *J*=4 Hz, C-3 H), 4.08 (s, 3H, OCH_3), 3.03 (m, 4H, C-5,7 H_2), 2.38 (m, 2H, C-6 H_2); Found: C, 60.66; H, 5.34; N, 5.15; S, 23.13%. Calcd for $C_{14}H_{15}NS_2O$: C, 60.62; H, 5.45; N, 5.05; S, 23.11%.

3 - Methyl - 1,3,4,5,6,7 - hexahydro -1- thioxocyclopenta[*d*][1,3]thiazine (IIId). A solution of I (5 g), acetaldehyde (5 g) and sulfuric acid (96%, 2 g) in methanol (150 m*l*) was allowed to stand at room temperature for 64 hr. The resulting reaction mixture was concentrated under reduced pressure and then water was added. The purple material which separated from the solution was recrystallized from methanol-water. Light orange plates (IIId): yield 4.5 g, 78%; mp 128—129°C; UV λ_{max}^{EtOH} 337, 405 mμ (log ε=3.72, 4.26); IR ($CHCl_3$), 3405 (s, NH), 1550 (vs, conjd C=C), 1515 cm^{-1} (vs. ring); NMR (CF_3COOH) δ 9.40 (br, 1H, NH), 5.17 (m, 1H, C-3 H), 2.92 (m, 4H, C-5,7 H_2), 2.25 (m, 2H, C-6 H_2), 1.85 (d, 3H, CH_3); Found: C, 51.83; H, 5.83; N, 7.62; S, 34.87%. Calcd for $C_8H_{11}NS_2$: C, 51.85; H, 5.99; N, 7.55; S, 34.61%.

3-Methyl-3-phenyl-1,3,4,5,6,7-hexahydro-1-thioxocyclopenta[*d*][1,3]thiazine (IIIe). A mixture of I (5 g), acetophenone (5 g), sulfuric acid (96%, 2 g) and methanol (150 m*l*) was refluxed for 3 hr and the reaction mixture was worked up as above. Light orange plates (IIIe): yield 1.6 g, 19.5%; mp 183—184°C (remelted at 195—197°C); UV λ_{max}^{EtOH} 340, 407 mμ (log ε=3.70, 4.30); IR ($CHCl_3$) 3400 (m, NH), 1550 (vs. conjd C=C), 1522 cm^{-1} (s, ring); NMR (CF_3COOH) δ 9.66 (br, 1H, NH), 7.51 (s, 5H, C_6H_5), 3.03 (m, 4H, C-5,7 H_2), 2.31 (m, 2H, C-6 H_2), 2.28 (s, 3H, CH_3); Found: C, 64.41; H, 5.77; N, 5.40; S, 24.73%. Calcd for $C_{14}H_{15}NS_2$: C, 64.32; H, 5.79; N, 5.36; S, 24.53%.

3 - (2 - Hydroxyphenyl) - 1,3,4,5,6,7 - hexahydro - 1-thioxocyclopenta[*d*][1,3]thiazine (IIIf). A solution of I (2 g), salicylaldehyde (2 g) and sulfuric acid (96%, 1 g) in methanol (70 m*l*) was refluxed for 10 min and then allowed to stand at room temperature for 1 hr. The reaction mixture was concentrated under reduced pressure, then water was added. The resulting red material was recrystallized from methanol-water. Red long plates (IIIf): yield 2.2 g, 67%; mp 201—215°C with dec. (slow heating), 211—227°C with dec. (rapid heating); UV λ_{max}^{EtOH} 341, 408 mμ (log ε=3.87, 4.20); IR ($CHCl_3$) 3260 (s, OH), 3160 (s, br, NH), 1560 (s, conjd C=C), 1495 cm^{-1} (vs. ring); NMR (CF_3COOH) δ 9.43 (s, br, 2H, OH and NH), 7.28 (m, 4H, C_6H_4), 6.58 (d, 1H, *J*=5 Hz, C-3 H), 3.02 (m, 4H, C-5,7 H_2), 2.35 (m, 2H, C-6 H_2); Found: C, 59.46; H, 4.92;

N, 5.25; S, 23.95%. Calcd for $C_{13}H_{13}NS_2O$: C, 59.28, H, 4.98; N, 5.32; S, 24.34%.

3-Phenyl-1,3,4,5,6,7-hexahydro-1- thioxocyclopenta[*d*][1,3]thiazine (IIIg). A solution of I (5 g), benzaldehyde (5 g) and sulfuric acid (96%, 2 g) in methanol (150 m*l*) was refluxed for 2 hr. The resulting material was recrystallized from methanol. Red prisms (IIIg): yield 5.1 g, 66%; mp 199—200°C; UV λ_{max}^{EtOH} 340, 408 mμ (log ε=3.86, 4.28); IR ($CHCl_3$) 3400 (s, NH), 1546 (vs. conjd C=C), 1515 cm^{-1} (s, ring); NMR (CF_3COOH) δ 9.45 (br, 1H, NH), 7.49 (m, 5H, C_6H_5), 6.13 (d, 1H, J=4 Hz, C-3 H), 2.97 (m, 4H, C-5,7 H_2), 2.31 (m, 2H, C-6 H_2); Found: C, 63.06; H, 5.11; N, 5.70; S, 25.79%. Calcd for $C_{13}H_{13}NS_2$: C, 63.12; H, 5.30; N, 5.66; S, 25.92%.

3-(2-Methoxypehnyl)-1,3,4,5,6,7-hexahydro-1-thioxocyclopenta[*d*][1,3]thiazine (IIIh). A mixture of I (5 g), *o*-methoxybenzaldehyde (5 g), sulfuric acid (96%, 2 g) and methanol (150 m*l*) was refluxed for 30 min and worked up as above. Light thick plates (IIIh): yield 5.3 g, 61%; mp 201°C; UV λ_{max}^{EtOH} 341, 408 mμ (log ε=3.88, 4.29); IR ($CHCl_3$) 3410 (s, NH), 1547 (vs. conjd C=C), 1510 cm^{-1} (s, ring); NMR (CF_3COOH) δ 9.35 (br, 1H, NH), 7.28 (m, 4H, C_6H_4), 6.56 (d, 1H, J=6 Hz, C-3 H), 3.97 (s, 3H, OCH_3), 3.00 (m, 4H, C-5,7 H_2), 2.36 (m, 2H, C-6 H_2); Found: C, 60.73; H, 5.57; N, 5.10; S, 23.10%. Calcd for $C_{14}H_{15}NS_2O$: C, 60.62; H, 5.45; N, 5.05; S, 23.11%

3-(4-Hydroxyphenyl)-1,3,4,5,6,7-hexahydro-1-thioxocyclopenta[*d*][1,3]thiazine (IIIi). A mixture of I (5 g), *p*-hydroxybenzaldehyde (5 g), sulfuric acid (96%, 2 g) and methanol (150 m*l*) was allowed to stand at room temperature for 30 min and worked up as above. Orange prisms (IIIi): yield 6.4 g, 77%; mp, 197—213°C with dec. (slow heating), 211—220°C with dec. (rapid heating); UV λ_{max}^{EtOH} 340, 408 mμ (log ε=3.88, 4.28); IR ($CHCl_3$) 3268 (s, OH), 3100 (m, br, NH), 1566 (s, conjd C=C), 1512 cm^{-1} (vs. ring); NMR (CF_3COOH) δ 9.49 (br, 1H, NH), 7.27 (q, 4H, C_6H_4), 6.18 (d, 1H, J=4 Hz, C-3 H), 3.00 (m, 4H, C-5,7 H_2), 2.31 (m, 2H, C-6 H_2); Found: C, 59.28; H, 4.83; N, 5.33; S, 24.37%. Calcd for $C_{13}H_{13}NS_2O$: C, 59.28; H, 4.98; N, 5.32; S, 24.34%.

3-(p-Tolyl)-1,3,4,5,6,7-hexahydro-1-thioxocyclopenta[*d*][1,3]thiazine(IIIj). A mixture of I (3 g), *p*-tolualdehyde (3 g), sulfuric acid (96%, 1 g) and methanol (100 m*l*) was refluxed for 30 min and then water was added. The solution was allowed to stand at room temperature for 12 hr. The resulting crystalline material was recrystallized from methanol and dried at 110°C under reduced pressure. Light orange prisms (IIIj): yield 2.3 g, 44%; mp 176—177°C; UV λ_{max}^{EtOH} 340, 408 mμ (log ε=3.91, 4.34); IR ($CHCl_3$) 3420 (s, NH), 1545 (s, conjd C=C), 1515 cm^{-1} (vs. ring); NMR (CF_3COOH) δ 9.50 (br, 1H, NH), 7.40 (s, 4H, C_6H_4), 6.17 (d, 1H, J=3 Hz, C-3 H), 3.08 (m, 4H, C-5,7 H_2), 2.42 (s, 3H, CH_3), 2.38 (m, 2H, C-6 H_2); Found: C, 64.58; H, 6.05; N, 5.36; S, 24.23%. Calcd. for $C_4H_{15}NS_2$: C, 64.32; H, 5.79; N, 5.36; S, 24.53%.

3-Ethyl-3-methyl-1,3,4,5,6,7-hexahydro-1-thioxocyclopenta[*d*][1,3]thiazine(IIIk). A mixture of I (5 g), methyl ethyl ketone (22 g), morpholine (15 g) and ethanol (100 m*l*) was refluxed for 10 hr. The white precipitates which separated from the solution were filtrated, the filtrate was concentrated under reduced pressure and then water was added. The resulting yellow material was recrystallized from ethanol-water and dried at 138°C under reduced pressure for 1 day. Yellow plates (IIIk): yield 4.4 g, 67%; mp 173—174°C; UV λ_{max}^{EtOH} 336, 406 mμ (log ε=3.68, 4.25); IR (KBr) 3180 (s, NH), 1565 (m, conjd C=C), 1520 cm^{-1} (vs. ring); NMR (CD_3COCD_3) δ 9.40 (br, 1H, NH), 3.00 (m, 4H, C-5,7 H_2), 2.25 (m, 4H, C-6 H_2 and CH_2CH_3), 1.85 (s, 3H, CH_3). 1.15 (t, 3H, CH_2CH_3); Found: C, 56.53; H, 7.00; N, 6.54; S, 29.99%. Calcd for $C_{10}H_{15}NS_2$: C, 56.32; H, 7.09; N, 6.57; S, 30.01%.

Compound IIIk was also obtained by refluxing a mixture of I (5 g), methyl ethyl ketone (5 g), sulfuric acid (96%, 2 g) and methanol (100 m*l*) for 1 hr; the yield was 57%.

3,3-Dimethyl-1,3,4,5,6,7-hexahydro-1-thioxocyclopenta[*d*][1,3]thiazine (IIII). A mixture of I (2.5 g), acetone (3 g), sulfuric acid (96%, 1 g) and methanol (100 m*l*) was refluxed for 1.5 hr and then worked up as above: yield 51%, mp 172—173°C, undepressed on admixture with an authentic specimen. IR and UV absorption spectra of IIII were also identical with those of authentic specimen.[2)]

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