REACTIONS OF 1,3-THIAZINE-2,6-DITHIONES. PART 8.1
FORMATION OF A NEW SERIES OF 2-PYRROLINE-4-THIONES BY
THE REARRANGEMENT OF 1,3-THIAZINE-6 SPIRO-2’-THIIRANE-2-
THIONES AND 2-METHYLTHIO-1,3(6H)-THIAZINE-6 SPIRO-2’-
THIIRANES AND SOME RELATED REACTIONS

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Abstract – 1,3(6H)-Thiazine-6-spiro-2’-thiirane-2-thiones 2a-c and 3’,3’-disubstituted 2-methylthio-1,3-thiazine-6-spiro-2’-thiiranes 12a-f were synthesized by the reaction of 1,3-thiazine-2,6-dithiones 1 or 11a-d, which are 2-methylthio derivatives of thiazinedithiones 1, with diazomethane derivatives. 1,3(6H)-Thiazine-6-spiro-2’-thiiranes 2a-c and 12a-f rearranged into a series of 2-pyrroline-4-thione derivatives 3a-c and methyl 4-thioxopyrroline-1-dithiocarboxylates 13a-f on treatment with a base or gentle heating. 2-Pyrroline-4-thione derivative 13c, upon heating to 140 °C for 1 h, reversely rearranged into the thiirane derivative 12c. The structure of the 2-pyrroline-4-thione 13e was determined by single-crystal X-ray analysis.

INTRODUCTION
Previously, we reported on the synthesis of 4,4-disubstituted thiazolizine-2,5-dithiones by the reaction of isothiocyanates with carbon disulfide in the presence of a strong base2 and this reaction resulted in the first synthesis of several 2-pyrroline-4-thiones3 by the transfragment reaction of the thiazolizine-2,5-dithiones with 3-aminoacrylonitrile or 3-aminocinnamnonitriles bearing an alkyl substituent at position-4 of the benzene ring.
Prior to our report, there were only two reports concerning the synthesis of the thiazolizine-2,5-dithiones. One of those reports was presented by Shahak and co-workers,4 and the other was the one by Shaumann and co-workers.5 Renznikov and Volodarskii also reported a method of synthesis of 2-pyrroline-4-thione6 in the same year (1990) as the report by us was presented.
Until now, there seems no other original report regarding the reactions of thiazolizine-2,5-dithiones including the formation of 1-aminoimidazolizine-2,5-dithiones and 2-pyrroline-4-thiones. Further, the authors tried to synthesize various new types of heterocyclic and fused heterocyclic compounds by the reactions of 1,3-thiazine-2,6-dithiones with many types of nucleophiles and found to be obtained fruitful results. Thus, in the reaction with 1,ω-diaminoalkanes, the 1,3-thiazine-2,6-dithiones produced imidazo[2,1-b]pyrimidine-5-thiones, pyrimido[2,1-b]-pyrimidine-4-thiones, pyrimido[2,1-b][1,3]diazepine-4-thiones, and pyrimidodiazepine-4-thiones. In contrast, the same 1,3-thiazine-2,6-dithiones yielded pyrimidobenzimidazole-4-thiones in the reaction with o-phenylenediamine. Various pyrimidine-2,4-dithione derivatives were formed by the reaction of these thiazinedithiones with hydrazines, hydroxylamine, and semicarbazide. Thiosemicarbazide took a different reaction course with those thiazinedithiones and yielded triazolopyrimidines. In reaction with 3-aminoacrylonitriles, the thiazinedithiones gave two kinds of products depending on the solvent used. When the reactions were conducted in THF, pyrimidine-4-thiones were obtained as a result of transfragment reaction and in the reaction using DMF as a polar aprotic solvent, 2-cyanomethyl-2,3-dihydro-1,3-thiazine-6-thiones were formed. Subsequent treatment of these 2,3-dihydro-1,3-thiazine-6-thiones with a strong base eliminated H₂S and 4-thiopyridone derivatives were produced. 1,3,5-Thiadiazine-4-thiones were also formed by the same transfragment reaction between the thiazinedithiones and thioureas. A unique reductive alkylation reaction of thiols with the thiazinethiones produced 2-alkylthio-2,3-dihydro-1,3-thiazine-6-thiones. In addition to the formation of these heterocyclic and fused heterocyclic compounds summarized above, the thiazinedithiones, in reactions with primary amines, alcohols or thiols, ring opening reactions also took place and yielded 3-thioureidocinnamthioamides and 3-[bis(alkylthio)methyleneamino]dithiocinnamic acid esters respectively.

RESULTS AND DISCUSSION

Our current interest is focused on the synthesis of new types of heterocyclic compounds through [3+2] cycloaddition of the 1,3-thiazine-2,6-dithiones with 1,3-dipolar compounds such as phenylidiazethane and diphenylidiazomethane.

Thus, when the 1,3-thiazine-2,6-dithiones bearing an aryl group at position-4 and an arylsulfonyl group at position-5, were allowed to react with diphenylidiazomethane at room temperature without catalyst, 3’,3’-diphenyl-1,3(6H)-thiazine-6-spiro-2’-thiiranes were isolated in fair to good yields. These 6-spiro-2’-thiirane derivatives were, probably, formed via two steps: first, [3+2] cycloaddition
between diphenyldiazomethane and the C=S double bond at position-6 of the thiazinedithiones produced unstable intermediate 1,3,4-thiadiazole derivatives, and second, the generated 1,3,4-thiadiazole derivatives promptly eliminated N\(_2\) to yield the thiiranes 2 (Scheme 1).

Furthermore, when these 6-spiro-2’-thiiane derivatives 2a-c were treated with a strong base such as sodium 1,1-dimethylpropoxide, which is very strongly basic and soluble in almost organic solvents and yet has no nucleophilicity, in THF, a new class of pyrroline-4-thione derivatives 3a-c were formed in fairly good yields through unique rearrangement of the 6-spiro-2’-thiiane derivatives 2a-c and subsequent rapid dedithiocarboxylation of the generated intermediates (2-pyrroline-4-thione-1-dithiocarboxylic acids formed by the rearrangement of the thiiranes 2. Refer to (Scheme 8).

The 6-spiro-2’-thiirane derivative 2d bearing an ethoxycarbonyl group at position-5 was also prepared by the reaction of 1,3-thiazine-2,6-dithione 1d with diphenyldiazomethane together with two other compounds, ethyl 6-diphenylmethylene-2-thioxo-4-p-tolyl-1,3-thiazine-5-carboxylate 4 and ethyl 2-(diphenylmethylthio)-1,3-thiazine-5-carboxylate 5a. The spiro-2’-thiirane derivative 2d, however, never afforded the expected pyrroline-4-thione derivative under reaction conditions similar to that used in the formation of compounds 3a-c, but it afforded an alkene-type product 4 as sole product by desulfurization in quantitative yield.

In the reaction with diphenyldiazomethane, thiazinedithione 1e having a cyano group at position-5, also did not produce the corresponding pyrroline-4-thione derivative, but gave only 2-(diphenylmethyl)thio-1,3-thiazine-4-thione 5b and two kinds of spirothiiranes 6 and 7 (Scheme 2).
In addition, spirothiiranes 9a-d which were synthesized by the reaction similar to the reaction of N-substituted thiazinedithiones 8 with diphenyldiazomethane, never rearranged to the corresponding pyrroline-4-thione derivatives on heating in both boiling toluene and boiling xylene; the starting spirothiiranes were recovered quantitatively. However, on heating to 190 °C in boiling ethyleneglycol, the spirothiiranes 9a-d, yielded alkene-type compounds 10a-d by thermal desulfurization (Scheme 3).

2-Methylthio-4-phenyl-5-phenylsulfonyl-1,3-thiazine-6-thione (11b), which was prepared by methylation of the corresponding 1,3-thiazine-2,6-dithione 1, and upon standing a solution of the methylthio
derivative 11b and diphenyl diazomethane in THF at room temperature, the pyrroline derivative 13b was obtained directly in quantitative yield. The methylthio derivatives 11a,c-e are very important because these compounds 11a,c-e are converted into the spiro-2'-thiiranes 12a,c-e which are able to rearrange to the pyrroline-4-thione derivatives 13a,c-e. High yields of thiiranes 12a,c-e were synthesized under the same reaction conditions as used for the formation of the pyrroline derivative 13b. Thiiranes 12b and 12f were, however, never obtained under the same reaction conditions. Instead, methyl 4-thioxopyrroline-1-dithiocarboxylate derivatives 13b and 13f were formed as sole product in high yields. The 2-methylthio derivatives 11b whose thiazine moiety bears a strongly electron-withdrawing phenylsulfonyl substituent at position-5 is unusually reactive. Thiirane 12b was obtained as the main product for the first time when a solution of 1,3-thiazine-6-thione derivative 11b was allowed to react with diphenyl diazomethane in THF at –50 °C.

This marked difference in the reaction results of (2-methylthio)thiazinethione 11b towards each diazomethane derivative was assumed to be due to the intermediate thiirane derivative 12b which has a phenylsulfonyl group at position-5 makes it much more reactive than other thiirane derivatives 12a,c-e under respective reaction conditions. Therefore, as soon as thiirane derivative 12b was formed, it would rearrange instantaneously into pyrroline-4-thione derivatives 13b (Scheme 4).

To the contrary, all of other thiiranes 12a,c-e are very stable at room temperature and were isolated in
high yields without converting it into the corresponding pyrroline-4-thione derivatives 13a,c-e. However, these very stable thiiranes 12a,c-e rearranged, in the end, to their respective pyrroline-4-thione derivatives 13a,c-e upon refluxing in boiling toluene, accompanied by the desulfurized products, 6-(diphenylmethylene)-1,3-thiazine derivatives 14a,c,d (Scheme 5).

Compared with the yields of the other pyrrolinethione derivatives 13, the yield of compound 13d was abnormally low because desulfurized by-product 14d formed competitively in the fixed reaction conditions.

Furthermore, when pyrroline-4-thione derivative 13c was refluxed in xylene at 140 °C, the 6-spiro-2'-thiirane derivative 12c was obtained in 35% yield by reverse rearrangement of the pyrroline derivative 13c. This reversible rearrangement that occurred between compound 12c and 13c is a very rare phenomenon and the authors tried persistently to find other cases of reversible rearrangement. However, the other pyrroline-4-thione 13d was never converted into 1,3-(6H)-thiazine-6-spiro-2'-thiirane-2-thione 12d. Instead, pyrroline-4-thione 13d yielded only desulfurized 1,3-thiazine derivatives 14d in low yield. The pyrrolines 13a,b,f, however, never changed on heating to 140 °C (Scheme 6).

In the case of the formation of 1,3-thiazine derivatives 14c,d upon heating the pyrroline derivatives 13c,d in boiling xylene, it is inevitable that spiro-2'-thiirane-2-thiones 12c,d, the precursors for the compounds 14, are formed by the inverse rearrangement of pyrroline derivatives 13c,d. The fact that the compound 12d was not isolated even in trace quantities is because of the following reason: under the fixed reaction conditions, as soon as the compound 12d formed, this thiirane 12d rapidly decomposed into 1,3-thiazine derivative 14d by thermal desulfurization.
The structure of representative pyrroline-4-thione derivative 13e was determined by X-ray crystal structure analysis in addition to confirmation by IR, $^1$H- and $^{13}$C-NMR spectra and elemental analysis. The ORTEP view of compound 13e is shown in Figure 1. The detailed data for the single-crystal X-ray analysis of pyrroline derivative 13e are shown in the Experimental Section (Figure 1).

The marked difference that the above-mentioned rearrangement takes place or does not, depending upon the substituent at position-5 of N-unsubstituted 3',3'-diphenyl-1,3(6H)-thiazine-6-spiro-2'-thiirane derivatives 2 is, seemingly, curious. However, from the result of calculated heat of reaction based on the
heat of formation by MOPAC PM5, it is ascertained obviously that the rearrangement yielding a new series of 2-pirrolime-4-thiones takes place or does not (Scheme 7).

For example, the heat of formation for intermediate 2-phenyl-3-phenylsulfonyl-5,5-diphenyl-4-thioxopyrroline-1-dithiocarboxylate anion C, which was formed via the rearrangement of transient acyclic dithiocarboxylate anion B, was estimated to be 32.4 kcal/mol and that for the anion A of the reactant thiirane derivative 2a was estimated to be 41.7 kcal/mol. As a result, the heat of reaction in this rearrangement is estimated to be $\Delta H = 9.3$ kcal, which means that the rearrangement of compound 2a to pyrroline derivative 3a is exothermic and the rearrangement proceeds smoothly.

On the other hand, similar calculation revealed that the heat of formation of the intermediate 3-ethoxycarbonyl-2-p-tolyl-4-thioxo-2-pyrroline-1-dithiocarboxylate anion F through transient acyclic dithiocarboxylate anion E and that for 5-ethoxycarbonyl-5,5-diphenyl-2-p-tolyl-1,3(6H)-thiazine-6-spiro-2-thiolate anion D, are very close. Accordingly, the heat of reaction for this rearrangement from

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\begin{align*}
\text{Scheme 7}
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1,3(6H)-thiazine-6-spiro-2'-thiirane-2-thiolate anion D to the pyrroline-1-dithiocarboxylate anion F was estimated to be $-\Delta H = 1.2$ kcal. Consequently, 1,3(6H)-thiazine-6-spiro-2'-thiirane derivative 2d did not yield expected pyrroline derivative but produced desulfurized ethyl 6-diphenylmethylene-2-thioxo-1,3(6H)-thiazine-5-carboxylate 4 in quantitative yield in the presence of sodium 1,1-dimethylethoxide.

In addition, the calculated heat of reactions of the pyrroline derivatives 13a,b,e produced by the rearrangement were estimated to be $-\Delta H = 2.6$–$9.7$ kcal. These results point out that the pyrroline-4-thione derivatives 13a,b,e by this rearrangement are all exothermic. The calculation results mentioned above suggest that the formation of pyrroline-4-thione derivatives 13a,b,e are formed in high yields. The pirrolinethiones 13a,b,e were really obtained in high to quantitative yields.

To the contrary, compared with each calculated heat of formation for 1,3(6H)-thiazine-6-spiro-2'-thiiranes 12c,d, those for pyrroline derivatives 13c,d were estimated to be high by 6.5–7.3 kcal/mol. These calculation results point out that these rearrangements are both endothermic and heating at high temperature for a long time in toluene is needed to form corresponding pyrroline derivatives 13c,d. Due to the drastic thermal condition, desulfurized products 14c,d were also formed as by-products.

![Scheme 8](image)

The rearrangement process that leads to the formation of pyrroline derivatives 3 and 13, starting with the reaction of 1,3-thiazine-2,6-dithiones or 2-methylthio-1,3-thiazine-6-thiones with higher analogs of
diazomethane, is expected to occur as follows: During the rearrangement of 2-methylthiothiazine-6-spirothiiranes 12 into methyl 4-thioxopyrroline-1-dithiocarboxylate derivatives 13, the 6-spirothiiranes 12 would first open the thiazine ring by reversible electrocyclic reaction to form acyclic intermediates H, which convert to isomeric intermediates I. Subsequent rearrangement of acyclic intermediates I would lead to methyl 4-thioxopyrroline-1-dithiocarboxylates by [1,5]sigmatropy of the intermediates I.

On the other hand, in the rearrangement of 1,3-thiazine-6-spiro-2′-thiirane-2-thiones 2 to the pyrrolinethiones 3, similar stepwise openings of both thiazine and thiirane rings would take place via electrocyclic reaction and would result in [1,5]sigmatropy of the ene-thiolate anions formed by a base. The generated intermediates J are neutralized to form dithiocarbamic acids K on acidification of the reaction mixture. The intermediates K are very unstable and dedithiocarboxylate swiftly to give N-unsubstituted pyrrolines 3 (Scheme 8).

EXPERIMENTAL

Mps were measured on a METTLER FP62 automatic melting point measurement apparatus and are uncorrected. NMR spectra were determined with a JEOL JNM-GX270-FT spectrometer at 270 MHz with tetramethylsilane as internal standard. IR spectra were determined with a JASCO FT-IR-5300 fourier transfer infrared spectrometer. UV and visible spectra were obtained on a Shimadzu UV-3100S UV-Vis recording spectrophotometer. All solvents used for each reaction and eluents for column chromatography were dried and distilled before use.

Starting Materials. 1,3-Thiazine-2,6-dithiones 1 and 3-substituted 1,3-thiazine-2,6-dithiones 8 were prepared by the reported method of synthesis by us.13 2-Methylthio-1,3-thiazine-6-thiones 11 were prepared by methylation of compounds 1 with iodomethane.4 Diphenyl diazomethane was prepared by usual method (oxidation of hydrazones by HgO)17 and 1-phenyl diazoethane was prepared by applying the synthesis of phenyl diazomethane.18 The concentration of phenyl diazomethane was determined by back titration.19

3′,3′-Diphenyl-5-phenylsulfonyl-1,3(6H)-thiazine-6-spiro-2′-thiirane-2-thione (2); To a solution of each 5-arylsulfonyl-1,3-thiazine-2,6-dithione (1a-c) (1 mmol) in THF (50 mL), was added dropwise a solution of diphenyl diazomethane (0.291 g, 1.5 mmol) in THF (5 mL) at room temperature. After 1 h, the reaction mixture was evaporated to dryness and then was added Et2O (50 mL). The resulting solid was collected, dried, and recrystallized from each mixed solvent in parentheses after each mp.

4,3′,3′-Triphenyl-5-phenylsulfonyl-1,3(6H)-thiazine-6-spiro-2′-thiirane-2-thione (2a); Yield 70%. Mp 201.5-202.0 °C (CH2Cl2-hexane). δH (DMSO-d6) 13.00 (s, br, 1H, NH) and 7.50-7.20 ppm (m, 20H, Ph×4). δC (DMSO-d6) 197.4, 152.6, 140.9, 138.9, 137.7, 132.8, 132.4, 132.1, 129.1, 129.0, 128.5, 128.0, 127.9, 127.66, 125.7, 116.1, 67.5, and 51.0 ppm. υmax (KBr) 3207 (NH), 3059, 2918, 1604, 1468, 1447,
1309 and 1141 (SO\(_2\)), 1257, 1179, 1074, 1037, 1024, 1001, 970, 941, 760, 727, 704, 667, 652, 629, and 500 cm\(^{-1}\). (Found: C, 63.79; H, 3.66; N, 2.58; S, 23.70. C\(_{29}\)H\(_{21}\)NO\(_2\)S\(_4\) requires C, 64.06; H, 3.89; N, 2.58; S, 23.59%)

4,3',3'-Triphenyl-5-p-tolylsulfonfyl-1,3(6H)-thiazine-6-spiro-2'-thiirane-2-thione (2b); Yield 67%. Mp 205.5 \(^\circ\)C (DMSO-H\(_2\)O). \(\delta\) (DMSO-\(d_6\)) 12.96 (s, br, 1H, NH), 7.5-7.1 (m, 14H, Ar), and 2.31 ppm (s, 3H, CH\(_3\)). \(\delta\) (DMSO-\(d_6\)) 197.30, 169.3, 152.8, 152.3, 143.3, 143.0, 139.5, 138.9, 138.1, 138.0, 137.8, 137.6, 133.0, 132.5, 131.0, 130.8, 129.0, 128.9, 128.8, 128.0, 127.9, 127.8, 127.7, 127.6, 116.4, 114.3, 67.5, 54.7, 51.1, 50.3, and 20.9 ppm. \(\nu_{\text{max}}\) (KBr) 3258 (NH), 3059, 2917, 1595, 1491, 1462, 1302, and 1142 (SO\(_2\)), 1257, 1074, 1022, 941, 758, 700, 665, 605, 557, and 530 cm\(^{-1}\). (Found: C, 64.68; H, 4.09; N, 2.52; S, 23.18. C\(_{30}\)H\(_{23}\)NO\(_2\)S\(_4\) requires C, 64.97; H, 4.16; N, 2.51; S, 22.99%)

3',3'-Diphenyl-4-p-tolylsulfonfyl-1,3(6H)-thiazine-6-spiro-2'-thiirane-2-thione (2c); Yield 80%. Mp 207.0 \(^\circ\)C (DMSO-H\(_2\)O). \(\delta\) (DMSO-\(d_6\)) 12.88 (s, br, 1H, NH), 7.5-7.1 (m, 18H, Ar), 2.35 (s, 3H, CH\(_3\)), and 2.31 ppm (s, 3H, CH\(_3\)). \(\delta\) (DMSO-\(d_6\)) 197.30, 169.3, 152.8, 152.3, 143.3, 143.0, 139.5, 138.9, 138.0, 137.8, 137.6, 133.0, 132.5, 131.0, 130.8, 129.0, 128.9, 128.8, 128.0, 127.9, 127.8, 127.7, 127.6, 116.4, 114.3, 67.5, 54.7, 51.1, 50.3, and 20.9 ppm. \(\nu_{\text{max}}\) (KBr) 3260 (NH), 3055, 3030, 2917, 1595, 1491, 1456, 1444, 1300, and 1140 (SO\(_2\)), 1256, 1184, 1074, 1037, 1020, 941, 810, 775, 743, 704, 664, 604, 556, and 530 cm\(^{-1}\). (Found: C, 65.05; H, 4.42; N, 2.46; S, 22.17. C\(_{31}\)H\(_{25}\)NO\(_2\)S\(_4\) requires C, 65.12; H, 4.41; N, 2.45; S, 22.43%)

3-Arylsulfonyl-5,5-diphenylpyrroline-4-thiones (3); A mixture of each 5-arylsulfonyl-3',3'-diphenyl-1,3(6H)-thiazine-6-spiro-2'-thiirane-2-thione 2 (1 mmol), sodium 1,1-dimethylpropoxide (0.220 g, 2 mmol), and THF or DMF (80 mL) was warmed at 60 \(^\circ\)C for 3 h. Water (150 mL) was added to the reaction mixture, and the resulting aqueous solution was acidified by adding 2 M-HCl at 0 \(^\circ\)C. The resulting solid was collected, dried, and recrystallized from each mixed solvent in parentheses next each mp.

2,5,5-Triphenyl-3-phenylsulfonylpyrroline-4-thione (3a); Yield 61%. Mp 209.0-209.5 \(^\circ\)C (DMF-EtOH-H\(_2\)O). \(\delta\) (DMSO-\(d_6\)) 12.00 (s, br, 1H, NH) and 7.85-7.10 ppm (m, 20H, Ph×4). \(\delta\) (DMSO-\(d_6\)) 217.2, 174.2, 141.8, 139.7, 132.6, 131.3, 129.2, 128.6, 128.3, 128.2, 128.1, 128.0, 127.8, 127.0, 125.0, and 86.2 ppm. \(\nu_{\text{max}}\) (KBr) 3207 (NH), 3059, 2879, 1535, 1489, 1458, 1418, 1352, 1307, and 1144 (SO\(_2\)), 1277, 1204, 1078, 1024, 999, 758, 735, 694, 623, 589, 557, and 532 cm\(^{-1}\). (Found: C, 71.62; H, 4.53; N, 2.94; S, 13.70. C\(_{29}\)H\(_{21}\)NO\(_2\)S\(_2\) requires C, 71.92; H, 4.53; N, 3.00; S, 13.72%)

2,5,5-Triphenyl-3-p-tolylsulfonfylpyrroline-4-thione (3b); Yield 67%. Mp 226.5 \(^\circ\)C (acetone-hexane). \(\delta\) (DMSO-\(d_6\)) 12.07 (s, br, 1H, NH), 7.73, 7.60, 7.31, and 7.20 (each m, 4+3+8+4H, Ph×3+tolyl) and 2.33 ppm (s, 3H, CH\(_3\)). \(\delta\) (DMSO-\(d_6\)) 217.0, 174.1, 142.9, 139.8, 139.0, 131.3, 129.2, 128.8, 128.6, 128.1, 128.0, 127.8, 127.1, 125.2, 86.1, and 20.9 ppm. \(\nu_{\text{max}}\) (KBr) 3190 (NH), 3059, 1541, 743, 704, 664, 604, 556, and 530 cm\(^{-1}\). (Found: C, 71.62; H, 4.53; N, 2.94; S, 13.70. C\(_{30}\)H\(_{23}\)NO\(_2\)S\(_4\) requires C, 71.92; H, 4.53; N, 3.00; S, 13.72%)
5,5-Diphenyl-2-p-tolyl-3-p-tolylsulfonylpyrroline-4-thione (3c); Yield 67%. Mp 225.0 °C (acetone-hexane). δH (DMSO-d6) 11.95 (s, br, 1H, NH), 7.71, 7.61, 7.36, (each d, each 2H, J = all 8 Hz, toyl×2), 7.39 and 7.16 (each m, 10+4H, Ph×2+tolyl), 2.42 (s, 3H, CH3), and 2.36 ppm (s, 3H, CH3).

Formation of 6-Spiro-2'-thiirane-5-carboxylate (2d), Ethyl 6-Diphenylmethylidene-2-thioxo-4-p-tolyl-1,3-thiazine-5-carboxylate (4), and Ethyl 2-Diphenylmethylthio-6-thioxo-4-p-tolyl-1,3-thiazine-5-carboxylate (5a) by the Reaction of Ethyl 2,6-Dithioxo-4-p-tolyl-1,3-thiazine-5-carboxylate (1d) with Diphenyldiazomethane. To a solution of ethyl 2,6-dithioxo-4-p-tolyl-1,3-thiazine-5-carboxylate (1d) (0.323 g, 1 mmol) in THF (10 mL), a solution of diphenyldiazomethane (0.291 g, 1.5 mmol) in THF (10 mL) was added at room temperature. After 10 min, the solvent was removed under reduced pressure and the residue was column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 20). Resulting each eluate was evaporated to dryness and each residue was washed with EtOH. Ethyl 3',3'-triphenyl-2-thioxo-4-p-tolyl-1,3(6H)-thiazine-6-spiro-2'-thiirane-5-carboxylate (2d) (0.166 g, 34%), ethyl 6-diphenylmethylidene-2-thioxo-4-p-tolyl-1,3-thiazine-5-carboxylate (4) (0.133 g, 29%), and ethyl 2-diphenylmethylthio-6-thioxo-4-p-tolyl-1,3-thiazine-5-carboxylate (5a) (0.059 g, 12%) were isolated respectively.

Ethyl 3',3'-Triphenyl-2-thioxo-4-p-tolyl-1,3(6H)-thiazine-6-spiro-2'-thiirane-5-carboxylate (2d); Yield 34%. Mp 219.0-220.0 °C (C6H6-hexane). δH (CDCl3) 9.05 (s, br, 1H, NH), 7.5-7.2 (m, 14H, Ar), 3.64 (q, 1H, J=8 Hz, OCH2), and 3.57 (q, 1H, J=8 Hz, OCH2), 2.37 (s, 3H, CH3), 0.73 ppm (t, 3H, J=8 Hz, CH3). δC (CDCl3) 196.9, 164.2, 144.3, 144.1, 143.7, 141.0, 140.2, 139.9, 139.0, 138.9, 131.3, 130.2, 129.6, 129.2, 128.9, 128.4, 128.2, 128.1, 128.0, 127.9, 111.6, 68.8, 61.0, 60.7, 56.6, 21.4, and 13.5 ppm. νmax (KBr) 3234 (NH), 3052, 3021, 2988, 2923, 1696 (COO), 1631, 1508, 1473, 1445, 1369, 1318, 1309, 1273, 1249, 1220, 1180, 1094, 1044, 1020, 825, 768, 746, 700, 615, 564, and 532 cm⁻¹. UV-Vis λmax (EtOH) 225.4 (log ε 4.38), 252.8 (4.15), 333.6 (4.08), and 295.2 nm (3.22) (Found: C, 66.10; H, 4.83; N, 2.87; S, 19.70. C27H23NO2S3 requires C, 66.23; H, 4.73; N, 2.86; S, 19.64%)

Ethyl 6-Diphenylmethylidene-2-thioxo-4-p-tolyl-1,3(6H)-thiazine-5-carboxylate (4); Yield 29%. Mp 227.0-228.0 °C (CH2Cl2-hexane). δH (CDCl3)12.38 (s, br, 1H, NH), 7.44 (d, 4H, J=7 Hz, Ph-2,6×2),
7.3-7.1 (m, 10H, Ar), 3.06 (q, 2H, \(J = 8\) Hz, OCH\(_2\)), 2.32 (s, 3H, CH\(_3\)), and 0.61 ppm (t, 3H, CH\(_3\))

\[\delta (\text{CDCl}_3) \ 191.3, 163.9, 144.8, 142.0, 139.1, 138.5, 130.4, 129.9, 129.5, 128.8, 128.6, 128.4, 128.0, 127.8, 127.7, 120.3, 111.9, 59.9, 20.9, and 13.1 ppm.\]

\[\nu_{\text{max}} (\text{NH}) 3164, 3080, 2987, 2932, 1714 (\text{COO}), 1623, 1510, 1484, 1441, 1365, 1305, 1284, 1260, 1199, 1149, 1104, 1052, 1025, 973, 906, 831, 775, 762, 728, 697, 623, and 578 cm\(^{-1}\).\]

\[\lambda_{\text{max}} (\text{EtOH}) 255.8 (\log \varepsilon 4.25), 293.6 (4.36), 325.6 (4.28), and 380.0 nm (3.73).\] (Found: C, 70.08; H, 5.08; N, 2.98; S, 14.32. \(\text{C}_{26}\text{H}_{23}\text{NO}_{2}\text{S}_2\) requires C, 70.08; H, 5.20; N, 3.14; S, 14.39%)

**Ethyl 2-Diphenylmethylthio-6-thioxo-4-\(p\)-tolyl-1,3(6\(H\))-thiazine-5-carboxylate (5a);** Yield 12%. Mp 239.5-240.5 °C (C\(_6\)H\(_6\)-hexane). \(\delta_H\) (DMSO-\(d_6\)) 7.50 (d, 4H, \(J = 7\) Hz, Ph-2,6×2), 7.39 (t, 4H, \(J = 7\) Hz, Ph-3,5×2), 7.24 (d, 2H, \(J = 8\) Hz, \(p\)-tolyl-2,6), 7.20 (d, 2H, \(J = 8\) Hz, \(p\)-tolyl-3,5), 6.49 (s, 1H, CH\(_2\)Ph), 4.10 (q, 2H, \(J = 7\) Hz, OCH\(_2\)), 2.35 (s, 3H, CH\(_3\)), and 1.06 ppm (t, 3H, CH\(_3\))

\[\delta (\text{DMSO-}\ 199.9, 176.1, 166.4, 150.3, 141.7, 138.8, 133.5, 129.1, 128.8, 128.6, 128.0, 127.8, 126.9, 61.6, 54.3, 20.9, and 13.4 ppm. \]

\[\nu_{\text{max}} (\text{KBr}) 3026, 2978, 2921, 2855, 1719 (\text{COO}), 1838, 1609, 1521, 1509, 1459, 1340, 1254, 1230, 1188, 1098, 1061, 952, 857, 839, 748, 727, 698, 629, and 421 cm\(^{-1}\).\]

\[\lambda_{\text{max}} (\text{EtOH}) 266.8 (\log \varepsilon 4.23), 324.0 (4.29), and 440.0 nm (3.93).\] (Found: C, 66.57; H, 4.74; N, 2.82; S, 19.94. \(\text{C}_{27}\text{H}_{23}\text{NO}_{2}\text{S}_3\) requires C, 66.23; H, 4.73; N, 2.86; S, 19.64%)

**Thermal Decomposition of Ethyl 3',3'-Triphenyl-2-thioxo-4-\(p\)-tolyl-1,3(6\(H\))-thiazine-6-spiro-2'-thiirane-5-carboxylate (2d).** A mixture of ethyl 3',3'-triphenyl-2-thioxo-4-\(p\)-tolyl-1,3(6\(H\))-thiazine-6-spiro-2'-thiirane-5-carboxylate (2d) (0.244 g, 0.5 mmol), sodium 1,1-dimethylpropoxide (0.110 g, 1 mmol), and THF (40 mL) was heated at 60 °C for 24 h. Water (100 mL) was added to separate ethyl 6-diphenylmethylidene-2-thioxo-4-\(p\)-tolyl-1,3-thiazine-5-carboxylate (4) in 99% (0.226 g) yield.

**Reaction of 2,6-Dithioxo-4-\(p\)-tolyl-1,3-thiazine-5-carbonitrile (1e) with Diphenyldiazo methane.** To the THF (10 mL) solution of 5-cyano-4-\(p\)-tolyl-1,3-thiazine-2,6-dithione (1e, 0.276 g, 1 mmol) in THF (10 mL), was added a (THF) solution of diphenyldiazo methane (0.291 g, 1.5 mmol) in THF (10 mL) at 0 °C. After the reaction mixture was allowed to stand at 0 °C for 90 min, the solvent was removed under reduced pressure and then the residue was subjected to column chromatography (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 20). Resulting each eluate was (were) evaporated to dryness, and (then) washed with (by) EtOH to give 2-diphenylmethyldithio-1,3-thiazine-6-thione (5b) and two kinds of spiro-2'-thiiranes (6) and (7). Physical and each spectral data for compounds 5b, 6 and 7 were as follows:

**2-Diphenylmethyldithio-1,3-thiazine-6-thione (5b);** Yield 37% (0.164 g). Mp 91.5-92.0 °C (EtOH). \(\delta_H\) (CDCl\(_3\)) 7.5-7.2 (m, 14H, Ar), 6.38 (s, 1H, CH), and 2.41 ppm (s, 3H, CH\(_3\)). \(\delta_C\) (CDCl\(_3\)) 198.8, 179.1, 159.1, 143.8, 138.2, 132.7, 130.2, 129.7, 129.3, 129.0, 128.7, 128.5, 128.3, 128.2, 115.4, 107.7, 55.9, and 21.8 ppm. \(\nu_{\text{max}}\) (KBr) 3058, 3026, 2978, 2917, 2214 (CN), 1605,
1490, 1432, 1401, 1245, 1185, 1078, 1031, 947, 824, 764, 747, 698, 627, 586, and 546 cm\(^{-1}\).

UV-Vis \(\lambda_{max} \) (EtOH) 250.0 (log \(\epsilon\) 4.11), 282.4 (4.12), 312.8 (4.16), and 429.6 nm (3.54).

(Found: C, 67.55; H, 4.12; N, 6.11; S, 21.56. C\(_{25}\)H\(_{18}\)N\(_2\)S\(_3\) requires C, 67.84; H, 4.10; N, 6.33; S, 21.73%)

3',3'-Diphenyl-3-diphenylmethyl-2-thioxo-4-p-tolyl-1,3(6\(H\))-thiazine-6-spiro-2'-thiirane-5-carbonitrile (6); Yield 10% (0.060 g). Mp 168.5 °C (EtOH). \(\delta\)_H (CDCl\(_3\)) 7.5-7.2 (m, 24H, Ar), 6.72 (s, 1H, CH), and 2.22 ppm (s, 3H, CH\(_3\)).

\(\delta\)_C (CDCl\(_3\)) 194.1, 158.8, 141.4, 137.9, 137.1, 136.2, 130.3, 130.3, 129.9, 129.8, 129.2, 128.5, 128.3, 128.1, 127.9, 127.7, 127.2, 127.0, 115.8, 71.7, 67.9, 51.8, and 21.4 ppm.

\(\nu_{max}\) (KBr) 3061, 3022, 2922, 2217 (CN), 1591, 1556, 1492, 1454, 1443, 1323, 1284, 1255, 1226, 1182, 1148, 1077, 1052, 1031, 1017, 1000, 937, 904, 819, 766, 743, 716, 698, 630, 617, 607, and 592 cm\(^{-1}\).

UV-Vis \(\lambda_{max} \) (EtOH) 250.0 (log \(\epsilon\) 4.11), 282.4 (4.12), 312.8 (4.16), and 429.6 nm (3.54). (Found: C, 75.09; H, 4.78; N, 4.52; S, 15.62. C\(_{38}\)H\(_{28}\)N\(_2\)S\(_3\) requires C, 74.96; H, 4.64; N, 4.60; S, 15.80%)

3',3'-Diphenyl-2-diphenylmethylthio-4-p-tolyl-1,3(6\(H\))-thiazine-6-spiro-2'-thiirane-5-carbonitrile (7); Yield 30% (0.182 g). Mp 104.0-105.0 °C (EtOH). \(\delta\)_H (CDCl\(_3\)) 7.1-7.5 (m, 24H, Ar), 6.35 (s, 1H, CH), and 2.24 ppm (s, 3H, CH\(_3\)).

\(\delta\)_C (CDCl\(_3\)) 168.6, 165.0, 159.4, 158.3, 146.3, 140.7, 140.6, 139.5, 139.4, 139.1, 137.9, 137.7, 133.1, 130.7, 130.4, 129.7, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 128.4, 128.3, 128.2, 128.1, 127.9, 127.8, 127.7, 116.6, 116.5, 116.4, 93.4, 39.0, 69.6, 54.7, 53.2, and 21.5 ppm. \(\nu_{max}\) (KBr) 3056, 3025, 2920, 2851, 2207 (CN), 1608, 1509, 1492, 1445, 1319, 1302, 1184, 1104, 1077, 1030, 984, 960, 900, 824, 747, 699, 632, 586, 367, and 352 cm\(^{-1}\). UV-Vis \(\lambda_{max} \) (EtOH) 253.4 (log \(\epsilon\) 4.25), 303.0 (4.30), and 409.6 nm (3.72). (Found: C, 75.19; H, 4.70; N, 4.70; S, 15.56. C\(_{38}\)H\(_{28}\)N\(_2\)S\(_3\) requires C, 74.96; H, 4.64; N, 4.60; S, 15.80%)

Reaction of 2-Diphenylmethylthio-6-thioxo-4-p-tolyl-1,3-thiazine-5-carbonitrile (5b) with Diphenyl-diazomethane. To the THF (10 mL) solution of 5-cyano-2-diphenylmethylthio-4-p-tolyl-1,3-thiazine-6-thione (5) (0.221 g, 0.5 mmol), a THF solution (10 mL) of diphenyldiazomethane (0.097 g, 0.5 mmol) was added at 0 °C. The reaction mixture was allowed to stand at 0 °C for 90 min. The solvent was removed at reduced pressure and then subjected to column chromatography (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 20). 3',3'-Diphenyl-2-diphenylmethylthio-4-p-tolyl-1,3(6\(H\))-thiazine-6-spiro-2'-thiirane-5-carbonitrile (7) was yielded in 15% (0.091 g).

3-Substituted 3',3'-Diphenyl-1,3(6\(H\))-thiazine-6-spiro-2'-thiirane-2-thiones (9); A mixture of each 3-substituted 1,3-thiazine-2,6-dithione 8 (1 mmol), diphenyldiazomethane (0.233 g, 1.2 mmol), and THF (50 mL) was allowed to stand for 1 h at room temperature. The solvent was removed at reduced pressure and then subjected to column chromatography (silica gel 60, 400 mesh, benzene) and recrystallized from each mixed solvent in parentheses.

3,4-Dimethyl-3',3'-diphenyl-2-thioxo-1,3(6\(H\))-thiazine-6-spiro-2'-thiirane-5-carbonitrile (9a); Yield
98%. Mp 243.0-246.5 °C (CH₂Cl₂-hexane). δH (CDCl₃) 7.4-7.2 (m, 10H, Ph×2), 3.83 (s, 3H, N-CH₃), and 2.36 (s, 3H, CH₃) ppm. δC (CDCl₃) 196.6, 153.7, 138.3, 129.7, 129.5, 129.1, 128.9, 128.7, 128.5, 128.4, 128.3, 128.2, 115.3, 99.1, 68.6, 51.4, 39.1, and 21.2 ppm. νmax (KBr) 2209 (CN), 1603, 1447, 1383, 1331, 1277, 1169, 1103, 1005, 822, 770, 747, 704, and 644 cm⁻¹. UV-Vis λmax (EtOH) 228.5 (log ε 4.06), 262.5 (3.20), 334.5 (4.13), and 403.5 nm (2.94). (Found: C, 63.28; H, 4.33; N, 7.25; S, 25.61. C₂₀H₁₆N₂S₃ requires C, 63.12; H, 4.24; N, 7.35; S, 25.28%)

3-Methyl-4',3',3'-triphenyl-2-thioxo-1,3(6H)-thiazine-6-spiro-2'-thiirane-5-carbonitrile (9b); Yield 89%. Mp 255.0-261.0 °C (CH₂Cl₂-hexane). δH (CDCl₃) 7.5-7.3 (m, 15H, Ph×3) and 3.51 ppm (s, 3H, NCH₃). δC (CDCl₃) 197.0, 156.3, 138.1, 137.8, 132.2, 131.4, 129.8, 129.3, 128.8, 128.6, 128.3, 127.9, 115.5, 99.7, 68.5, 51.5, and 42.5 ppm. νmax (KBr) 2216 (CN), 1593, 1489, 1445, 1426, 1331, 1321, 1290, 1263, 1231, 1198, 1113, 1080, 1053, 1028, 1001, 976, 928, 895, 847, 785, 774, 750, 704, and 675 cm⁻¹. UV-Vis λmax (EtOH) 230.0 (log ε 4.12), 263.0 (3.95), 338.5 (4.09), and 418.0 nm (3.49). (Found: C, 67.87; H, 4.27; N, 6.18; S, 21.55. C₂₅H₁₈N₂S₃ requires C, 67.84; H, 4.10; N, 6.33; S, 21.73%)

3-Methyl-3',3'-diphenyl-2-thioxo-4-p-tolyl-1,3(6H)-thiazine-6-spiro-2'-thiirane-5-carbonitrile (9c); Yield 93%. Mp 289.0 °C (CH₂Cl₂-hexane). δH (CDCl₃) 7.57 (d, 2H, J = 7 Hz, NPh-o), 7.53 (d, 2H, J = 7 Hz, 3-Ph-o), 7.4-6.9 (m, 16H, Ph×4), 3.40 and 3.37 (each q, each 1H, J = 7 Hz, OCH₂), and 0.55 (t, 3H, J = 7 Hz, CH₃) ppm. δC (CDCl₃) 196.0, 164.1, 146.5, 139.9, 139.0, 133.4, 130.1, 129.8, 129.6, 128.9, 128.7, 128.5, 128.2, 127.8, 115.6, 99.2, 68.5, 51.5, 42.6, and 21.5 ppm. νmax (KBr) 2216 (CN), 1591, 1560, 1508, 1491, 1458, 1442, 1340, 1313, 1294, 1265, 1219, 1186, 1157, 1109, 1076, 1020, 993, 939, 846, 819, 769, 735, 700, and 669 cm⁻¹. UV-Vis λmax (EtOH) 229.0 (log ε 4.15), 272.5 (4.01), 338.5 (4.14), and 422.0 nm (3.41). (Found: C, 68.10; H, 4.28; N, 5.86; S, 20.88. C₂₆H₂₀N₂S₃ requires C, 66.83; H, 4.41; N, 6.13; S, 21.06%)

Ethyl 3,4,3',3'-Tetraphenyl-2-thioxo-1,3(6H)-thiazine-6-spiro-2'-thiirane-5-carboxilate (9d); Yield 71%. Mp 156.0-158.0 °C (CH₂Cl₂-hexane). δH (CDCl₃) 7.57 (d, 2H, J = 7 Hz, NPh-o), 7.53 (d, 2H, J = 7 Hz, 3-Ph-o), 7.4-6.9 (m, 16H, Ph×4), 3.40 and 3.37 (each q, each 1H, J = 7 Hz, OCH₂), and 0.55 (t, 3H, J = 7 Hz, CH₃) ppm. δC (CDCl₃) 196.0, 164.1, 146.5, 139.9, 139.0, 133.4, 130.1, 129.8, 129.6, 128.9, 128.7, 128.5, 128.2, 127.7, 119.7, 68.1, 60.8, 53.1, and 13.2 ppm. νmax (KBr) 1714 (COO), 1624, 1591, 1543, 1489, 1444, 1367, 1311, 1275, 1213, 1178, 1086, 1016, 966, 922, 895, 856, 812, 750, 692, and 661 cm⁻¹. UV-Vis λmax (EtOH) 232.5 (log ε 4.42), and 331.0 (4.09), 415.5 nm (2.83). (Found: C, 69.42; H, 4.76; N, 2.59; S, 17.23. C₃₂H₂₅NO₂S₃ requires C, 69.66; H, 4.57; N, 2.54; S, 17.43%)

Thermal Decomposition of N-Substituted 3',3'-Diphenyl-1,3(6H)-thiazine-6-spiro-2'-thiirane-2-thiones (9); The ethylene glycolic solution (40 mL) of each 3-substituted 3',3'-diphenyl-1,3(6H)-thiazine-6-spiro-2'-thiirane-2-thione 9 (1 mmol) was heated at 190 °C for 1 h. The resulting each solution was cooled to 0 °C to separate each solid. Each collected
was washed with EtOH, dried, and recrystallized from each mixed solvent in parentheses.

**3,4-Dimethyl-6-diphenylmethyldene-2-thioxo-1,3-thiazine-5-carbonitrile (10a)**; Yield 72%. Mp 250.0-151.0 °C (CH$_2$Cl$_2$-hexane). $\delta_H$ (CDCl$_3$) 7.37 (m, 6H, Ph-$m,p$), 7.15 and 7.07 (each m, each 2H, Ph-$o$), 3.70 (s, 3H, NCH$_3$), and 2.45 (s, 3H, CH$_3$) ppm. $\delta_C$ (CDCl$_3$) 195.0, 152.0, 139.0, 138.9, 130.4, 129.2, 129.0, 128.5, 128.4, 115.8, 115.0, 97.8, 38.9, and 20.5 ppm. $\nu_{\text{max}}$ (KBr) 2212 (CN), 1560, 1491, 1429, 1379, 1340, 1315, 1277, 1192, 1105, 1059, 1006, 953, 923, 856, 771, 754, 704, and 627 cm$^{-1}$. UV-Vis $\lambda_{\text{max}}$ (EtOH) 232.5 (log $\varepsilon$ 3.79), 260.5 (4.03), 301.0 (4.32), 325.0 (3.70), and 375.0 nm (4.26). (Found: C, 68.75; H, 4.69; N, 7.83; S, 18.11. C$_{20}$H$_{16}$N$_2$S$_2$ requires C, 68.93; H, 4.63; N, 8.04; S, 18.40%)

**3-Methyl-4-phenyl-6-diphenylmethyldene-2-thioxo-1,3-thiazine-5-carbonitrile (10b)**; Yield 71% Mp 263.0-267.0 °C (CH$_2$Cl$_2$-hexane). $\delta_H$ (CDCl$_3$) 7.5-7.3 (m, 11H, Ph), 7.27 (m, 2H, Ph-$o$), and 3.36 ppm (s, 3H, NCH$_3$). $\delta_C$ (CDCl$_3$) 195.2, 154.5, 144.6, 139.1, 138.8, 132.4, 131.1, 130.9, 130.4, 130.1, 129.3, 129.1, 128.9, 128.6, 128.4, 116.0, 114.8, 98.9, and 42.4 ppm. $\nu_{\text{max}}$ (KBr) 2214 (CN), 1591, 1556, 1487, 1456, 1342, 1294, 1271, 1157, 1109, 991, 931, 841, 769, 698, 667, and 642 cm$^{-1}$. UV-Vis $\lambda_{\text{max}}$ (EtOH) 235.0 (log $\varepsilon$ 4.07), 262.5 (4.24), 306.5 (4.32), and 374.5 nm (3.77). (Found: C, 72.34; H, 4.56; N, 6.74; S, 15.21. C$_{25}$H$_{18}$N$_2$S$_2$ requires C, 73.14; H, 4.42; N, 6.82; S, 15.40%)

**3-Methyl-6-diphenylmethyldene-4-$p$-tolyl-2-thioxo-1,3-thiazine-5-carbonitrile (10c)**; Yield 97%. Mp 296.0-298.0 °C (CH$_2$Cl$_2$-hexane). $\delta_H$ (CDCl$_3$) 7.5-7.4 (m, 6H, Ar), 7.4-7.2 (m, 6H, Ar), 7.10 (m, 2H, Ar), 3.38 (s, 3H, NCH$_3$), and 2.40 ppm (s, 3H, CH$_3$) ppm. $\delta_C$ (CDCl$_3$) 195.3, 154.8, 144.5, 141.7, 139.2, 138.8, 130.5, 130.1, 130.0, 129.4, 129.3, 129.1, 128.8, 128.6, 116.0, 114.8, 98.9, and 21.5 ppm. $\nu_{\text{max}}$ (KBr) 2216 (CN), 1591, 1556, 1487, 1456, 1342, 1294, 1271, 1157, 1109, 991, 931, 841, 769, 698, 667, and 642 cm$^{-1}$. UV-Vis $\lambda_{\text{max}}$ (EtOH) 230.0 (log $\varepsilon$ 4.04), 265.0 (4.15), 302.0 (4.30), and 377.5 nm (3.71). (Found: C, 73.56; H, 4.59; N, 6.42; S, 15.22. C$_{26}$H$_{20}$N$_2$S$_2$ requires C, 73.55; H, 4.75; N, 6.60; S, 15.10%)

**Ethyl 3,4-Diphenyl-6-diphenylmethyldene-2-thioxo-1,3-thiazine-5-carboxylate (10d)**; Yield 96%. Mp 189.0-189.5 °C (CH$_2$Cl$_2$-hexane). $\delta_H$ (CDCl$_3$) 7.4-7.1 (m, 20H, Ph), 3.00 (q, 2H, J=7 Hz, OCH$_2$), and 0.55 (t, 3H, J=7 Hz, CH$_3$) ppm. $\delta_C$ (CDCl$_3$) 194.5, 164.9, 146.7, 144.1, 140.2, 139.7, 134.2, 130.08, 130.2, 129.0, 128.4, 128.4, 128.2, 127.9, 127.3, 119.6, 118.9, 60.6, and 13.1 ppm. $\nu_{\text{max}}$ (KBr) 1713 (COO), 1589, 1489, 1443, 1366, 1327, 1288, 1232, 1190, 1153, 1089, 1030, 918, 843, 808, 768, 704, and 640 cm$^{-1}$. UV-Vis $\lambda_{\text{max}}$ (EtOH) 301.0 nm (log $\varepsilon$ 4.44). (Found: C, 74.16; H, 4.66; N, 2.53; S, 12.10. C$_{32}$H$_{25}$NO$_2$S$_2$ requires C, 73.96; H, 4.85; N, 2.70; S, 13.34%)

Formation of 1,3(6H)-Thiazine-6-spiro-2'-thiiranes (12) Except for the 6'-Spiro-2'-thiiranes 12b and 12g by the Reaction of 2-Methylthio-1,3-thiazine-6-thiones (11) with Diphenylidazaomethane.
5-Methylsulfonyl-2-methylthio-4,3’,3’-triphenyl-1,3(6H)-thiazine-6-spiro-2’-thiirane (12a). To a solution of 2-methylthio-4-phenyl-5-methylsulfonyl-1,3-thiazine-6-thione (11a) (0.329 g, 1 mmol) in THF (10 mL), a solution of diphenyldiazomethane (0.291 g, 1.5 mmol) in THF (10 mL) was added at room temperature and was allowed to stand at room temperature for 1 h. The solvent of reaction mixture was removed under reduced pressure to dryness at 0 °C. The solid remained was column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 10) at 0 °C. Yield 94% (0.465 g) (gradually decomposed during recrystallization). Mp 147.5-148.0 °C (benzene-hexane).

δH (CDCl3) ca. 7.2 (m, 15H, 3 × C6H5), 2.57 (s, 3H, SCH3), and 2.36 ppm (s, 3H, SO2CH3). δC (CDCl3) 176.8, 158.8, 138.4, 137.6, 130.8, 129.9, 129.4, 129.2, 128.3, 128.2, 128.0, 117.3, 68.7, 46.2, and 15.7 ppm. vmax (KBr) 3057, 1926, 1520, 1487, 1450, 1302, and 1134 (SO2), 1262, 1175, 1076, 992, 623, 891, 787, 756, 712, 629, 584, 561, 517, 450, 442, and 405 cm⁻¹. UV-Vis λmax (EtOH) 230.5 (log ε 4.05), 299 (3.93), 400.5 (3.47), and 408.0 nm (3.48). (Found: C, 60.28; H, 4.37; N, 2.93; S, 25.60. C25H21NO2S4 requires C, 60.58; H, 4.27; N, 2.83; S, 25.87%)

2-Methylthio-4,3’,3’-triphenyl-5-phenylsulfonyl-1,3(6H)-thiazine-6-spiro-2’-thiirane (12b); Compound 12b was first obtained when the reaction was carried out at –50 °C. Thus, to a solution of 2-methylthio-4-phenylsulfonyl-1,3-thiazine-6-thione (11b) (0.391 g, 1 mmol) in THF (10 mL), a solution of diphenyldiazomethane (0.291 g, 1.5 mmol) in THF (10 mL) was added at –50 °C. The reaction mixture was allowed to stand at –50 °C for 2 h and then the solvent was removed thoroughly under reduced pressure at 0 °C. The remained solid was column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 10) at 0 °C. Yield 71% (0.395 g) (gradually decomposed during recrystallization). Mp 135.0-135.5 °C.

δH (CDCl3) ca. 7.4 (m, 20H, 4 × C6H5) and 2.57 ppm (s, 3H, SCH3).
δC (CDCl3) 76.0, 158.0, 141.4, 137.9, 137.3, 137.2, 136.8, 132.2, 130.1, 129.8, 129.6, 129.5, 128.7, 128.3, 128.0, 127.8, 127.8, 127.3, 117.3, 67.4, 51.1, and 15.8 ppm. vmax (KBr) 3075, 3030, 2926, 1597, 1582, 1443, 1308, and 1144 (SO2), 1265, 1172, 1082, 1034, 993, 968, 926, 909, 889, 843, 831, 787, 756, 725, 708, 693, 660, and 631 cm⁻¹. (Found: C, 63.98; H, 4.37; N, 2.24; S, 23.11. C30H23NO2S4 requires C, 64.60; H, 4.16; N, 2.51; S, 22.99%)

Ethyl 2-Methylthio-4,3’,3’-triphenyl-1,3(6H)-thiazine-6-spiro-2’-thiirane-5-carboxylate (12c): Compound 12c was obtained and purified similarly to 5-methylsulfonyl-6-spiro-2’-thiirane 12a. Yield 96%. Mp 170 °C (dec.) (benzene-hexane). δH (CDCl3) ca. 7.3 (m, 15H, 3 × C6H5), 3.51 and 3.49 (each q, each 1H, J=7.3 Hz, OCH2), 2.54 (s, 3H, SCH3), and 0.56 ppm (t, 3H, J=7.3 Hz, CH3). δC (CDCl3) 166.3, 165.8, 150.5, 139.0, 138.3, 130.0, 129.6, 128.6, 128.0, 127.9, 127.8, 127.5, 114.7, 69.6, 60.6, 54.0, 14.9, and 13.2 ppm. vmax (KBr) 3057, 3022, 2980, 2920, 1705 (COO), 1582, 1559, 1530, 1491, 1464, 1445, 1392, 1368, 1319, 1308, 1285, 1240, 1221, 1175, 1067, 1030, 984, 939, 922, 893, and 862 cm⁻¹. UV-Vis
λ_max (EtOH) 220.5 (log ε 4.26), 235.0 (4.32), 279.5 (4.39), and 316.5 nm (4.20). (Found: C, 65.98; H, 4.83; N, 2.69; S, 19.55. C_{27}H_{23}NO_2S_3 requires C, 66.23; H, 4.73; N, 2.86; S, 19.64%).

2-Methylthio-3',3'-diphenyl-4-m-tolyl-1,3(6H)-thiazine-6-spiro-2'-thiirane-5-carbonitrile (12d):
Compound 12d was also obtained and purified similarly to the 5-methylsulfonyl-6-spiro-2'-thiirane 12a. Yield 70%. Mp 148 °C (dec.) (EtOAc-hexane). δ_H (CDCl_3) ca. 7.4 (m, 14H, Ar), 2.064 (s, 3H, CH_3), and 2.37 ppm (s, 3H, SCH_3).

C_{27}H_{23}NO_2S_3 requires C, 66.23; H, 4.73; N, 2.86; S, 19.64%.

3'-Methyl-5-methylsulfonyl-2-methylthio-4,3'-diphenyl-1,3(6H)-thiazine-6-spiro-2'-thiirane (12e):
To a solution of 2-methylthio-5-methylsulfonyl-4-phenyl-1,3-thiazine-6-thione (11a) (0.329 g, 1 mmol) in THF (10 mL), was added a solution of 1-phenyldiazoethane (1.5 mmol) in THF (10 mL) at room temperature. The reaction mixture was allowed to stand at room temperature for 20 min. Then the solvent was removed under reduced pressure and was column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 4 : 1). Yield 97% (0.480 g). Mp 114 °C (dec.) (benzene-hexane).

δ_H (CDCl_3) 7.3-7.0 (m, 8H, 2×Ph), 6.88 (d, 2H, J=7 Hz, Ph-2,6), and 2.72 (s, 3H, SO_2CH_3), 2.49 (s, 3H, SCH_3), 2.00 ppm (s, 3H, CH_3).

C_{26}H_{20}NO_2S_3 requires C, 55.40; H, 4.42; N, 3.34; S, 29.30.

Methyl 5-Methyl-2,5-diphenyl-3-phenylsulfonyl-4-thioxopyrroline-1-dithiocarboxylate (13f):
Compound 13f was obtained similarly to the formation of the 5-methylsulfonyl-6-spiro-2'-thiirane 12e from the reactants, 2-methylthio-4-phenyl-5-phenylsulfonyl-1,3-thiazine-6-thione 11b (0.391 g, 1 mmol) and 1-phenyldiazoethane (1.5 mmol). After the reaction mixture was allowed to stand at room temperature for 3 min, the solvent was removed under reduced pressure and column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 10). Yield 82% (0.457 g). Mp 172.5-175.5 °C (benzene-hexane).

δ_C (CDCl_3) 221.7, 204.3, 173.5, 140.8, 139.0, 133.0, 131.5, 130.5, 129.5, 128.3, 128.2, 127.8, 127.7, 125.7, 88.4, 25.1, and 21.6 ppm. v_max (KBr) 3061, 1601, 1582, 1508, 1447, 1387, 1335, 1273, and 1132 (SO_2), 1073, 1040, 928, 907, 858, 760, 747, 735, 714, 691, 662, and 637 cm⁻¹. UV-Vis λ_max (EtOH) 210.5 (4.36), 292.5 (4.07), and 401.0 nm (3.42). (Found: C, 55.65; H, 4.47; N, 6.10; S, 21.22. C_{20}H_{19}NO_2S_4 requires C, 55.40; H, 4.42; N, 3.34; S, 29.30.

C_{20}H_{19}NO_2S_4 requires C, 55.40; H, 4.42; N, 3.34; S, 29.30. 

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210.5 (log ε 4.49), 292.5 (4.12), 328.5 (3.94), 404.0 (4.34), and 478.0 nm (3.24). (Found: C, 60.39; H, 4.57; N, 2.83; S, 25.59. C\textsubscript{25}H\textsubscript{21}NO\textsubscript{2}S\textsubscript{4} requires C, 60.58; H, 4.27; N, 2.83; S, 25.87%)

Thermal Rearrangement of 1,3(6\textsubscript{H})-Thiazine-6-spiro-2'-thiiranes (12a-d) into Methyl 3-Methylsulfonyl-2,5,5-triphenylpyrroline-4-thioxo-1-dithiocarboxylate (13a). A solution of 2-methylthio-5-methylsulfonyl-4,3',3'-triphenyl-1,3-thiazine-6-spiro-2'-thiirane (12a) (0.248 g, 0.5 mmol) in toluene (50 mL) was refluxed at 110 °C for 4 min. The reaction mixture was evaporated to dryness and the residue was column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 10). Yield 76% (0.376 g) (direct 0%). Mp 186.5-187.5 °C (benzene-hexane). δ\textsubscript{H} (CDCl\textsubscript{3}) ca. 7.5 (m, 15H, 3 × C\textsubscript{6}H\textsubscript{5}), 3.13 (s, 3H, SO\textsubscript{2}CH\textsubscript{3}), and 2.13 ppm (s, 3H, SCH\textsubscript{3}). δ\textsubscript{C} (CDCl\textsubscript{3}) 223.1, 205.6, 173.3, 137.4, 131.9, 131.2, 129.9, 129.2, 128.9, 128.3, 128.0, 127.7, 96.2, 42.3, and 21.4 ppm. \(\text{v}_{\text{max}}\) (KBr) 3057, 1516, 1470, 1364, 1318, and 1141 (SO\textsubscript{2}), 1277, 1084, 1036, 999, 947, 880, 758, 739, 698, 584, 540, 515, 480, and 421 cm\(^{-1}\). UV-Vis \(\lambda_{\text{max}}\) (EtOH) 249.0 (log ε 4.05), 409.0 (4.25), and 471.0 nm (3.08). (Found: C, 61.48; H, 4.49; N, 2.66; S, 25.59. C\textsubscript{25}H\textsubscript{21}NO\textsubscript{2}S\textsubscript{4} requires C, 60.58; H, 4.27; N, 2.83; S, 25.87%)

Compound 14a was isolated together with compound 13a as by-product; 5-Methylsulfonyl-2-methylthio-4-phenyl-6-diphenylmethylidene-1,3-thiazine (14a); Yield 19%. Mp 168.5-169.0 °C (benzene-hexane). δ\textsubscript{H} (CDCl\textsubscript{3}) ca. 7.2 (m, 15H, 3 × C\textsubscript{6}H\textsubscript{5}), 2.51 (s, 3H, SCH\textsubscript{3}), and 2.07 ppm (s, 3H, SO\textsubscript{2}CH\textsubscript{3}). δ\textsubscript{C} (CDCl\textsubscript{3}) 163.8, 162.3, 148.6, 140.6, 139.9, 134.0, 130.0, 129.8, 129.7, 129.3, 129.0, 128.4, 128.3, 128.2, 126.7, 125.0, 43.7, and 16.5 ppm. \(\text{v}_{\text{max}}\) (KBr) 3032, 2926, 1532, 1485, 1443, 1314, and 1140 (SO\textsubscript{2}), 1244, 1074, 1028, 964, 936, 883, 761, 702, 631, 613, 583, 559, 536, 494, 440, and 403 cm\(^{-1}\). UV-Vis \(\lambda_{\text{max}}\) (EtOH) 241.0 (log ε 4.20), 285.0 (4.14), and 399.5 nm (3.05). (Found: C, 64.36; H, 4.31; N, 3.22; S, 20.87. C\textsubscript{25}H\textsubscript{21}NO\textsubscript{2}S\textsubscript{3} requires C, 64.76; H, 4.57; N, 3.02; S, 20.75%)

Methyl 2,5,5-Triphenyl-3-phenylsulfonyl-4-thioxopyrroline-1-dithiocarboxylate (13b); A solution of 2-methylthio-4,3',3'-triphenyl-5-phenylsulfonyl-1,3-thiazine-6-spiro-2'-thiirane (12b) (0.278 g, 0.5 mmol) in benzene (50 mL) was allowed to stand at room temperature for 20 min. After being evaporated to dryness, the solid residue was column chromatographed (silica gel 60, 400 mesh, benzene). Yield 100% (0.278 g). Mp 188-190 °C (benzene-hexane). δ\textsubscript{H} (CDCl\textsubscript{3}) ca. 7.5 (m, 20H, 3 × C\textsubscript{6}H\textsubscript{5}) and 2.10 ppm (s, 3H, SCH\textsubscript{3}). δ\textsubscript{C} (CDCl\textsubscript{3}) 221.8, 205.4, 173.4, 140.3, 137.2, 132.6, 131.8, 130.7, 129.9, 129.8, 129.6, 128.6, 128.3, 128.0, 127.9, 127.8, 127.5, 96.1, and 21.3 ppm. \(\text{v}_{\text{max}}\) (KBr) 3059, 2917, 1603, 1582, 1512, 1493, 1464, 1445, 1373, 1323, and 1151 (SO\textsubscript{2}), 1285, 1250, 1127, 1082, 1036, 999, 965, 949, 914, 880, 795, 756, 737, and 716 cm\(^{-1}\). UV-Vis \(\lambda_{\text{max}}\) (EtOH) 299.0 (log ε 4.12), 407.5 (4.28), and 487.0 nm (3.06). (Found: C, 64.84; H, 4.34; N, 2.51; S, 23.21. C\textsubscript{30}H\textsubscript{23}NO\textsubscript{2}S\textsubscript{4} requires C, 64.60; H, 4.16; N, 2.51; S, 22.99%)

Direct Formation of Methyl 2,5,5-Triphenyl-3-phenylsulfonyl-4-thioxopyrroline-1-dithio-
carboxylate (13b). To a solution of 2-methylthio-4-phenyl-5-phenylsulfonyl-1,3-thiazine-6-thione (11a) (0.391 g, 1 mmol) in THF (10 mL), diphenyldiazomethane (0.291 g, 1.5 mmol) in THF (10 mL) was added at room temperature. The mixture was allowed to stand at room temperature for 20 min, then the solvent was removed under reduced pressure to dryness and the residue was column chromatographed (silica gel 60, 400 mesh, benzene). Yield 98% (0.546 g).

Ethyl 1-(Methylthio)thiocarbonyl-2,5,5-triphenyl-4-thioxo-3-carboxylate (13c); Compound 13c was obtained similarly to compound 13a from ethyl 2-methylthio-3′,3′-triphenyl-1,3-thiazine-6-spiro-2′-thiirane-5-carboxylate (12c) (0.489 g, 1 mmol) by refluxing in toluene at 110 °C for 2 h and isolated similarly to the isolation of compound 13a. Yield 69% (0.337 g). Mp 183.5-186.0 °C (EtoAc-hexane). δH (CDCl3) ca. 7.5 (m, 15H, 3 × C6H5), 4.13 (q, 2H, J = 7.0 Hz, OCH2), 2.13 (s, 3H, SCH3), and 1.03 ppm (t, 3H, J = 7.0 Hz, CH3). δC (CDCl3) 225.0, 205.3, 170.3, 163.4, 137.9, 131.2, 131.0, 29.3, 129.0, 128.6, 128.2, 128.1, 127.9, 127.6, 95.8, 61.1, 20.9, and 13.8 ppm. νmax (KBr) 3063, 2992, 1726 (COO), 1553, 1491, 1445, 1404, 1296, 1213, 1154, 1032, 1017, 901, 768, 727, 696, and 602 cm⁻¹. UV-Vis λmax (EtOH) 210.5 (log ε 4.55), 299.0 (4.14), and 417.5 nm (4.31). (Found: C, 66.00; H, 4.90; N, 2.90; S, 19.35. C27H23NO2S3 requires C, 66.23; H, 4.73; N, 2.86; S, 19.64%). Desulfurized compound, ethyl 6-diphenylmethylidene-2-methylthio-4-phenyl-1,3-thiazine-5-carboxylate (14c) was also isolated as by-product. Yield 25%. Mp 199.5-211.5 °C (benzene-hexane). δH (CDCl3) ca. 7.3 (m, 15H, 3 × C6H5), 3.21 (q, 2H, J = 6.5 Hz, OCH2), 2.52 (s, 3H, SCH3), and 0.66 ppm (t, 3H, J = 6.5 Hz, CH3). δC (CDCl3) 167.5, 152.8, 146.0, 140.6, 140.2, 138.6, 131.2, 130.6, 128.7, 128.6, 128.3, 128.0, 127.8, 127.7, 115.7, 60.5, 14.6, and 13.1 ppm. νmax (KBr) 3057, 2980, 2922, 1713 (COO), 1532, 1485, 1443, 1327, 1304, 1192, 1088, 1074, 1030, 988, 775, and 702 cm⁻¹. UV-Vis λmax (EtOH) 210.5 (log ε 4.51), 254.5 (4.35), 287.5 (4.35), and 390.5 nm (3.78). (Found: C, 70.76; H, 5.19; N, 2.64; S, 13.87. C27H23NO2S2 requires C, 70.87; H, 5.07; N, 3.06; S, 14.01%)

Methyl 3-Cyano-5,5-diphenyl-4-thioxo-5-m-tolylpyrroline-1-dithiocarboxylate (13d); Compound 13d was obtained similarly to compound 12a from 2-methylthio-3′,3′-diphenyl-4-m-tolyl-1,3-thiazine-6-spiro-2′-thiirane-5-carbonitrile (12d) (0.228 g, 0.5 mmol) by refluxing in toluene (50 mL) at 110 °C for 20 h and isolated similarly to the isolation of compound 13a. Yield 41% (0.093 g). Mp 196.5-197.5 °C (EtOAc-hexane). δH (CDCl3) ca. 7.74 (s, 1H, m-tolyl-2), 7.59-7.53 (m, 4H, Ar), 7.59-7.53 (m, 4H, Ar), 4.41-7.37 (m, 8H, Ar), 2.45 (s, 3H, CH3), and 2.20 ppm (s, 3H, SCH3). δC (CDCl3) 224.5, 205.4, 174.2, 139.4, 137.2, 133.9, 133.6, 130.4, 129.8, 129.2, 129.0, 128.8, 128.7, 128.0, 127.2, 125.6, 114.2, 109.7, 96.4, 21.5, and 21.2 ppm. νmax (KBr) 3048, 2945, 2228 (CN), 1584, 1530, 1491, 1476, 1443, 1375, 1293, 1263, 1148, 1130, 1036, 999, 959, 928, 899, 878, 849, 802, 781, 762, 741, 721, 710, 697, 675, 608, and 579 cm⁻¹. UV-Vis λmax (EtOH) 302.5 (log ε 4.57) and 418.5 nm (4.71). (Found: C, 68.39; H, 4.55; N, 6.06; S, 21.11.
C\textsubscript{26}H\textsubscript{20}N\textsubscript{2}S\textsubscript{3} requires C, 68.39; H, 4.41; N, 6.13; S, 21.06\%). Compound 14d: 2-Methylthio-6-diphenylmethylidene-4-m-tolyl-1,3-thiazine-5-carbonitrile was also isolated as by-product. Yield 28\% (0.059 g). Mp 188.5-189.5 °C (EtOAc-hexane). δ\textsubscript{H} (CDCl\textsubscript{3}) ca. 7.65-7.61 (m, 2H, Ar), 7.41-6.99 (m, 12H, Ar), 2.57 (s, 3H, CH\textsubscript{3}), and 2.38 ppm (s, 3H, SCH\textsubscript{3}). δ\textsubscript{C} (CDCl\textsubscript{3}) 166.7, 158.5, 146.6, 139.6, 137.9, 136.1, 131.2, 130.7, 130.4, 129.4, 129.1, 128.4, 128.2, 126.2, 21.5, and 15.0 ppm. ν\textsubscript{max} (KBr) 3040, 2910, 2209 (CN), 1499, 1443, 1312, 1192, 1157, 1115, 1076, 1030, 972, 927, 885, 835, 795, 768, 700, 681, 637, 613, 584, 519, and 442 cm\textsuperscript{-1}. UV-Vis λ\textsubscript{max} (EtOH) 250.0 (log ε 4.78), 297.5 (4.84), and 408.5 nm (4.21). (Found: C, 73.56; H, 4.89; N, 6.35; S, 1488. C\textsubscript{26}H\textsubscript{20}N\textsubscript{2}S\textsubscript{2} requires C, 73.55; H, 4.75; N, 6.60; S, 15.10\%).

Thermal Rearrangement of 3’-Methyl-2-methylthio-5-methylsulfonyl-4,3’-diphenyl-1,3(6H)-thiazine-6-spiro-2’-thiirane (12e) to Methyl 5-Methyl-3-methylsulfonyl-2,5-diphenyl-1,3(6H)-thioxopyrroline-1-dithiocarboxylate (13e). 3’-Methyl-2-methylthio-5-methylsulfonyl-4,3’-diphenyl-1,3(6H)-thiazine-6-spiro-2’-thiirane (12e) (0.217 g, 0.5 mmol) was refluxed for 10 min in benzene (50 mL) and evaporated to dryness. The residue was column chromatographed (silica gel 60, 400 mesh, benzene), and recrystallized from benzene-hexane. Yield 100\% (0.217 g). Red prisms. Mp 217.5-226.0 °C. δ\textsubscript{H} (CDCl\textsubscript{3}) ca. 7.5 (m, 10H, 2 × C\textsubscript{6}H\textsubscript{5}), 3.24 (s, 3H, SO\textsubscript{2}CH\textsubscript{3}), 2.31 (s, 3H, SCH\textsubscript{3}), and 2.04ppm (s, 3H, CH\textsubscript{3}). δ\textsubscript{C} (CDCl\textsubscript{3}) 222.9, 204.4, 173.3, 138.7, 131.6, 130.6, 129.0, 128.3, 127.7, 125.7, 88.6, 42.7, 25.3, and 21.7 ppm. ν\textsubscript{max} (KBr) 2922, 1510, 1468, 1445, 1370, and 1142 (SO\textsubscript{2}), 1312, 1275, 1219, 1165, 1040, 961, 910, 862, 791, 764, 743, 721, 696, 658, and 629 cm\textsuperscript{-1}. UV-Vis λ\textsubscript{max} (EtOH) 210.5 (log ε 4.38), 264.5 (3.66), 297.0 (3.85), 333.0 (3.73), 402.5 (4.14), and 471.0 nm (3.01). (Found: C, 55.61; H, 4.55; N, 3.12; S, 29.88. C\textsubscript{20}H\textsubscript{19}NO\textsubscript{2}S\textsubscript{4} requires C, 55.40; H, 4.42; N, 3.23; S, 29.58\%)

X-Ray crystallographic data of compound 13e:

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Reverse Rearrangement of Ethyl 1-Methylthiothiocarbonyl-4-thioxo-2,5,5-triphenylpyrroline-3-carboxylate (13c) into Ethyl 2-Methylthio-4,3′,3′-triphenyl-1,3(6H)-thiazine-6-spiro-2′-thiirane-5-carboxylate (12c). The solution of ethyl 1-methylthiothiocarbonyl-4-thioxo-2,5,5-triphenylpyrroline-3-carboxylate (13c) was refluxed in xylene at 140 °C for 1 h. The solvent was evaporated to dryness in vacuo and the residue was column chromatographed (silica gel 60, 400 mesh, EtOAc : pentane = 1 : 10). Reversely rearranged ethyl 2-methylthio-4,3′,3′-triphenyl-1,3-thiazine-6-spiro-2′-thiirane-5-carboxylate (12c) was obtained in 35% yield and 42% of compound 13c was recovered. On the other hand, when the above solution was continued to reflux for 1 day, compound 12c could not be obtained, but desulfurized ethyl 6-diphenylmethylidene-2-methylthio-4-phenyl-1,3-thiazine-5-carboxylate (14c) was formed in 48% yield and compound 13c was recovered in 14% yield.

Thermal Decomposition of Methyl 3-Cyano-5,5-diphenyl-4-thioxo-2-m-tolylpyrroline-1-dithiocarboxylate (13d). Looking forward to similar reverse rearrangement to take place for compound 12d, the solution of methyl 3-cyano-5,5-diphenyl-4-thioxo-2-m-tolylpyrroline-1-dithiocarboxylate (13d) was also refluxed in xylene at 140 °C for 1 h, but compound 12d was never obtained. (Compound 13d was recovered in 76% yield.) Moreover, prolonged heating of the above solution in xylene for 24 h at 140 °C merely gave 2-methylthio-6-diphenylmethylidene-4-m-tolyl-1,3-thiazine-5-carbonitrile (14d) in 71% yield.

REFERENCES AND NOTES