Thermal Rearrangement of 1,3-Thiazolidine Sulfoxides: Thiolsulfinate and Thioaldehyde Intermediates

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Stereospecific ring opening of the sulfoxides *cis*-**13** and *trans*-**14** in refluxing toluene gave the corresponding sulfenic acids **9**, **10** intermediates respectively. The sulfenic acid **9** dimerized to the thiolsulfinate **17** by dual function of the sulfenic acid as *S*-nucleophile/*S*-electrophile with loss of water while the sulfenic acid **10** was unchanged. The stereospecific recyclization of **10** to the parent sulfoxide **14** increases the higher pi-electron density of the double. The thermolysis of the thiolsulfinate **17** gave the transient sulfenic acid **9**, which dimerized again to repeat the process and unisolable thioaldehyde **21**. The thioaldehyde **21** was converted to either pyrrole **15** by the action of a sulfinic acid **20** catalyst formed inevitably by hydrolysis of **17** under the reaction conditions, or thiazole **18** under neutral conditions. In these rearrangements, the amide carbonyl group facilitated the elimination of a neighboring hydrogen.

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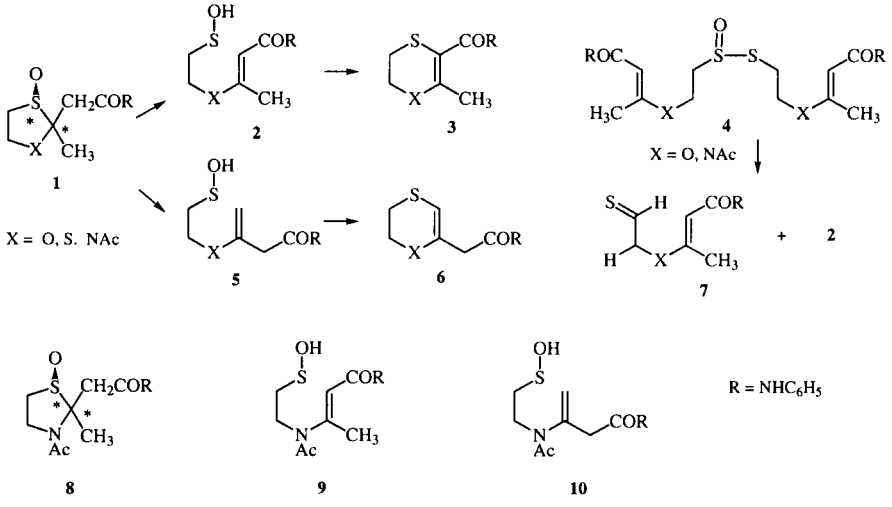
Introduction.

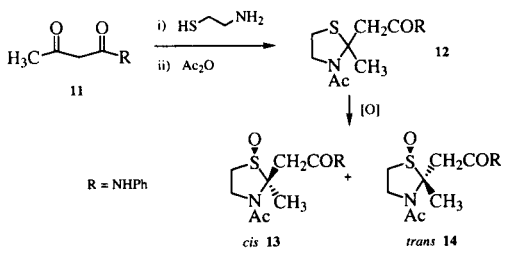
The rearrangement of appropriately substituted cyclic sulfoxides to a ring expansion product is of considerable mechanistic interest as well as synthetic utility. We reported ring expansions of some cyclic sulfoxides **1** to 6-membered cyclic sulfides **3** or **6** *via* the corresponding sulfenic acid intermediates **2** or **5** [1]. An important feature of the cyclic sulfoxide **1** is the presence of both carbonyl-activated methylene and unactivated hydrogens β to the C-S bond being ruptured to give the corresponding sulfenic acids **2**, **5**. Depending on the spatial arrangement of the sulfoxide oxygen the ring opening reaction proceeded either by a [2,3]-sigmatropic rearrangement under neutral conditions, or through a protonated sulfoxide in the presence of an acid catalyst. In our previous paper [2], we reported that the pyrolytic transformation of thiolsulfinate **4** afforded the corresponding reactive intermediates, a thioaldehyde **7** and the sulfenic acid **2** by S-S bond cleavage and a labile α-sulfenyl hydrogen transfer [3]. As an extension of our studies on the reactivity and synthetic uses of the sulfoxide and the sulfenic acid, we now report the thermal rearrangement of 1,3-thiazolidine sulfoxide **8** in refluxing toluene. This investigation provides interesting results on the reactivity of the sulfenic acids **9** or **10** generated from the sulfoxides **8** when to compared with the reported [1,2].

Results and Discussion.

As shown in Scheme 1, the parent 1,3-thiazolidines **12** were obtained from the hemithioketalization of acetoacetanilide (**11**) with 2-aminoethanethiol followed by an acetylation. Oxidation of **12** with aqueous hydrogen peroxide in the presence of benzeneseleninic acid as the catalyst [4] gave a 3:2 mixture of *cis*-**13** and *trans*-**14** 1,3-thiazolidine sulfoxides, which were separated by chromatography. We have named that isomer as *cis* where the sulfoxide oxygen and CH_2COR group are on the same face of the thiazolidine ring and *trans* where they are on opposite faces. Assignment of stereochemistry to the *cis*-**13** and *trans*-**14** isomers was based on the ^1H nmr data and by a deuterium incorporation reaction [1b]. When the *cis*-sulfoxide **13** was



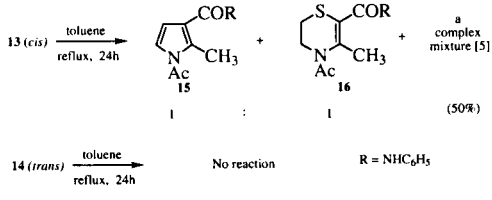
Scheme 1



refluxed in toluene for 24 hours to give a 1:1 mixture of a new pyrrole **15** and dihydro-1,4-thiazine **16** in 50% yield, while the *trans* sulfoxide **14** was recovered, being unchanged under the same reaction conditions (Scheme 2).

The structure of pyrrole **15** was elucidated by the spectral data, elemental analysis, and independent synthesis (see the experimental section).

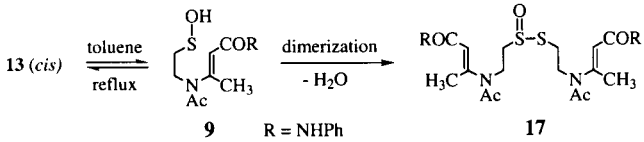
Scheme 2



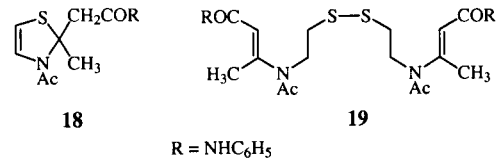
cis-Sulfoxide.

In general, alkyl sulfoxides, when heated in aprotic solvents, undergo pyrolysis readily and yield an olefin and sulfenic acid [6]. Undoubtedly, the *cis*-sulfoxide **13** was converted into a sulfenic acid **9** by ring opening of the carbonyl-activated methylene hydrogen through [2,3]-sigmatropic rearrangement in refluxing toluene since the sulfoxide oxygen and the CH_2COR group are on the same face of the thiazolidine ring (Scheme 3) [1].

Scheme 3



It has been known that sulfenic acids are unstable, dimerizing to a thiolsulfinate with loss of water [7]. Because the formation of pyrrole **15** strongly suggested that the reactive thioaldehyde **21** (see Scheme 6) was generated in the pyrolysis of the thiolsulfinate, we synthesized intermediate **17** independently. In the mass spectrum of **17** [8], although the molecular ion was not found, fragments at m/z 294 and 276 resulting from S-S bond cleavage and a hydrogen transfer from sulfenyl to the sulfinyl moiety was found. This decomposition is due to a weak S-S bond and a labile α-sulfenyl hydrogen, characteristic of thiolsulfinate [3]. Surprisingly, no significant amount of pyrrole **15** was found when the thiolsulfinate **17** was refluxed in toluene for 6 hours. Instead a mixture of thiazole **18** (40%), and *cis*-sulfoxide **13** (30%) was produced (entry 2 in Table 1) [2b]. An additional experiment (entry 3) including refluxing of the thiolsulfinate **17** in toluene for a prolonged period (24 hours) afforded the increased amount of pyrrole **15** (20%) with a corresponding decrease of *cis*-sulfoxide **13** (trace). An interesting phenomenon was that a significant amount of **15** (25%) in comparison with thiazole **18** (8%) was formed when the *cis*-sulfoxide **13** was refluxed in toluene for 24 hours (entry 1).



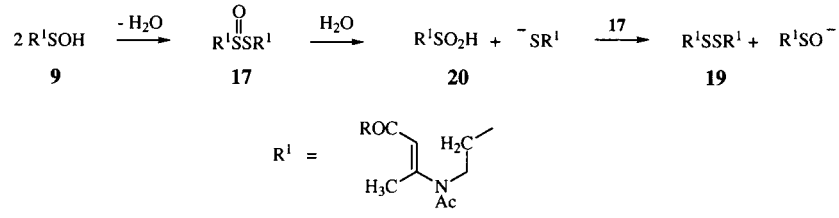
Therefore, we concluded that the reaction pathway of the themolysis of the *cis*-sulfoxide **13** is different from that of the thiolsulfinate **17**. Isolation of the disulfide **19** (8%) from a complex mixture generated from the pyrolysis of the *cis*-sulfoxide **13** provided a clue to the mechanistic pathway to pyrrole **15**. Dimerization of sulfenic acid **9** produced thiolsulfinate **17** with release of water, subsequently hydrolyzing thiolsulfinate **17** to yield a disulfide **19** and an unisolable sulfinic acid **20** (Scheme 4) [9,10], which may catalyze the reaction.

An overall plausible mechanism is suggested in Scheme 5. Pyrolysis of thiolsulfinate **17** gave thioaldehyde **21** with generation of sulfenic acid **9** which dimerizes again with loss of water to repeat the process. Alternatively, in the presence of

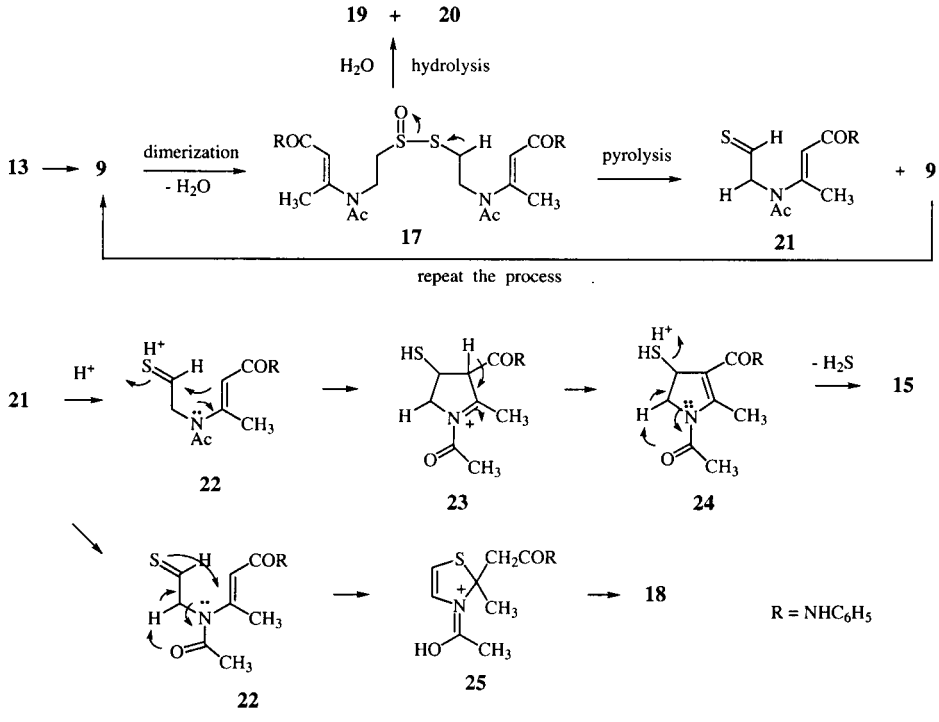
Table 1
Pyrolysis of *cis*-Sulfoxide **13**, and Thiolsulfinate **17** in Refluxing Toluene.

Entry	Starting Material	Reaction Time (hours)	Key Products (%) *cis*-sulfoxide **13**	pyrrole **15**	thiazole **18**	dihydro-1,4-thiazine **16**
1	*cis*-sulfoxide **13**	24	0	25	8	25
2	thiolsulfinate **17**	6	30	trace	40	trace
3	thiolsulfinate **17**	24	2	20	40	5

Scheme 4

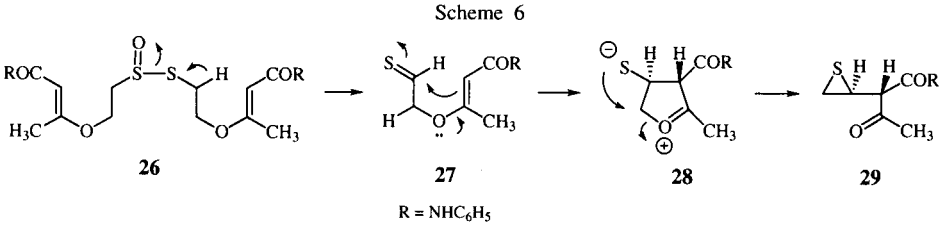


Scheme 5



water, the hydrolysis of **17** takes place to give disulfide **19** and sulfinic acid **20**. The thioaldehyde **21** produced by the pyrolysis of **17** proceeds *via* two pathways. Whereas only a few cases of thioaldehyde isolation have been reported [12], other reports mention the isolation of products which suggest the intermediacy of a thioaldehyde [13]. In our case, however, in the presence of an acid catalyst, the protonated thiocarbonyl carbon in **22** suffered an attack by the internal double bond, activated by the lone pairs of the vinyl amide, to form an iminium ion **23**. The iminium ion **23** releases the acidic proton followed by elimination of hydrogen sulfide [14] to afford the pyrrole **15**. In the conversion of **24** to **15**, the amide carbonyl group possibly facilitates the elimination of a neighboring hydrogen to enhance the elimination of hydrogen sulfide. In comparison, in the absence of the acid catalyst, the amide carbonyl group promotes the removal of a neighboring hydrogen to elevate the Michael type nucleophilic attack of the thiocarbonyl sulfur that results in thiazole **18** through **25**. The conversion of an analogous thioaldehyde **27** generated from an oxygen analogue **26** to episulfide **29** [2a] possibly through an oxonium ion **28** proves the effect of the amide group could have in these reactions (Scheme 6).

Scheme 6



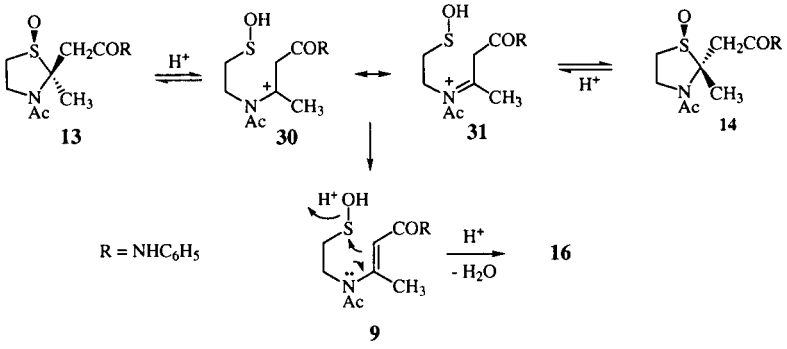
Isolation of a small amount of the *trans*-sulfoxide **14** (14%) from the mixture further supports the acid catalyzed reaction. In contrast to the stereospecific cyclization of sulfenic acid **9** intermediate to *cis*-sulfoxide **13** under neutral conditions, the *cis*-sulfoxide **13** isomerizes the *trans*-sulfoxide **14** through **30** and **31** *via* a stepwise mechanism in the presence of the acid catalyst (Scheme 7) [1b]. Apparently, the formation of dihydro-1,4-thiazine **16** (4%) arises from the acid catalyzed dehydration of sulfenic acid **9**. In the presence of the acid catalyst, the electrophilic character of the sulfenic acid for the internal double bond as assisted by the oxygen lone pairs predominates over its nucleophile component of the sulfenic acid, which resulted in the cyclization to **16**.

bond in **9**, facilitates the reversal of the previously reported [1b] [2,3]-sigmatropic ring opening, and in stereospecific cyclization to *trans*-sulfoxide **14** (Scheme 8).

EXPERIMENTAL

Melting points were determined on a Thomas-Hoover capillary melting point apparatus. All ^1H and ^{13}C nmr spectra were recorded either on a Bruker AM-200 or on a Varian Gemini 300 spectrometer. Chemical shift (δ) are in ppm and coupling constants (J) are in Hz. Infrared (ir) spectra were obtained with Perkin-Elmer 16F-PC FT-IR and are reported in cm^{-1}. Mass spectra (ms) were recorded on a Hewlet Packard 5890 series GC/MSD. Electron impact high-resolution mass spectra (hrms)

Scheme 7



trans-Sulfoxide.

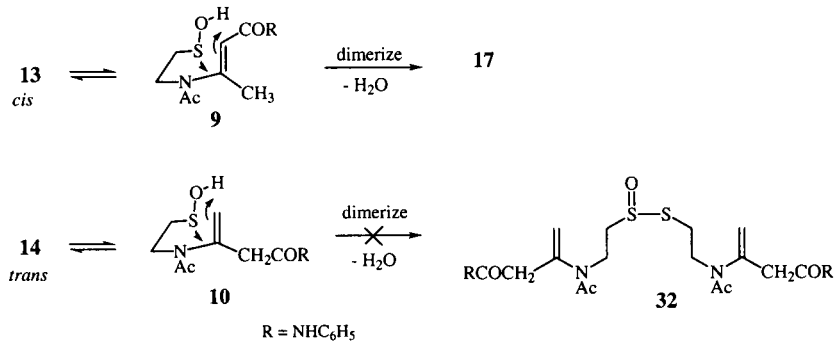
As described above, sulfenic acid **9** generated from *cis*-sulfoxide **13** dimerizes the thiolsulfinate **17** by a dual function of the sulfenic acid as *S*-nucleophile/*S*-electrophile [7]. In contrast, when the *trans*-sulfoxide **14** was refluxed for 3 hours in toluene, the starting material was recovered unchanged. The deuterium incorporation reaction [1b] of the *trans*-sulfoxide **14** suggests that sulfenic acid **10** intermediate cyclizes to the *trans*-sulfoxide **14** without formation of a corresponding thiolsulfinate **32**. In sulfenic acid **10**, the higher pi-electron density of the isolated double bond in comparison with the carbonyl deactivated double

were obtained on a VG70-VSEQ (VG analytical) high-resolution mass spectrometer at 70eV. Elemental analyses were performed using a Fisons EA1108 analyzer. Flash chromatographic isolation was accomplished on silica gel GF254 (230-400 mesh).

Preparation of 1,3-Thiazolidine **12**.

A solution of acetoacetanilide (**11**) (51.67 g, 0.292 mole), a mixture of 2-aminoethanethiol hydrochloride (36.8 g, 0.324 mole) and triethylamine (45.2 ml), and *p*-toluenesulfonic acid monohydrate (2.77 g) in benzene (300 ml) was refluxed for 6 hours under a Dean-Stark water separator and then cooled to room temperature. The reaction mixture was washed with water and dried (sodium sulfate). The solvent was removed *in vacuo* to give a yellow oily liquid (67.19 g, 98%). This oily residue dissolved in acetic

Scheme 8



anhydride (121 ml) and stirring was continued for 4 hours at rt. The white precipitate which was thiazolidine **12** was collected by filtration (72.5 g, 91%), mp 197-204° (recrystallized from ethanol); ^{1}H nmr (300 MHz, dimethyl-d_6 sulfoxide): 1.83 (s, 3H, 2-CH_3), 2.03 (s, 3H, $COCH_3$), 2.95 (t, J = 5.7, 2H, 5-CH_2), 3.15 and 3.24 (2d, J = 14.6, AB pattern, 2H, 2-CH_2CO), 3.77-3.85 and 3.88-3.95 (m, 2H, 4-CH_2), 6.98-7.59 (m, 5H, ArH), 9.90 (br. s, 1H, NH); ^{13}C nmr (78.5 MHz, dimethyl-d_6 sulfoxide): 25.4, 27.3, 28.2, 45.0, 53.4, 71.9, 119.1, 123.0, 128.6, 139.1, 167.9, 168.1; ms: m/z 278 (M^+); ir (potassium bromide): 1680, 1630.

Anal. Calcd. for $C_{14}H_{18}N_2O_2S$: C, 60.41; H, 6.52; N, 10.06. Found: C, 60.22; H, 6.69; N, 10.05.

Preparation of 1,3-Thiazolidine Sulfoxides **13** and **14**.

To an ice-cooled solution of 1,3-thiazolidine **12** (13.9 g, 50 mmoles) and benzeneseleninic acid (90 mg) in methylene chloride (100 ml) was added 35% hydrogen peroxide in water (8 ml, about 80 mmoles) dropwise with vigorous stirring at room temperature. The reaction mixture was stirred for 18 hours, washed with sodium bicarbonate solution, cold water, and then dried (sodium sulfate). The solvent was removed under reduced pressure to obtain a white foamy solid (12.7g, 86%) consisting of a 3:2 mixture of *cis*-**13** and *trans*-**14** sulfoxide, which were separated by chromatography using chloroform:methanol = 50:1 as an eluent.

The *cis*—sulfoxide **13** had mp 49-51° (recrystallized from methylene chloride and cyclohexane); ^{1}H nmr (300 MHz, dimethyl-d_6 sulfoxide): 1.60 (s, 3H, 2-CH_3), 2.10 (s, 3H, $COCH_3$), 2.78 and 3.95 (2d, J = 16.6, AB pattern, 2H, 2-CH_2CO), 3.00-3.05 (m, 2H, 5-CH_2), 4.01-4.09 and 4.19-4.23 (2m, 2H, 4-CH_2), 7.00-7.57 (m, 5H, ArH), 10.09 (br. s, 1H, NH); ir (potassium bromide): 1670 (C=O), 1625 (C=O), 1040 (S->O); ms: m/z 294 (M^+).

Anal. Cacld. for $C_{14}H_{18}N_2O_3S$: C, 57.52; H, 6.10; N, 9.27; S, 10.92. Found: C, 57.2; H, 6.26; N, 9.54; S, 10.8.

The *trans*-sulfoxide **14** had mp 149.5-150.5° (recrystallized from methylene chloride and cyclohexane); ^{1}H nmr (300 MHz, dimethyl-d_6 sulfoxide): 1.83 (s, 3H, 2-CH_3), 2.03 (s, 3H, $COCH_3$), 2.96 (t, J = 5.50 Hz, 2H, 5-CH_2), 3.13 and 3.31 (2d, J = 14.5, AB pattern, 2H, 2-CH_2), 3.78-3.85 and 3.88-3.95 (2m, 2H, 4-CH_2), 6.99-7.58 (m, 5H, ArH), 9.88 (br. s, 1H, NH); ir (potassium bromide): 1675 (C=O), 1625 (C=O), 1060 (S->O); ms: m/z 294 (M^+).

Anal. Cacld. for $C_{14}H_{18}N_2O_3S$: C, 57.52; H, 6.10; N, 9.27; S, 10.92. Found: C, 57.12; H, 6.16; N, 9.52; S, 10.89.

Thermolysis of *cis*-Sulfoxide **13**.

A solution of *cis*-sulfoxide **13** (820 mg, 278 mmoles) in toluene (80 ml) was refluxed under a Dean-Stark water separator for 24 hours. Evaporation of the solvent gave a brown oily residue, consisting a 25:25:14:14:8:8:6 mixture of pyrrole **15**, dihydro-1,4-thiazine **16**, *trans*-sulfoxide **14**, 1,3-thiazolidine **12**, 1,3-thiazole **18**, disulfide **19**, and isomeric dihydro-1,4-thiazine **33**, respectively. The mixture was separated by preparative tlc (silica gel GF254) using chloroform:methanol = 95:5 and then ethyl acetate: *n*-hexane = 1:1 as eluents to give **15** (R_f 0.83, 82 mg), **16** (R_f 0.50, 103 mg), **14** (R_f 0.23, 11 mg), **12** (R_f 0.45, 6 mg), **18** (R_f 0.63, 8 mg), **19** (R_f 0.40, 7 mg), and **33** (R_f 0.33, 5 mg).

Pyrrole **15** had mp 112° (recrystallized from ethyl ether and petroleum ether); ^{1}H nmr (200 MHz, deuteriochloroform): 2.53 (s, 3H, $COCH_3$), 2.80 (s, 3H, 2-CH_3), 6.43 (d, J = 3.6, 1H, 4-CH), 7.01 (d, J = 3.6, 1H, 5-CH), 7.00-7.58 (m, 5H, ArH), 7.71 (br. s, 1H, NH); ^{13}C nmr (50.3 MHz, deuteriochloroform): 14.1, 24.5, 100.7, 100.8, 109.9, 119.7, 120.2, 124.2, 128.9, 138.0, 163.3, 169.6; ir (potassium bromide): 1718 (C=O), 1661 (C=O); ms: m/z 242 (M^+).

Anal. Calcd. for $C_{14}H_{14}N_2O_2$: C, 69.41; H, 5.82; N, 11.56. Found: C, 69.27; H, 5.65; N, 11.32.

1,3-Thiazole **18** had mp 164-166°; ^{1}H nmr (300 MHz, deuteriochloroform): 2.05 (s, 3H, $COCH_3$) 2.12 (s, 3H, 2-CH_3), 3.36 and 3.59 (2d, J = 14.8, AB pattern, 2H, 2-CH_2), 5.62 (d, J = 4.9, 1H, 5-CH), 6.17 (d, J = 4.9, 1H, 4-CH), 7.07-7.51 (m, 5H, ArH), 7.83 (br. s, 1H, NH); ir (potassium bromide): 1680 (C=O), 1640 (C=O); hrms Calcd. for $C_{14}H_{16}N_2O_2S$: m/z 276.0933. Found: m/z 276.0939; ms: m/z 276 (M^+).

Anal. Calcd. for $C_{14}H_{16}N_2O_2S$: C, 60.85; H, 5.84; N, 10.14. Found: C, 60.60; H, 5.79; N, 9.85.

Disulfide **19** had mp 202° (recrystallized from ethanol); ^{1}H nmr (300 MHz, dimethyl-d_6 sulfoxide and deutriochloroform): 1.88 (s, 6H, $COCH_3$), 2.00 (s, 6H, CH_3), 2.50-2.97 (m, 4H, SCH_2), 3.42-3.84 (2m, 4H, NCH_2), 6.08 (s, 2H, vinyl CH), 6.94-7.56 (m, 10H, ArH), 9.84 (br. s, 2H, NH); ir (potassium bromide): 3274 (NH), 1684 (C=O); hrms Cacld. for $C_{28}H_{34}N_4O_4S_2$: m/z 554.2021 (not found). Found: m/z 276.0925 ($SCH_2CH_2N(COCH_3)CC(CH_3)$-$CHCONHC_6H_5$).

Anal. Calcd. for $C_{28}H_{34}N_4O_4S_2$: C, 60.62; H, 6.18; N, 10.10; S, 11.56. Found: C, 60.70; H, 6.19; N, 9.94; S, 11.70.

Thiolsulfinate **17** (obtained either by separation of the reaction mixture quenched halfway of the pyrolysis of *cis*-sulfoxide **13** or by oxidation [2b] of disulfide **19**) had mp 169° (recrystallized from acetone); ^{1}H nmr (300 MHz, dimethyl-d_6 sulfoxide + deuteriochloroform): 3.30 and 3.42 (2s, 6H, 2xCH_3), 3.45 and 3.49 (2s, 6H, $COCH_3$), 4.25-5.60 (m, 8H, SCH_2CH_2N), 7.51 and 7.56 (2s, 2H, vinyl CH), 8.40-8.99 (m, 10H, ArH), 11.40 and 11.44 (br. 2xs, 2H, NH); ir (potassium bromide): 3300 (NH), 1682 (C=O); hrms Calcd. for $C_{28}H_{34}N_4O_5S_2$: m/z 570.1951 (not found). Found: m/z 294.1026 ($HOSCH_2CH_2N(COCH_3)CC(CH_3)CHCONHC_6H_5$ and m/z 276.0925 ($CHSCH_2N(COCH_3)CC(CH_3)CHCONHC_6H_5$).

Anal. Calcd. for $C_{28}H_{34}N_4O_5S_2$: C, 58.92; H, 6.00; N, 9.82; S, 11.24. Found: C, 58.8; H, 6.04; N, 9.54; S, 11.4.

The *trans*-sulfoxides **14**, 1,3-thiazolidine **12**, dihydro-1,4-thiazine **16** and isomeric dihydro-1,4-thiazine **33** had identical ^{1}H nmr and ir spectra with those obtained previously [1b].

Pyrolysis of Thiosulfinic *S*-Ester **18**.

A solution of **17** (0.13 g, 0.23 mmoles) in toluene (30 ml) was refluxed for 24 hours. Evaporation of the reaction mixture gave a light brown oily residue (110 mg), which was chromatographed using chloroform:methanol = 95:5 as an eluent to afford pyrrole **15** (10 mg, 9%), 1,3-thiazole **18** (47 mg, 43%), dihydro-1,4-thiazine **16** (12 mg, 11%), *cis*-sulfoxide **13** (13 mg, 12%). All of the above had identical ^{1}H nmr and ir spectra with those obtained by the previous methods.

Independent Synthesis of Pyrrole **15**.

To vinyl acetate (15 g, 0.174 mole) was added dropwise bromine (9 ml, 0.174 mole) at 0-5° in an ice water bath over 20 minutes. The cooling bath was removed and the stirring was continued for 2 hours in an oil bath at 55°. Fractional distillation of the reaction mixture gave 1,2-dibromovinyl acetate (bp 130-135°, 30.24 g, 71%). A mixture of acetoacetanilide (13.29 g, 74.9 mmoles), 1,2-dibromovinyl acetate (18.42 g, 74.9 mmoles) and 29% aqueous ammonia (60 ml, 0.496 mole) was placed in an oil bath (70°) and heated for 30 minutes with stirring. The reaction

mixture was diluted with methylene chloride (70 ml), washed with water, and then dried (sodium sulfate). The solvent was removed under reduced pressure to give an oily residue (15.5 g), which was chromatographed using ethyl acetate:*n*-hexane = 1:1 as the eluent to afford 2-methylpyrrole-3-carboxanilide (11.52 g, 77%) [15]. To a solution of this anilide (0.4 g, 2 mmoles) in dimethylformamide (10 ml) was added 60% sodium hydride in oil under a nitrogen atmosphere at room temperature. The reaction mixture was treated with acetyl chloride (0.14 ml, 2 mmoles) for 1 hour under reflux. The precipitates were filtered and the filtrate was evaporated to give an oily residue, which was dissolved in methylene chloride, washed with water twice, and then dried (sodium sulfate). Removal of the solvent under reduced pressure afforded a brown oil, which was chromatographed using benzene:ethyl acetate = 7:3 as the eluent to give **15** (0.118 g, 24%) as a white solid, which had an identical ^{1}H nmr spectrum with that described above.

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REFERENCES AND NOTES

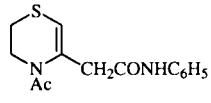
[1a] W. S. Lee, H. G. Hahn and K. D. Nam, *J. Org. Chem.*, **51**, 2789 (1986); [b] H. D. Mah and W. S. Lee, *J. Heterocyclic Chem.*, **26**, 1447 (1989); [c] W. S. Lee, K. Lee, K. D. Nam and Y. J. Kim, *Tetrahedron*, **47**, 8091 (1991); [d] W. S. Lee, K. D. Nam and H. G. Hahn, *J. Heterocyclic Chem.*, **30**, 1105 (1993).

[2a] H. G. Hahn and W. S. Lee, *J. Chem. Res. (S)*, 86 (1995); *J. Chem. Res. (m)*, 0630 (1995); [b]. H. Mah, K. D. Nam and H. G. Hahn, *Heterocycles*, **45**, 1999 (1997).

[3] E. Block, *J. Am. Chem. Soc.*, **94**, 642, 644 (1972).

[4] H. J. Reich, F. Chew and S. L. Peake, *Synthesis*, 299 (1978).

[5] This is a 7:7:4:4:3 mixture of *trans*-sulfoxide **14**, 1,3-thiazolidine **12**, 1,3-thiazole **18**, disulfide **19**, and isomeric dihydro-1,4-thiazine **33** respectively by ^{1}H nmr spectroscopy.



33

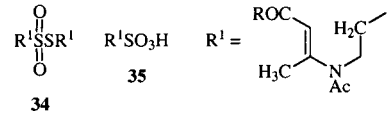
[6a] D. N. Jones, D. R. Hill, D. A. Lewton and C. Sheppard, *J. Chem. Soc. Perkin Trans., 1*, 1574 (1977); [b] D. N. Jones, D. R. Hill and D. A. Lewton, *Tetrahedron Letters*, **27**, 2235 (1975).

[7a] D. R. Hogg, Comprehensive Organic Chemistry, Pergamon Press, Oxford, 1979, **3**, pp262-267; [b] F. A. Davis and R. L. Billmers, *J. Am. Chem. Soc.*, **103**, 7016 (1981); [c] E. Block and J. O'Connor, *ibid* **96**, 3929 (1974).

[8] Although tlc clearly revealed the presence of **17**, it was too scarce to isolate it by chromatography. We prepared **17** by an independent synthesis [2b].

[9] S. Oae, Organic Sulfur Chemistry: Structure and Mechanism, CRCPress, London, 1991, pp 134-135.

[10] Sulfinic acid is known to be thermally unstable and undergo acid-catalyzed, dehydrative disproportionation to yield thiosulfonate and sulfonic acid [11]. However, we could not isolate either **34** or **35**.



34 **35**

[11] S. Oae, Organic Sulfur Chemistry: Structure and Mechanism, CRC Press, London, 1991, p 304.

[12] A. Ishii, T. Ishida, N. Kumon, N. Fukuda, N. Oyama, N. Inamoto, F. Iwasak and R. Okazaki, *Bull. Chem. Soc. Japan*, **69**, 709 (1996).

[13a] D. R. Dice and R. P. Steer, *Can. J. Chem.*, **52**, 3518 (1974); [b] A. G. Anastassiou, J. C. Wetzel and B. Chao, *J. Am. Chem. Soc.*, **98**, 6405 (1976); [c] E. Vedejs, M. J. Arnost, J. M. Dolphin and J. Eustache, *J. Org. Chem.*, **45**, 2601 (1980); [d] E. Vedejs, T. H. Eberlein and D. L. Varie, *J. Am. Chem. Soc.*, **104**, 1445 (1982); [e] J. E. Baldwin and R. C. G. Lopez, *J. Chem. Soc., Chem. Commun.*, 1029 (1982); J. E. Baldwin and R. C. G. Lopez, *Tetrahedron*, **39**, 1487 (1983).

[14] Black precipitates were observed by the treatment of cupric chloride dissolved in 1*N* hydrochloric acid with the stream of vapor of the reaction mixture during the reaction.

[15] H. Shinohara, S. Misaki and E. Imoto, *Nippon Kagaku Zasshi*, **83**, 637 (1962).