The product was light yellow. The 2030-cm^{-1} band and the yellow color disappeared on warming to -110 to -100 °C and the sample became opaque. Benzonitrile and sulfur were identified after warming to room temperature.

Pyrolysis of 1 at 400 °C with isolation of the products in Ar matrix on a BaF_2 window at 20 K was carried out at ca. 10^{-5} torr at an argon/substance ratio of 500:1. The IR spectrum (Figure 1) had the following bands: 3060 (m), 2228 (s), 2175 (vw), 2125 (vw), 2030 (s), 1700 (acetone), 1620 (water), 1595 (m), 1485 (m), 1440 (m), 1408 (w), 1360 (m), 1285 (w), 1230 (w), 1190 (w), 1175 (w), 1155 (w), 1090 (w), 1065 (w), 1020 (w), 995 (vw), 920 (m), 750 (s) cm^{-1}.

No 1 was present in this spectrum, and no 1 was detectable after warming this sample to room temperature. Benzonitrile, sulfur, and a trace of phenyl isothiocyanate were the only products still detectable at room temperature.

Photolysis of 1 in Ar matrix at 11 K at 310 ± 11 nm (Hanovia 1000-W high-pressure Hg lamp with Schoeffel GM 250 monochromator) for 2 h caused the appearance of a weak band at 2030 cm^{-1} and a still weaker one at 2228 cm^{-1}.

Irradiation at 254 nm (75-W low-pressure Hg lamp) for 3 h caused the appearance of two equally strong bands at 2030 and 2228 cm^{-1} together with very weak absorptions at 2190 and 2120 cm^{-1}, the latter ascribed to phenyl isothiocyanate.

Registry No. 1, 34733-85-2; N_2S, 56400-02-3; PhNCS, 103-72-0; PhCN, 100-47-0.

Reactions of 4,5-Dihydro-2-thiazolamine with Phenyl Isothiocyanate and Phenyl Isocyanate: A Reinvestigation

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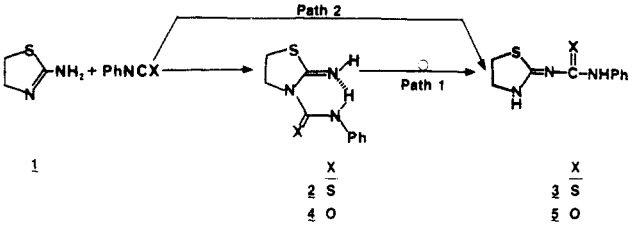
In 1928, Fromm and Kapeller-Adler reported the reaction of 4,5-dihydro-2-thiazolamine (1) with phenyl isothiocyanate under "starker Kühlung" conditions, which initially produced the unstable 2-imino-*N*-phenyl-3-thiazolidinecarbothioamide (**2**).[1] Fromm et al. hypothesized that **2** rearranged during the heating process to *N*-phenyl-*N'*-2-thiazolidinylidenethiourea (**3**), which melted at a higher temperature. Klayman, Maul, and Milne were unable to repeat the earlier work after "careful repetition" of Fromm's conditions.[2,3] Instead, Klayman et al. obtained a single product to which structure **2** was assigned based on an "unequivocal" synthesis.[2] Later, Klayman retracted structure **2**, along with its alleged synthesis, then reassigned structure **3** to this product,[3] which later was confirmed by X-ray crystallography.[4] The X-ray data could not distinguish the tautomeric composition of **3** because both C=N bond lengths were similar. However, Klayman et al. stated that "the intermediacy of **2** in the formation of **3** could not be precluded."[3]

Klayman, Maul, and Milne also examined the reaction of 1 with phenyl isocyanate in acetonitrile in an attempt to prepare 2-imino-*N*-phenyl-3-thiazolidinecarboxamide (**4**).[2] The only product isolated was *N*-phenyl-*N'*-2-thiazolidinylideneurea (**5**) whose structure was deduced by ^{15}N-labeling and degradation experiments. Klayman et al. concluded that phenyl isocyanate had reacted *only* with the exocyclic amino group of **1**.[2]

Scheme I



1 | 2 X = S | 3 X = S | 4 X = O | 5 X = O

a. X = S, 1·HBr, KOH/EtOH, -4 to -2 °C.
b. X = S, 1, Et_2O, -7 to -5 °C.
c. X = O, 1, Et_2O, -16 to -12 °C.

In our hands, reaction of 1 with phenyl isothiocyanate (Scheme Ia) resulted in almost exclusive formation of thiocarbanilide **2**, when compared on TLC with an authentic sample of thiourea **3**.[3] A small amount of **3** was observed in the crude product. Recrystallization in the cold furnished pure **2** in 51% yield,[5,6] the TLC of which indicated some dissociation to 1 and phenyl isothiocyanate (verified by two-dimensional TLC). We also prepared carbothioamide **2** under more convenient Scheme Ib, conditions, which provided pure **2** in 53% yield. Scheme Ia,b conditions appear to show incomplete reaction of 1 with phenyl isothiocyanate, even in the presence of excess (10-20%) 1 during reaction times of up to 3 h. These observations are consistent with the reversible dissociation of pure **2** to 1 and PhNCS in solution and, probably, also during fusion of neat **2**. As a result, during experiments in which **2**, neat or in solution, is heated causing conversion to **3**, the presence of PhNCS allows formation of varying amounts of a byproduct derived from cyclization of a bis adduct of 1 with phenyl isothiocyanate, as previously reported by Klayman et al.[7] Thiocarbanilide **2** was also unstable in the solid state at -20 °C since the presence of **3** was detected after 1 month.

Reaction of 1 with an equimolar quantity of phenyl isocyanate at 0-5 °C in acetonitrile gave **4** as the major product along with small amounts of 1, **5**, and a bis adduct.[3] At ambient temperature, **5** became the major product (ca. 67% by ^1H NMR). However, when phenyl isocyanate was allowed to react with a 10% excess of 1 under Scheme Ic conditions, a 73% yield of pure carboxanilide **4** was obtained directly from the reaction mixture. Amide **4** was significantly more stable than thio counterpart **2** in the solid state and in solution (vide infra). Conversion of **4** to **5** was essentially quantitative when heated neat or in solution. The structure of **4** (and **2** by analogy) has been verified by X-ray crystallography.[8]

^1H NMR spectra of **2** were obtainable by dissolution in CD_2Cl_2 in the cold and immediately recording the spectra at -50 °C probe temperature. In DMF-d_7, dissociation of **2** to 1 and phenyl isothiocyanate was so rapid at -30 °C that clean spectra could not be obtained. ^{13}C NMR verified the presence of PhNCS and ^1H NMR showed varying amounts (ca. 1-2 H) of resonances ascribable to the 4,5-protons of 1. In contrast, carboxanilide **4** was significantly

(1) Fromm, E.; Kapeller-Adler, R. *Justus Liebigs Ann. Chem.* **1928**, *467*, 240. Mp 60 °C, resolidification at 80 °C, remelting at 129 °C.
(2) Klayman, D. L.; Maul, J. J.; Milne, G. W. A. *Tetrahedron Lett.* **1967**, 281.
(3) Klayman, D. L.; Maul, J. J.; Milne, G. W. A. *J. Heterocycl. Chem.* **1968**, *5*, 517.
(4) Flippen, J. L.; Karle, I. L. *J. Phys. Chem.* **1970**, *74*, 769.
(5) We were generally unable to observe spontaneous crystallization after **2** melted. Crystallization of the melt was induced by scratching with a slender glass boiling stick.
(6) The mps of **2-5** were variable (ca. ±2 °C) with the rate of heating.
(7) Klayman, D. L.; Milne, G. W. A. *Tetrahedron* **1969**, *25*, 191.
(8) We gratefully acknowledge the contribution of Professor Roy A. Olofson and D. S. Morrison of the Pennsylvania State University for providing the X-ray crystallographic data for **4**: Rasmussen, C. R.; Villani, F. J., Jr.; Griffin, E. A.; Morrison, D. S.; Olofson, R. A. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1984**, *C40*, 2120.

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more stable in DMF, since satisfactory ^1H NMR were obtainable at −30 °C. Thus, the transformations of carboxanilides **2** and **4**, each with a well-defined A_2X_2 pattern, to their respective ureas **3** and **5**, which had similar A_2B_2 patterns, were clearly observable when these solutions were heated. Our NMR results correlated well with the work of Yamamoto, Yoda, and Matsumura,[9,10] who have studied the reactions of **1** with methyl and ethyl isothiocyanates. These authors concluded that the structural assignments made by Cherbuliez et al. on various isothiocyanate adducts of a series of 2-*N*-substituted-amino thiazolines[11] were in error.

From these experiments we suggest that initial reactions of **1** with isocyanates and isothiocyanates (kinetic control) essentially occur exclusively at endocyclic sp^2 nitrogen to produce **2** and **4**. These adducts may then undergo intramolecular $N \rightarrow N'$ rearrangement (path 1) and/or dissociate to reactants and recombine at exocyclic nitrogen to form the thermodynamically more stable ureas **3** and **5** (path 2). Thus, the initial work of Fromm and Kapeller-Adler, which had come into question, has been verified; and the reaction scope has been extended to include phenyl isocyanate.[12]

Experimental Section

Thin-layer chromatograms were carried out on Whatman MK6F 200 μ silica gel fluorescent 1 × 3 in. slides and Analtech silica gel GF 250 μ 5 × 20 and 20 × 20 cm plates with either CH_2Cl_2 (compounds **2** and **3**) or $CHCl_3$–acetone (9:1) (for compounds **4** and **5**) as eluting solvents. Fresh CH_2Cl_2 solutions of the unstable **2** and **4** for TLC analyses were prepared in an ice–H_2O bath *immediately* before *each* application in order to minimize dissociation and/or conversions to **3** and **5**. ^1H NMR spectra were recorded on a JEOL JNM-FX60Q Fourier transform spectrometer with Me_4Si as internal standard. IR spectra were obtained on a Perkin-Elmer 283. Melting points were determined on a Thomas-Hoover apparatus and are corrected. 4,5-Dihydrothiazol-2-amine (**1**) and phenyl isothiocyanate were purchased from Aldrich Chemical Co. Phenyl isocyanate was obtained from Kodak Laboratory Chemical Co. 4,5-Dihydrothiazol-2-amine was purified by successive recrystallizations from benzene and Et_2O, mp 80–81 °C [lit.[13a] mp 86 °C; lit.[13b] mp 79–80 °C]. The HBr salt of **1** was prepared by treatment of an ethereal solution of **1** with HBr (48%) followed by successive triturations with anhydrous Et_2O and acetone. Recrystallization of the resulting solid from EtOH (95%) furnished pure **1**·HBr, mp 175–176 °C [lit.[14] mp 175–176 °C].

2-Imino-*N*-phenylthiazolidinecarbothioamide (2): Procedure a. Fromm and Kapeller-Adler-Like Conditions.[3] To a cold (−3 °C) stirring solution of 1.28 g (0.02 mol) of KOH (88%) in 5 mL of EtOH (95%) were added 4.03 g (0.022 mol) of 4,5-dihydro-2-thiazolamine hydrobromide (**1**·HBr) and 7 mL of rinse EtOH. The stirring slurry was recooled to −4 °C, and 2.70 g (0.02 mol) of phenyl isothiocyanate was added followed by 2 mL of rinse EtOH. The resulting mixture was stirred at −4 to −2 °C for 3 h, and then ice was added over ca. 5 min with vigorous stirring until a final volume of ca. 75 mL was attained. Filtration gave the crude product **2**, which was washed well with H_2O, allowed to dry under suction for 5 min, and then air-dried, furnishing 4.16 g (88%) of **2** (R_f 0.65) containing a small amount of **3** (R_f 0.18) (CH_2Cl_2). Dissociation of **2** to **1** (R_f 0.0) and PhNCS (R_f 0.91) was verified by two-dimensional TLC on 20 × 20 cm plates. Two recrystallizations from CH_2Cl_2–hexane (dissolution in a minimal amount of CH_2Cl_2, filtration, and then dilution with cold hexane to the cloud point) furnished 2.40 g (51%) of pure **2**, mp 69–71, resolidification,[5,6] remelting at 142–143 °C [lit.[1] mp 60 °C, resolidification at 80 °C, remelting 129 °C].

Procedure b. A solution of 1.12 g (0.011 mol) of **1** in 50 mL of Et_2O was cooled with stirring to −7 °C. Then 1.35 g (0.01 mol) of PhNCS was added drop by drop over 5 min. After the mixture was stirred for 1 h at −7 to −5 °C, 50 mL of hexane was added and the reaction mixture concentrated *in vacuo* below 0 °C to ca. 30 mL. The precipitate was collected, washed well with H_2O, and dried at ambient temperature, affording 1.58 g (67%) of crude product containing a trace of **3**. One recrystallization from CH_2Cl_2–hexane gave 1.25 g (53%) of pure **2**, mp 69–71 °C, resolidification,[5,6] remelting at 142–144 °C. NMR samples were prepared by dissolution in CD_2Cl_2 at <−30 °C and immediately used for recording at −50 °C probe temperature: ^1H NMR (CD_2Cl_2) δ 14.34 (1 H br s, NH), 8.28 (1 H br s, N′H), 7.39 (5 H, m, Ph H), 4.77 (2 H, t, J = 7 Hz, 4-CH_2), 3.18 (2 H, t, J = 7 Hz, 5-CH_2); IR (KBr) 3470 (br), 3226, 1644, 1574, 1520 cm^{-1}. Anal. Calcd for $C_{10}H_{11}N_3S_2$: C, 50.61; H, 4.67; N, 17.70. Found: C, 50.73; H, 4.71; N, 17.70.

Alternate Preparation of *N*-Phenyl-*N*′-2-thiazolidinylidenethiourea (3). A solution of 4.16 g (0.031 mol) of phenyl isothiocyanate in 30 mL of dry DMF was added over 25 min to a solution of 5.32 g (0.052 mol) of **1** in 50 mL of dry DMF. After the mixture was stirred at room temperature for 3 h, addition of H_2O caused precipitation of crude **3**, which, after drying, was recrystallized once from CH_2Cl_2 (filtration to remove a small amount of insoluble material) and, finally, slowly from MeCN–Et_2O, affording pure **3**; mp 149–152 °C (lit.[3] mp 148–149 °C). Fast precipitation of **3** from MeCN by addition of excess Et_2O gave a polymorph, mp 137–139 °C, whose ^1H NMR and solution IR ($CHCl_3$) spectra and TLC behavior were essentially identical with the higher melting polymorph but whose solid-state (KBr) spectra differed markedly: IR ($CHCl_3$) [both polymorphs] 3411 (NH), 1624 (C=N), 1577, 1503 cm^{-1}; IR (KBr) [mp 137–139 °C] 3458, 1631, 1617, 1581, 1539, 1500 [mp 149–152 °C] 3208, 1577, 1517 cm^{-1}; ^1H NMR (DMF-d_7) δ 10.46 (1 H, br s, NH), 9.77 (1 H, br s, N′H), 8.04–7.15 (5 H, m, Ph H), 3.48 (4 H, m, CH_2CH_2). Anal. Calcd for $C_{10}H_{11}N_3S_2$: C, 50.61; H, 4.67; N, 17.70. Found: C, 50.65; H, 4.69; N, 17.69.

Conversion of 2 to 3. Procedure a. An NMR tube containing 50 mg (0.21 mmol) of pure **2** was treated with 0.4 mL of dry DMF-d_7 and immediately heated for 5 min in the steam bath. ^1H NMR indicated essentially complete generation of **3**, when compared with the ^1H NMR spectrum of pure **3**. Examination of the tube contents on TLC indicated the presence of small amounts of **1**, PhNCS, and cyclized bis adduct.[7]

Procedure b. A melting point capillary charged with pure **2** was heated to 69–71 °C. Scratching the melt with a slender glass boiling stick induced crystallization. The tube was heated slowly to ca. 120 °C and held there until complete crystallization occurred. The tube was removed from the oil and wiped clean and the melt extracted into acetone. TLC indicated complete conversion of **2** to **3**. A small front-running impurity (R_f 0.57) which did not correspond to either **2** or PhNCS was observed. TLC of a sample melted at 148–151 °C indicated the presence of small amounts of two decomposition products (R_f 0.57 and 0.61, respectively).

2-Imino-*N*-phenyl-3-thiazolidinecarboxamide (4). A stirring solution of 1.12 g (0.011 mol) of **1** in 50 mL of anhydrous Et_2O under argon was cooled to −16 °C. The cooling process caused reprecipitation of **1**. Then 1.19 g (0.01 mol) of phenyl isocyanate in 2 mL of Et_2O was added drop by drop over 10 min. The reaction mixture was stirred at −16 to −12 °C for 0.75 h. The product was collected, washed with hexane, and dried, furnishing 1.62 g (73%) of pure **4** (R_f 0.68), mp 98–99 °C, spontaneous resolidification, remelting at 152–153 °C. Crystals suitable for X-ray studies were obtained from Et_2O–hexane by slow recrystallization at −20 °C: ^1H NMR (CD_2Cl_2 at −50 °C) δ 12.30 (1 H, br s, NH), 7.86 (1 H, br s, N′H), 7.42 (5 H, m, Ph H), 4.27 (2 H, t, J = 7 Hz), 4-CH_2), 3.17 (2 H, t, J = 7 Hz, 5-CH_2); IR (KBr) 3277 (NH), 1666 (C=O), 1602 (C=N), 1568 cm^{-1}. Anal. Calcd

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(12) Reaction of **1** with 4-tolyl isocyanate in the cold also produced the analogous **4** in 72% yield, mp 114–116 °C spontaneous recrystallization, remelting at 163–167 °C. Anal. Calcd for $C_{11}H_{13}N_3OS$: C, 56.15; H, 5.57; N, 17.86. Found: C, 56.10; H, 5.60; N, 17.82.
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(14) Doherty, D. G.; Shapira, R.; Burnett, W. T., Jr. *J. Am. Chem. Soc.* **1957**, *79*, 5667.

for $C_{10}H_{11}N_3OS$: C, 54.28; H, 5.01; N, 18.99. Found: C, 54.27; H, 5.04; N, 18.90.

***N*-Phenyl-*N'*-2-thiazolidinylideneurea (5).** To a stirring solution of 5.12 g (0.05 mol) of 1 in 60 mL of dry DMF at ambient temperature was added drop by drop over 25 min a solution of 4.77 g (0.04 mol) of phenyl isocyanate in 20 mL of dry DMF. The mixture was allowed to stir for 3 h and then poured onto excess ice and the crude solid collected, washed with H_2O, and dried. Recrystallization from EtOH and DMF-H_2O gave 9.0 g (81%) of pure **5** (R_f 0.1): mp 150-152 °C (lit.[3] mp 149.5-150 °C; lit.[15] mp 157-159 °C): ^{1}H NMR (DMF-d_7) δ 9.66 (1 H, br s, NH), 8.70 (1 H, s, N'H), 8.0-6.9 (5 H, m, Ph H), 3.44 (4 H, m, CH_2CH_2); IR (KBr) 3220 (NH), 1685 (C=O), 1620 (C=N) cm^{-1}. Anal. Calcd for $C_{10}H_{11}N_3OS$: C, 54.28; H, 5.01; N, 18.99. Found: C, 54.23; H, 5.02; N, 18.95.

Heating pure **4** neat and in solution in the same manner as **2** gave essentially clean conversion to **5**. Small amounts of two impurities (R_f 0.59 and 0.64, respectively) were observed on TLC. TLC of the 150-152 °C melt indicated significant amounts of **1**, the two front-running materials described, and an additional small impurity at R_f 0.73.

Preparation of **5** according to the directions of Klayman (1 mol:1 mol) in refluxing benzene also led, in our hands, to the formation of small amounts of bis adduct.[3]

Registry No. **1**, 1779-81-3; **1**·HBr, 13483-03-9; **2**, 101418-75-1; **3**, 13945-09-0; **4**, 14033-35-3; **5**, 14033-37-5; PhNCS, 103-72-0; PhNCO, 103-71-9.

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Reduction of Chiral β-Hydroxy Sulfoxides: Application to the Synthesis of Both Enantiomers of 4-Substituted Butenolides

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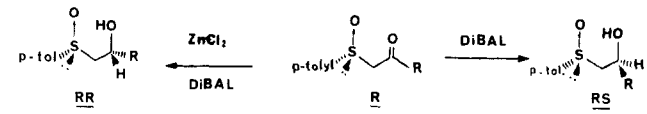
γ-Lactones and butenolides (1) are widely found as a moiety in many naturally occuring compounds such as insect pheromones or flavors. Numerous syntheses of such molecules in racemic form have been described,[1] but only a few reports of chiral synthesis of optically active butenolides have been published. Most of them deal with optical resolution of an intermediate[2] or transformation of an optically active precursor.[3] To our knowledge, only one asymmetric synthesis has been reported: asymmetric reduction of α,β-acetylenic ketones with lithium aluminum hydride complexed by *N*-methylephedrine and 3,5-dimethylphenol, yielding chiral propargylic alcohols which were transformed into butenolides.[4]

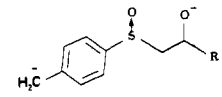
Scheme I



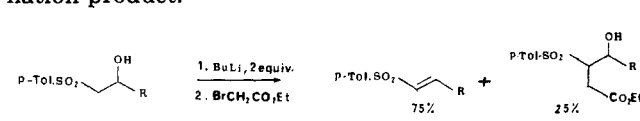
We recently reported[5,6] that the reduction of β-keto sulfoxides afforded both diastereomers of the corresponding β-hydroxy sulfoxides in high ee depending on the experimental conditions of the reduction (Scheme I). We report now the application of such a methodology to the chiral synthesis of butenolides.

For the synthesis of butenolides **1** (Scheme II), 2*R*-β-keto sulfoxides were prepared from the corresponding ethyl esters and (*R*-(+)-*p*-tolyl methyl sulfoxide.[6] The reduction step was performed either directly with DIBAL in THF at -78 °C affording the diastereomer (*RS*)-**3** or after complexation with zinc chloride followed by addition of DIBAL to give the diastereomer (*RR*)-**3**. Diastereomeric excesses were easily determined by ^{1}H NMR at 200 MHz. The two diastereomers (*RS*)-**3** and (*RR*)-**3** show quite different nonequivalences for the two protons α to the sulfoxide as well as quite different chemical shifts for the *tert*-butyl protons. The absolute configuration was deduced from our preceeding study on the reduction mechanism.[5] As indicated in Scheme II this reduction step was highly stereospecific. The smaller de observed with **3c** was the result of a reverse addition of DIBAL as shown in the preceeding paper[5] (method B).

β-Hydroxy *p*-tolyl sulfoxide **3** could not be alkylated on the carbon atom α to the sulfoxide. We demonstrated by labeling experiments that such a molecule gives a dianion having the following structure:



Therefore it was necessary to oxidize the sulfoxide to a sulfone. However, the alkylation of the corresponding dianion with ethyl bromoacetate gave mainly the elimination product:



Recently Tanaka[7] reported that the alkylation of racemic β-hydroxy sulfones could be performed by using sodium iodoacetate instead of any haloacetic ester. We have been able to repeat this experiment on the optically active sulfone (*S*)-**4** and (*R*)-**4** and without isolation of intermediates, convert the resulting hydroxyacids into the corresponding butenolides (*S*)-**1** and (*R*)-**1** by lactonisation in presence of *p*-toluenesulfonic acid and elimination of the sulfonyl group with triethylamine.

The enantiomeric purity of butenolide (*S*)-**1a** could be checked by NMR in presence of the chiral complex Eu(Tfc)$_3$. The racemic compound showed that for a molar ratio [Eu]/[butenolide] = 4, two nonequivalent *tert*-butyl groups can be detected ($\Delta\nu$ = 1.5 Hz). In these conditions

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