H, C3-H), 3.82 (ddd, J = 9.6, 9.2, 2.4 Hz, 1 H, C5-H), 3.45 (s, 3 H, OCH_3), 3.23 (dd, J = 10.3, 2.4 Hz, 1 H, C6-H_a), 3.13 (dd, J = 10.3, 9.2 Hz, 1 H, C6-H_b), 0.68 (s, 9 H, $SiC(CH_3)_3$), −0.05 (s, 3 H, $SiCH_3$), −0.24 (s, 3 H, $SiCH_3$); IR (neat) ν_{max} 1728, 1514, 1261 cm^{-1}; ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 156.0, 136.5, 133.9, 130.3, 129.9, 128.9, 128.9, 128.9, 128.7, 99.5, 75.8, 71.4, 70.6, 67.6, 66.2, 56.3, 56.1, 26.2, 25.9, 18.1, 4.8, −4.0, −4.0; CIMS (NH_3), m/e (relative intensity) 656 (M^+ + H, 35), 624 (50), 547 (65), 530 (30), 498 (base).

Anal. Calcd for $C_{28}H_{38}NO_7SiI$: C, 51.30; H, 5.84; N, 2.14. Found: C, 51.36; H, 5.81; N, 2.11.

(2*S*,3*R*,4*R*)-4-Acetoxy-3-benzoxy-2-[*N*-(benzoxycarbonyl)amino]-5-hexenal (11a). A solution of iodo sugar **10a** (3.0 g, 5.3 mmol) in 95% EtOH (25 mL) was treated with activated zinc dust (6.9 g, 105.4 mmol, 20 equiv), and the reaction mixture was warmed at reflux for 1 h under N_2. The reaction mixture was cooled to ambient temperature, filtered through a plug of alumina and silica (EtOH wash, 3 × 25 mL), and concentrated in vacuo. The residue was redissolved in EtOAc (50 mL), washed with saturated aqueous $NaHCO_3$ (50 mL) and saturated aqueous NaCl (2 × 30 mL), dried (Na_2SO_4), and concentrated in vacuo to provide aldehyde **11a** (2.2 g, 2.2 g theoretical, 100%) as a pale yellow oil, which was used without further purification. A sample of crude aldehyde **11a** was purified by flash chromatography (0.9 × 15 cm silica, 30% EtOAc/hexanes) to afford pure **11a**, which was characterized: ^1H NMR (500 MHz, $CDCl_3$) δ 9.60 (s, 1 H, CHO), 7.35–7.27 (m, 10 H, ArH), 5.79 (ddd, J = 17.4, 10.7, 6.4 Hz, 1 H, C*H*=CHH), 5.64 (br d, J = 7.6 Hz, 1 H, NH), 5.43 (dd, J = 6.4, 5.2 Hz, 1 H, C4-H), 5.30 (d, J = 17.4 Hz, 1 H, *trans*-CH=C*H*H), 5.24 (d, J = 10.7 Hz, 1 H, *cis*-CH=CH*H*), 5.11 (AB q, J = 12.2 Hz, $\Delta\nu$ = 20.1 Hz, 2 H, NC(O)OCH_2Ph), 4.66 (AB q, J = 11.6 Hz, $\Delta\nu$ = 40.6, 2 H, OCH_2Ph), 4.43 (dd, J = 7.6, 3.4 Hz, 1 H, C2-H), 4.21 (dd, J = 5.2, 3.4 Hz, 1 H, C3-H), 2.00 (s, 3 H, CH_3CO); ^{13}C NMR (75 MHz, $CDCl_3$), δ 199.0, 169.7, 156.2, 137.0, 135.9, 132.1, 128.6, 128.5, 128.4, 128.3, 128.2, 128.1, 119.5, 78.5, 74.6, 73.4, 67.4, 60.3, 20.9; IR (neat) ν_{max} 3032, 2867, 1736, 1720 cm^{-1}; CIMS (NH_3), m/e (relative intensity) 412 (M^+ + H, 72), 352 (18), 304 (16), 246 (41), 197 (45), 169 (28), 108 (79), 91 (base).

(2*R*,3*R*,4*R*)-4-Acetoxy-3-benzoxy-2-[*N*-(benzoxycarbonyl)amino]-5-hexen-1-ol (12a). A solution of aldehyde **11a** (3.68 g, 9.0 mmol) in THF (50 mL) at −43 °C under N_2 was treated with solid sodium borohydride (3.38 g, 90 mmol, 10 equiv) followed by water (2.5 mL). The reaction mixture was allowed to stir overnight at −43 °C and was quenched by the slow addition of saturated aqueous NH_4Cl (15 mL, caution!: liberation of H_2). The aqueous layer was extracted with EtOAc (3 × 25 mL) and the combined organic extracts were washed with 5% aqueous HCl (15 mL), saturated aqueous $NaHCO_3$ (2 × 25 mL), and saturated aqueous NaCl (2 × 25 mL), dried ($MgSO_4$), and concentrated in vacuo to provide a colorless oil. Purification of the residue by flash chromatography (3.6 × 15 cm silica, 30–40% EtOAc/hexanes) afforded alcohol **12a** (2.53 g, 3.70 g theoretical, 68%) as a colorless oil: ^1H NMR (500 MHz, $CDCl_3$) δ 7.49–7.28 (m, 10 H, ArH), 5.82 (ddd, J = 17.4, 10.7, 6.7 Hz, 1 H, C*H*=CHH), 5.48 (dd, J = 7.3, 6.7 Hz, 1 H, C4-H), 5.30 (d, J = 17.4 Hz, 1 H, *trans*-CH=C*H*H), 5.27 (br d, J = 9.5 Hz, 1 H, NH), 5.22 (d, J = 10.7 Hz, 1 H, *cis*-CH=CH*H*), 5.05 (s, 2 H, NC(O)OCH_2Ph), 4.69 (AB q, J = 11.3 Hz, $\Delta\nu$ = 78.9 Hz, 2 H, OCH_2Ph), 3.89 (apparent dd, J = 9.5, 5.5 Hz, 1 H, C2-H), 3.84 (dd, J = 7.3, 1.5 Hz, 1 H, C3-H), 3.59 (dd, J = 10.7, 5.5 Hz, 1 H, C1-H), 3.45 (dd, J = 10.7, 7.6 Hz, 1 H, C1-H), 2.53 (s, 1 H, OH), 2.02 (s, 3 H, CH_3CO); ^{13}C NMR (125 MHz, $CDCl_3$), δ 170.4, 156.8, 138.1, 136.6, 132.8, 129.0, 128.9, 128.6, 128.5, 128.4, 128.3, 119.5, 78.2, 75.5, 75.4, 67.4, 63.0, 53.0, 21.5; IR (neat) ν_{max} 3438, 3032, 1722 cm^{-1}; EIMS, m/e (relative intensity) 413 (M^+, 1), 382 (3), 314 (12), 270 (7), 219 (4), 160 (15), 119 (10), 91 (base); HRMS, m/e calcd for $C_{23}H_{27}NO_6$ 413.1828, found 413.1846.

Anal. Calcd for $C_{23}H_{27}NO_6$: C, 66.81; H, 6.58; N, 3.39. Found: C, 66.72; H, 6.59; N, 3.36.

(2*R*,3*R*,4*R*)-2-[*N*-(Benzoxycarbonyl)amino]-4-(benzoyloxy)-3-[(*tert*-butyldimethylsilyl)oxy]-5-hexen-1-ol (12b). A solution of iodide **10b** (0.77 g, 1.18 mmol) in 95% EtOH (20 mL) was treated with activated zinc dust (1.52 g, 23.4 mmol, 20 equiv). The reaction mixture was warmed at reflux under N_2 for 1 h and the warm reaction mixture was filtered through a mixed pad of Celite and neutral Al_2O_3 (3 × 10 mL EtOH wash). The filtrate containing crude aldehyde **11b** was cooled to 0 °C and was treated with $NaBH_4$ (22.2 mg, 0.59 mmol, 2.0 equiv). After 15 min at 0 °C, aqueous 5% HCl was slowly added to the reaction mixture until gas evolution ceased. The mixture was diluted with saturated aqueous $NaHCO_3$ (40 mL) and extracted with EtOAc (4 × 40 mL). The combined organic extracts were washed with saturated aqueous NaCl (60 mL) and were dried ($MgSO_4$). The solvent was removed in vacuo and the residue was purified by flash chromatography (2 × 12 cm silica, 20–40% EtOAc/hexanes) to afford alcohol **12b** (0.50 g, 0.60 g theoretical, 84% based on iodide **10b**): ^1H NMR (300 MHz, $CDCl_3$) δ 8.06 (d, J = 7.2 Hz, 2 H, PhCO), 7.54 (apparent t, J = 7.4 Hz, 1 H, PhCO), 7.43 (apparent t, J = 7.5 Hz, 2 H, PhCO), 7.35–7.30 (m, 5 H, $C_6H_5CH_2O$), 5.93 (ddd, J = 17.3, 10.7, 5.9 Hz, 1 H, C*H*=CH_2), 5.56 (dd, J = 6.2, 5.9 Hz, 1 H, C4-H), 5.32 (d, J = 17.3 Hz, 1 H, *trans*-CH=C*H*H), 5.24 (d, J = 8.8 Hz, 1 H, NH), 5.14 (d, J = 10.7 Hz, 1 H, *cis*-CH=CH*H*), 5.06 (s, 2 H, PhCH_2O), 4.20 (apparent d, J = 6.2 Hz, 1 H, C3-H), 3.98 (apparent dd, J = 15.0, 6.9 Hz, 1 H, C2-H), 3.70–3.60 (m, 1 H, C1-H), 3.55–3.45 (m, 1 H, C1-H), 2.72 (t, J = 5.7 Hz, 1 H, OH), 0.86 (s, 9 H, $SiC(CH_3)_3$), 0.13 (s, 3 H, $SiCH_3$), 0.09 (s, 3 H, $SiCH_3$); IR (neat) ν_{max} 3442, 1722, 1504, 1267 cm^{-1}; ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 156.4, 136.4, 133.3, 132.0, 130.0, 130.0, 130.0, 128.5, 128.3, 117.9, 75.8, 70.8, 67.0, 63.1, 53.2, 25.9, 18.1, −4.2, −4.8; EIMS, m/e (relative intensity) 499 (M^+, 2), 468 (15), 442 (10), 338 (25), 230 (30), 179 (80), 91 (base); HRMS, m/e calcd for $C_{23}H_{28}NO_6Si$ (M^+ − $C(CH_3)_3$) 442.1686, found 442.1691.

Anal. Calcd for $C_{27}H_{37}NO_6Si$: C, 64.90; H, 7.46; N, 2.80. Found: C, 64.78; H, 7.51; N, 2.74.

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Registry No. **4**, 4704-15-8; **5a**, 141438-52-0; **5b**, 141438-53-1; **6a**, 93000-10-3; **6b**, 141438-54-2; **7**, 87907-35-5; **8**, 141438-55-3; **9**, 141438-56-4; **10a**, 141438-57-5; **10b**, 141438-58-6; **10c**, 141438-59-7; **10d**, 56733-36-9; **11a**, 141438-60-0; **12a**, 141438-61-1; **12b**, 141438-62-2; **12c**, 141438-63-3; **12d**, 141438-64-4; *p*-anisaldehyde dimethyl acetal, 2186-92-7.

Supplementary Material Available: Experimental procedures and spectral characterization for **6a**, **6b**, **10c,d**, **11c,d**, and **12c,d** (6 pages). Ordering information is given on any current masthead page.

A Novel Photochemical Isomerization of *N*-(2′,2′-Dimethyl-3′-butenoyl) Cyclic Dithiocarbamates, Cyclic Thionocarbamates, and Thiolactams to Thiolactones

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Introduction

The photochemistry of thiocarbonyl compounds has received much attention from both synthetic and mechanistic viewpoints. It is well-known that thioamides[1] and

Scheme I

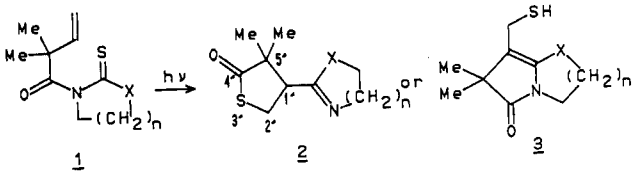


Table I. Photolysis of Monothioimides 1[a]

monothioimide	n	X	product (yield, %)
1a	1	S	**2a** (74)
1b	1	O	**2b** (56)
1c	1	C	**2c** (70)
1d	2	S	**3d** (64)
1e	2	O	**2e** (77)

[a] 500-W high-pressure Hg lamp, benzene solution, rt, ca. 0.5 h.

thioimides,[2] in which the carbon of the thiocarbonyl group is also joined, by single bonds, to a carbon and a nitrogen, cycloadd to carbon–carbon double bonds, both inter- and intramolecularly, to produce thietanes. In contrast, the [2 + 2] cycloaddition to carbon–carbon double bonds of related compounds, i.e., those in which the carbon of the thiocarbonyl group is bonded both to a nitrogen and to an atom other than carbon, e.g., nitrogen, oxygen, or sulfur, has been little studied. For example, 1,3-disubstituted thioparabanates, which are cyclic thioureas, cycloadd intermolecularly to olefins.[3] We have already studied the intramolecular [2 + 2] cycloaddition of thioimides to carbon–carbon double bonds and the Norrish type II reactions of *N*-acyl cyclic thionocarbamates and *N*-acyl cyclic dithiocarbamates.[4] We now wish to report that photolysis of *N*-(2′,2′-dimethyl-3′-butenoyl) cyclic thionocarbamates and cyclic dithiocarbamates gives γ-thiolactones via intermediate thietanes. What are described are the first examples of the intramolecular [2 + 2] cycloaddition to a carbon–carbon double bond of thiocarbonyl compounds in which the carbon of the thiocarbonyl group is joined, by single bonds, to two heteroatoms.

Results and Discussion

All *N*-acyl cyclic dithiocarbamates **1a** and **1d**, cyclic thionocarbamates **1b** and **1e**, and thiolactam **1c** were easily obtained by condensing 2,2-dimethyl-3-butenoyl chloride with the corresponding cyclic dithiocarbamates, cyclic thionocarbamates, or thiolactam in the presence of triethylamine. When a benzene solution of *N*-(2′,2′-dimethyl-3′-butenoyl)thiazolidine-2-thione (**1a**) in a Pyrex vessel was irradiated under argon atmosphere with the UV light from a high-pressure mercury lamp until the starting material had disappeared, 2-(5′,5′-dimethyl-4′-oxo-3′-thiolanyl)-2-thiazine (**2a**) was obtained in 74% yield (Scheme I). The structure of **2a** was inferred from the results of elemental analysis and spectral data. The IR spectrum of **2a** exhibits absorptions at 1610 and 1680 cm^{-1} attributable to C=N and C=O bonds, respectively. The ^1H NMR spectrum shows three double-doublets assignable to the protons on C-1′ and C-2′ and the absence of olefinic proton signals. The ^{13}C NMR spectrum exhibits a singlet, not present in the spectrum of **1a**, at 168.3 (C=N) and a doublet at 53.4 (C-1′). No signal which could be attributed to the thiocarbonyl group carbon is observed. The structure of **2a** was unequivocally established by X-ray crystallographic analysis (Figure 1).[5]

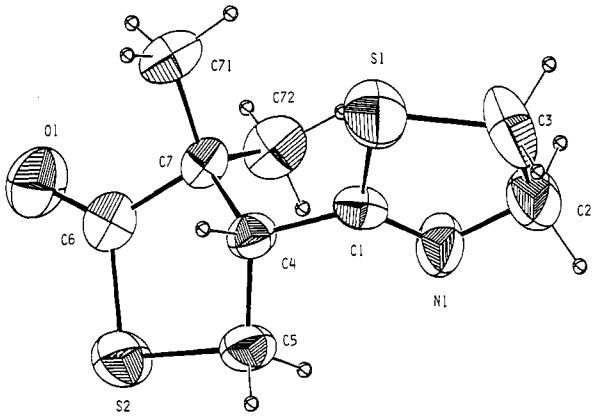
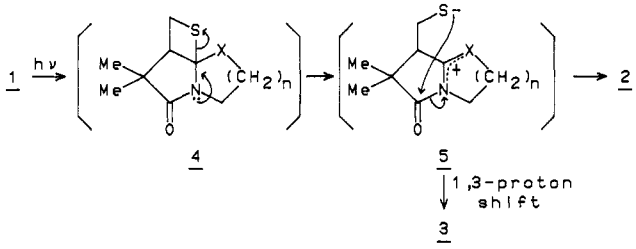


Figure 1. ORTEP diagram of **2a**.

Scheme II



The photolysis of two other five-membered compounds, *N*-acyl cyclic thionocarbamate **1b** and thiolactam **1c**, gave similar results, i.e., the corresponding thiolactones **2b** and **2c** were produced (Table I). Earlier, we reported[4b] that the photolysis of **1c** gave what we believed to be a bicyclic lactam. However, the similarities between the ^1H and ^{13}C NMR spectra of **2a** and those of the photoproduct from **1c** suggested that the latter also possesses a thiolactone moiety. Furthermore, the results of applying COSY techniques permitted the assignment of the multiplet signals. After carefully comparing the spectra of **2a** with those of the photoproduct from **1c**, we concluded that the latter is not a bicyclic lactam but a thiolactone **2c**. From the photolysis of **1d**, a bicyclic ene thiol, 8,8-dimethyl-7-(mercaptomethyl)-5-thia-1-azabicyclo[4.3.0]-6-nonen-9-

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(5) Crystal and experimental data for **2a**: $C_9H_{13}NOS_2$, MW 215, colorless, space group with a = 6.889 (2) Å, b = 10.630 (2) Å, c = 14.674 (5) Å, β = 100.138 (1)°, V = 1057.800 Å^3, z = 4, ρ = 1.35 g/cm^3, and μ = 4.4 cm^{-1}. Data were collected at 23 ± 1 °C with Mo Kα radiation (λ = 0.70930 Å) on an Enraf-Nonius CAD-4. A total of 1044 reflections within 2θ = 50.0° were measured by the $\omega - 2\theta$ scan method with a scan rate of 1–5°/min. The structure was solved by direct methods and refined by the method of full-matrix least-squares. Convergence on 811 reflections [$Fo^2 > 3.0\sigma(Fo^2)$] and 157 parameters resulted in R = 0.053 and R_w = 0.056.

one (**3d**), was the main photoproduct. The structure of **3d** was inferred from the results of elemental analysis and spectral data. Thus, the IR spectrum of **3d** exhibits an absorption at 1680 cm^{-1} due to the carbonyl group. The ^1H NMR spectrum shows a D_2O-exchangeable triplet at δ 1.78 and a doublet at δ 3.34, indicative of the presence of a mercaptomethyl group at the 7-position. The ^{13}C NMR spectrum exhibits singlets due to the olefinic carbons C-6 and C-7. No signal which could be attributed to the thiocarbonyl carbon is seen. The photolysis of **1e**, like that of **1a–1c**, gave a thiolactone **2e**.

The formation of the thiolactones **2** can be reasonably explained in terms of the intermediacy of a tricyclic thietane **4** (Scheme II). Presumably the angle strain in **4** is relieved by ring-opening to the zwitterionic intermediate **5**. We were unsuccessful in attempts to directly observe **4a** by ^1H NMR spectroscopy during the photolysis of **1a** at −20 °C. Only the thiolactone **2a** was detected, even at that temperature. In an attempt to trap the zwitterion **5a** as a methoxy derivative, a methanolic colution of **1a** was irradiated. However, an intractable mixture, in which not even **2a** was detected, was produced.

We postulate that the bicyclic lactam **3d** is formed as the result of the 1,3-shift of a proton within the zwitterion **5d** (Scheme II). Why only **1d** gives an ene thiol **3d** can be explained in terms of the stability of the zwitterion **5d**. Species **5d** would be expected to be more stable than the zwitterions derived from **1a–1c** and **1e** because its cationic center is stabilized by a resonance interaction involving the lone pair of electrons on the adjacent sulfur and also because the strain in a six-membered ring is slightly less than that in a five-membered ring. We established that the bicyclic lactams **3** are not intermediates in the transformation of compounds **1** into thiolactones **2**. Thus, heating **3d** or exposing it to acidic conditions gave intractable mixtures, in which the thiolactone **2d** was not found.

In conclusion, the photolysis of various *N*-(2′,2′-dimethyl-3′-butenoyl) cyclic dithiocarbamates, cyclic thionocarbamates, and thiolactams gave, via the initially formed tricyclic thietanes and the zwitterions derived therefrom, thiolactones; except in the case of the tetrahydro-1,3-thiazine derivative **1d**, photolysis of which gave a bicyclic ene thiol. Ring-opening, which relieves the angle strain in the tricyclic thietanes **2**, is facilitated by the electron-donating effect of the two heteroatoms adjacent to the thietane ring. What are shown are the first examples of the intramolecular [2 + 2] cycloaddition of cyclic thionocarbamates and cyclic dithiocarbamates to a carbon–carbon double bond. Cycloaddition is followed by a novel isomerization of the initially formed product. The reaction should prove useful for preparing certain γ-thiolactones.

Experimental Section

IR spectra of $CHCl_3$ solutions were recorded with a Jasco IRA-1 spectrophotometer. ^1H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded with Hitachi R-600 and GEOL GSX-500 spectrometers, respectively. An Eikohsya 500-W high-pressure Hg lamp was used in the irradiations. Silica gel (Merck, Kieselgel 60, 230–400 mesh) was used for flash chromatography.

Preparation of *N*-Acyl Cyclic Dithiocarbamates 1a and 1d, *N*-Acyl Cyclic Thionocarbamates 1b and 1e, and *N*-Acyl Thiolactam 1c. To a cold (0 °C) stirred solution of the thioamide (3.0 mmol), Et_3N (3.6 mmol), and THF (30 mL) was added 2,2-dimethylbutenoyl chloride (3.6 mmol) drop-by-drop under N_2. The mixture was stirred for 2 h at rt. The Et_3N·HCl that precipitated was removed by filtration through a Celite 545 column. The solvent was evaporated from the filtrate in vacuo. The residue was purified by flash chromatography on silica gel (benzene–EtOAc (50:1–10:1)). The crystalline monothioimides so isolated were recrystallized from $CHCl_3$/hexane.

***N*-(2′,2′-Dimethyl-3′-butenoyl)thiazolidine-2-thione (1a)**: 75% yield; bp 60–63 °C (1 mmHg); IR 1720 cm^{-1}; ^1H NMR δ 1.44 (s, 6 H, 2′-CH_3), 3.45 (t, J = 7 Hz, 2 H, 5-CH_2), 4.17 (t, J = 7 Hz, 2 H, 4-CH_2), 5.10 (d, J = 10 Hz, 1 H, 4′-CH), 5.11 (d, J = 18 Hz, 1 H, 4′-CH) and 6.05 (dd, J = 10 and 18 Hz, 1 H, 3′-CH); ^{13}C NMR δ 25.6 (q, 2′-Me), 31.2 (t, 5-C), 49.7 (s, 2′-C), 57.1 (t, 4-C), 114.9 (t, 4′-C), 141.7 (d, 3′-C), 182.5 (s, C=O) and 200.5 (s, C=S). Anal. Calcd for $C_9H_{13}NOS_2$: C, 50.20; H, 6.08; N, 6.50. Found: C, 50.06; H, 6.01; N, 6.40.

***N*-(2′,2′-Dimethyl-3′-butenoyl)oxazolidine-2-thione (1b)**: 95% yield; mp 68–70 °C; IR 1710 cm^{-1}; ^1H NMR δ 1.20 (s, 6 H, 2′-CH_3), 4.0–4.8 (m, 4 H, 2-CH_2 and 3-CH_2), 5.10 (d, J = 18 Hz, 1 H, 4′-CH), 5.11 (d, J = 10 Hz, 1 H, 4′-CH) and 6.05 (dd, J = 18 and 10 Hz, 1 H, 3′-CH); ^{13}C NMR δ 26.0 (q, 2′-Me), 48.4 (s, 2′-C), 49.1 (t, 4-C), 67.2 (t, 5-C), 114.7 (t, 4′-C), 141.6 (d, 3′-C), 176.5 (s, C=S), and 185.7 (s, C=O). Anal. Calcd for $C_9H_{13}NO_2S$: C, 54.24; H, 6.57; N, 7.02. Found: C, 54.35; H, 6.62; N, 6.88.

***N*-(2′,2′-Dimethyl-3′-butenoyl)tetrahydro-1,3-thiazine-2-thione (1d)**: 99% yield; mp 48–49 °C; IR 1710 cm^{-1}; ^1H NMR δ 1.48 (s, 6 H, 2′-CH_3), 2.0–2.4 (m, 2 H, 5-CH_2), 3.00 (t, J = 6 Hz, 2 H, 6-CH_2), 3.50 (m, J = 6 Hz, 2 H, 4-CH_2), 5.10 (d, J = 10 Hz, 1 H, 4′-CH), 5.11 (d, J = 18 Hz, 1 H, 4′-CH) and 6.09 (dd, J = 18 and 10 Hz, 1 H, 3′-CH); ^{13}C NMR δ 21.3 (t, 5-C), 25.8 (q, 2′-Me), 30.6 (t, 6-C), 49.2 (t, 4-C), 50.3 (s, 2′-C), 114.4 (t, 4′-C), 142.5 (d, 3′-C), 186.8 (s, C=O), and 191.8 (s, C=S). Anal. Calcd for $C_{10}H_{15}NOS_2$: C, 52.36; H, 6.59; N, 6.10. Found: C, 52.24; H, 6.52; N, 6.00.

***N*-(2′,2′-Dimethyl-3′-butenoyl)tetrahydro-1,3-oxazine-2-thione (1e)**: 86% yield; mp 41–42 °C; IR 1720 cm^{-1}; ^1H NMR δ 1.48 (s, 6 H, 2′-CH_2), 2.13 (quint, J = 6 Hz, 2 H, 5-CH_2), 3.43 (t, J = 6 Hz, 2 H, 4-CH_2), 4.28 (t, J = 6 Hz, 2 H, 6-CH_2), 5.05 (d, J = 10 Hz, 1 H, 4′-CH), 5.06 (d, J = 17 Hz, 1 H, 4′-CH) and 6.09 (dd, J = 10 and 17 Hz, 1 H, 3′-CH); ^{13}C NMR δ 20.7 (t, 5-C), 26.4 (q, 2′-Me), 45.9 (t, 4-C), 50.5 (s, 2′-C), 68.0 (t, 6-C), 114.4 (t, 4′-C), 142.7 (d, 3′-C), 183.8 (s, C=O or C=S), and 184.4 (s, C=O or C=S). Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 56.31; H, 7.08; N, 6.56. Found: C, 56.16; H, 6.95; N, 6.51.

General Procedure for the Photolysis of the Monothioimides 1a–1e. A benzene solution of the monothioimide under Ar was irradiated at rt with the UV light from a 500-W high-pressure Hg lamp until the starting material had disappeared (ca. 0.5 h in all cases). The residue obtained by concentrating the reaction mixture was purified by flash chromatography (benzene/EtOAc (4:1–2:3)). The crystalline products were recrystallized from $CHCl_3$/hexane.

2-(5′,5′-Dimethyl-4′-oxo-3′-thiolanyl)-2-thiazine (2a): 74% yield; mp 46–47 °C; IR 1610 and 1680 cm^{-1}; ^1H NMR δ 1.05 (s, 3 H, 5′-Me), 1.36 (s, 3 H, 5′-Me), 3.21 (dd, J = 10.2 and 6.2 Hz, 1 H, 1′-CH), 3.3–3.4 (m, 3 H, 5-CH_2 and 2′-CH), 3.64 (dd, J = 11.5 and 10.2 Hz, 1 H, 2′-CH), and 4.2–4.4 (m, 2 H, 4-CH_2); ^{13}C NMR δ 19.3 (q, 5′-Me), 24.0 (q, 5′-Me), 30.9 (t, 2′-C), 33.8 (t, 5-C), 51.4 (s, 5′-C), 53.4 (d, 1′-C), 64.1 (t, 4-C), 168.3 (s, C=N), and 210.6 (s, C=O). Anal. Calcd for $C_9H_{13}NOS_2$: C, 50.20; H, 6.08; N, 6.50. Found: C, 50.48; H, 6.14; N, 6.41.

2-(5′,5′-Dimethyl-4′-oxo-3′-thiolanyl)-2-oxazine (2b): 56% yield; mp 33–34 °C; IR 1655 and 1690 cm^{-1}; ^1H NMR δ 1.05 (s, 3 H, 5′-Me), 1.32 (s, 3 H, 5′-Me), 3.05 (dd, J = 11.1 and 6.5 Hz, 1′-CH), 3.33 (dd, J = 11.7 and 6.5 Hz, 1 H, 2′-CH), 3.59 (dd, J = 11.1 and 11.7 Hz, 1 H, 2′-CH), 3.8–3.9 (m, 2 H, 5-CH_2) and 4.2–4.4 (m, 2 H, 4-CH_2); ^{13}C NMR δ 19.5 (q, 5′-Me), 23.8 (q, 5′-Me), 29.6 (t, 2′-C), 48.2 (d, 1′-C), 51.2 (s, 5′-C), 54.1 (t, 5-C), 67.6 (t, 4-C), 165.7 (s, C=N), and 210.7 (s, C=O). Anal. Calcd for $C_9H_{13}NO_2S$: C, 54.24; H, 6.57; N, 7.02. Found: C, 54.15; H, 6.56; N, 7.00.

2-(5′,5′-Dimethyl-4′-oxo-3′-thiolanyl)-2-pyrroline (2c): 70% yield; bp 68 °C (10^{-3} mmHg); IR 1620 and 1680 cm^{-1}; ^1H NMR δ 0.99 (s, 3 H, 5′-Me), 1.33 (s, 3 H, 5′-Me), 1.8–2.0 (m, 2 H, 4-CH_2), 2.45–2.55 (m, 1 H, 3-CH), 2.55–2.65 (m, 1 H, 3-CH), 3.09 (dd, J = 10.3 and 6.2 Hz, 1 H, 1′-CH), 3.30 (dd, J = 11.7 and 6.2 Hz, 1 H, 2′-CH), 3.63 (dd, J = 11.7 and 10.3 Hz, 1 H, 2′-CH), and 3.8–3.95 (m, 2 H, 5-CH_2); ^{13}C NMR δ 19.5 (q, 5′-Me), 22.7 (t, 4-C), 24.4 (q, 5′-Me), 30.6 (t, 2′-C), 38.2 (t, 3-C), 51.3 (s, 5′-C), 53.0 (d, 1′-C), 60.5 (t, 5-C), 175.1 (s, C=N), and 211.6 (s, C=O); MS m/e 197 (M^+). Anal. Calcd for $C_{10}H_{15}NOS$: C, 60.87; H, 7.66; N, 7.09. Found: C, 62.28; H, 7.98; N, 6.62.

8,8-Dimethyl-7-(mercaptomethyl)-5-thia-1-azabicyclo-[4.3.0]-6-nonen-9-one (3d): 64% yield; mp 82–84 °C; IR 1680 cm^{-1}; ^1H NMR δ 1.24 (s, 6 H, 8-CH_3), 1.78 (t, J = 6.9 Hz, 1 H, D_2O exchangeable, SH), 2.1–2.2 (m, 2 H, 3-CH_2), 2.9–3.0 (m, 2 H, 4-CH_2), 3.34 (d, J = 6.9 Hz, 2 H, CH_2SH), and 3.5–3.6 (m, 2 H, 2-CH_2); ^{13}C NMR δ 18.3 (t, 7-CH_2SH), 22.8 (q, 8-Me), 24.0 (t, 3-C), 24.6 (t, 4-C), 39.4 (t, 2-C), 47.4 (s, 8-C), 118.6 (s, 7-C), 126.9 (s, 6-C), 181.8 (s, C=O). Anal. Calcd for $C_{10}H_{15}NOS_2$: C, 52.36; H, 6.59; N, 6.10. Found: C, 52.15; H, 6.53; N, 6.06.

2-(5',5'-Dimethyl-4'-oxo-3'-thiolanyl)-2-oxazine (2e): 77% yield; mp 77–79 °C; IR 1660 and 1685 cm^{-1}; ^1H NMR δ 1.04 (s, 3 H, 5'-Me), 1.29 (s, 3 H, 5'-Me), 1.8–1.9 (m, 2 H, 5-CH_2), 2.84 (dd, J = 10.8 and 6.6 Hz, 1 H, 1'-CH), 3.18 (dd, J = 11.7 and 6.6 Hz, 1 H, 2'-CH), 3.4–3.5 (m, 2 H, 6-CH_2), 3.55 (dd, J = 11.7 and 10.8 Hz, 2'-CH) and 4.1–4.2 (m, 2 H, 4-CH_2); ^{13}C NMR δ 19.6 (q, 5'-Me), 21.9 (t, 5-C), 24.4 (q, 5'-Me), 29.5 (t, 2'-C), 42.2 (t, 6-C), 51.4 (s, 5'-C), 53.8 (d, 1'-C), 65.0 (t, 4-C), 157.4 (s, C=N), and 211.7 (s, C=O). Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 56.31; H, 7.08; N, 6.56. Found: C, 56.25; H, 7.06; N, 6.55.

Registry No. **1a**, 141249-21-0; **1b**, 141249-22-1; **1c**, 125880-12-8; **1d**, 141249-23-2; **1e**, 141249-24-3; **2a**, 141249-25-4; **2b**, 141249-26-5; **2c**, 141249-27-6; **2e**, 141249-28-7; **3d**, 141249-29-8; 2,2-dimethylbutenoyl chloride, 57690-96-7; thiazolidine-2-thione, 96-53-7; oxazolidine-2-thione, 5840-81-3; pyrrolidine-2-thione, 2295-35-4; tetrahydro-1,3-thiazine-2-thione, 5554-48-3; tetrahydro-1,3-oxazine-2-thione, 17374-18-4.

Sulfonation of Aromatic Compounds in HSO_3F–SbF_5

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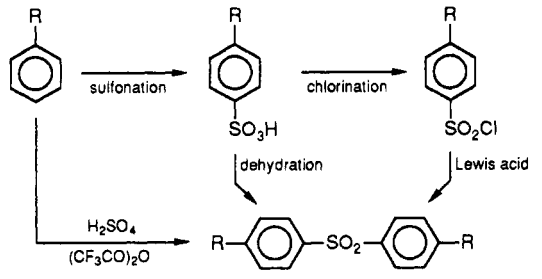
Sulfonyl compounds are useful raw materials for engineering plastics which are clear and thermostable. The synthesis of diaryl sulfones and disulfonyl compounds has been extensively studied and reviewed.[1,2] Generally, diaryl sulfones have been prepared from aromatic compounds by two- or three-step reactions via aryl sulfonic acids or sulfonyl chlorides.



The main synthetic methods for preparing diaryl sulfones have been Friedel–Crafts sulfonylations between arylsulfonyl halides and aromatic compounds in the presence of a suitable Lewis acid.[1] Other synthetic methods are the condensation of arylsulfonic acids with aromatic compounds using dehydration reagents[3] such as H_3PO_4 and P_2O_5. A one-pot synthesis of diaryl sulfones from aromatic compounds using H_2SO_4 and $(CF_3CO)_2O$ has been reported.[4]

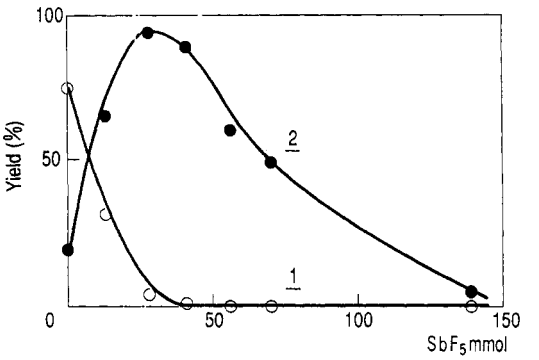
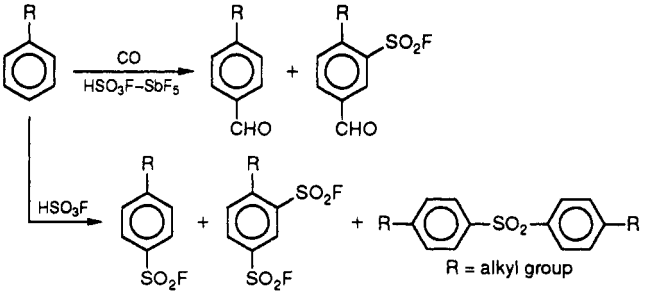


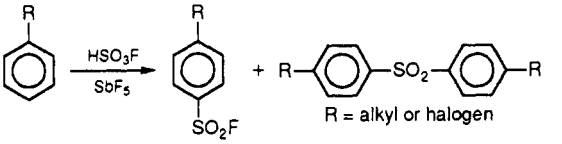
Figure 1. Influence of HSO_3F–SbF_5 Compositions. Sulfonation was carried out using 174 mmol of HSO_3F and 20 mmol of benzene at 50 °C for 1 h: (1) benzenesulfonyl fluoride; (2) diphenyl sulfone.

In our previous work on the formylation of alkylbenzenes with CO in HSO_3F–SbF_5, unexpected products, namely bis(alkylphenyl) sulfones and alkylbenzenedisulfonyl fluorides, were formed in a one-pot reaction as follows:[5]



Therefore, we focused on a convenient synthesis of diaryl sulfones and disulfonyl compounds in HSO_3F–SbF_5 and wish to report herein the results of these studies.

Aromatic compounds reacted with HSO_3F[6] in the presence of a suitable amount of SbF_5 to give arylsulfonyl fluorides and diaryl sulfones as the main products at 0–50 °C:



The results of application of this reaction to a variety of aromatic compounds are summarized in Table I. Diaryl sulfones were obtained in high yield from benzene, toluene, xylenes, 1,2,4-trimethylbenzene, and fluoro-, chloro-, and bromobenzene by a one-pot reaction when an excess amount of SbF_5 relative to the substrate was added to HSO_3F. The appropriate amount of SbF_5 depended on the reactivity of the aromatic compounds for the electrophilic substitution, and the required amount of SbF_5 decreased with increasing reactivity of the aromatic compounds. In the case of polyalkylbenzenes such as 1,3,5- and 1,2,3-trimethylbenzene and tetramethylbenzenes, attempts to obtain diaryl sulfones with good yield were unsuccessful, and arylsulfonyl fluorides were formed as the main products. Although the sulfonyl group was mainly

(1) Olah, G. A. *Friedel-Crafts and Related Reaction*; Wiley-Interscience: New York, 1964; Vol. III, p 1319.
(2) See ref 1, p 1355.
(3) (a) Graybill, B. M. *J. Org. Chem.* **1967**, *32*, 2931. (b) Sipe, H. J., Jr.; Clary, D. W.; White, S. B. *J. Chem. Soc., Chem. Commun.* **1984**, 283. (c) Ueda, M.; Uchiyama, K.; Kano, T. *J. Chem. Soc., Chem. Commun.* **1984**, 323. (d) Tedder, J. M. *Chem. Rev.* **1955**, *55*, 787. (e) Field, L. *J. Am. Chem. Soc.* **1952**, *74*, 394.
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(6) (a) Baker, W.; Coates, G. E.; Glockling, F. *J. Chem. Soc.* **1951**, 1376. (b) Baker, B. R.; Cory, M. *J. Med. Chem.* **1971**, *14*, 119.

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