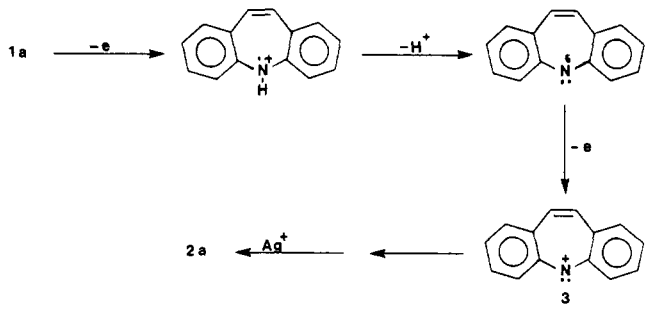
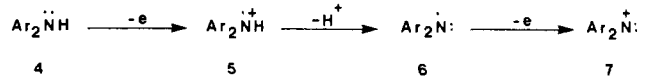
Scheme I



Scheme II



mmol) of dibenz[*b*,*f*]azepine (**1a**) in 25 mL of methylene chloride. The orange solution of **1a** immediately turned black and silver metal precipitated. Analysis of the reaction mixture by GC-MS indicates **1a** had been completely converted to **2a** within minutes. The reaction mixture was filtered to yield 1.10 g (10.2 mmol) of metallic silver. The solvent was evaporated from the mother liquor and the resulting brown solid redissolved in a mixture of 50 mL of ether and 50 mL of 1 N sodium hydroxide. The layers were separated, the aqueous layer was extracted with ether (2 × 50 mL), the ether layers were combined and dried over anhydrous sodium sulfate, and the solvent was evaporated to yield the crude product **2a**.[5] Recrystallization from ethanol/water yields 0.44 g (2.5 mmol, 94%) of **2a**, mp 107–109 °C. The NMR and mass spectra along with the GC retention time are identical with an authentic sample of **2a**. The GC confirms the purity of the recrystallized product.

An aliquot of the filtered reaction mixture from above was analyzed for formic acid and trifluoroacetic acid using HPLC. Elution on a DuPont Zorbax NH_2 (4.6 mm × 25 cm) column with 1.5% KH_2PO_4 (pH 2.20) indicated a quantitative yield of both acids.

Acknowledgment. Support of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the University of Scranton Faculty Research and Development Fund is gratefully acknowledged. The GC-MS used in this work was purchased with the aid of a CSIP grant from National Science Foundation to T. A. Dickneider who assisted in obtaining the GC-MS data.

(5) GC-MS indicates that the crude product is acridine contaminated with a small amount of a compound whose parent ion has a mass to charge ratio of 253.

Synthesis and Crystal Structure of 4-*tert*-Butyl-2(3*H*)-oxazolethione

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One of the most generally useful reagents for the cyclization of ω-hydroxy carboxylic acids to macrocyclic lactones is 2,2′-bis(4-*tert*-butyl-1-isopropylimidazolyl) disulfide.[1] During attempts to synthesize an analogous polymer-supported bis(imidazolyl) disulfide via 4-*tert*-butyl-2-mercaptoimidazole (**1**), we obtained 4-*tert*-butyl-2(3*H*)-oxazolethione (**3**) instead. Our synthetic method was analogous to that for 4-*tert*-butyl-1-isopropyl-2-mercaptoimidazole (**2**).[1] Treatment of 1-bromopinacolone with an excess of ammonia (instead of isopropylamine) followed by evaporation of the ammonia and treatment with KSCN in 1 M HCl in 50/50 v/v ethanol/water gave **3**. Oxidation of **3** with MnO_2 gave 2,2′-bis(4-*tert*-butyl-oxazolyl) disulfide (**4**).

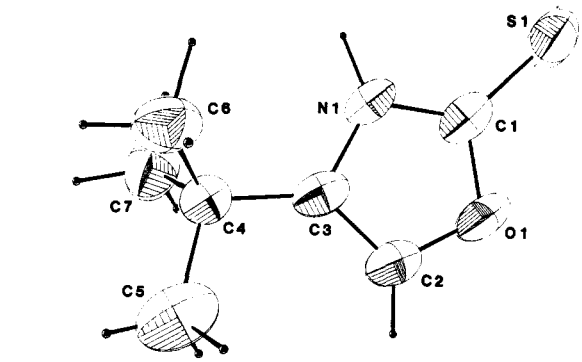
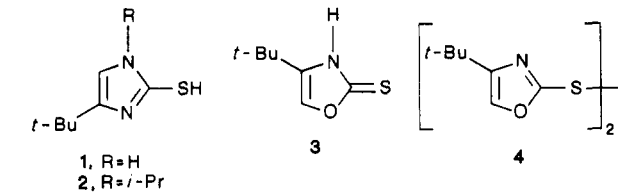
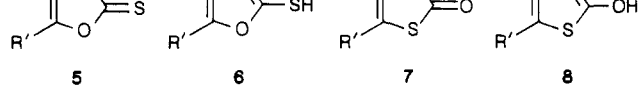


Figure 1. ORTEP drawing of oxazolethione **3**.



The structure of the new oxazolethione was determined as follows: Elemental analysis and the high resolution mass spectrum indicated the molecular formula to be $C_7H_{11}NOS$. Possible structures considered were **5**, **6**, **7**, and **8**.



The structures of 4- and 5-substituted 2(3*H*)-thiazolones are known to adopt the oxo form **7** rather than the hydroxyl form **8**.[2] The IR spectrum of the new compound does not show the required carbonyl band at 1695 cm^{-1} for thiazolone **7**. The ^1H and ^{13}C NMR data also do not match those reported for thiazolones **7**.[2] A ^{13}C NMR peak at 178.6 ppm supports thione structure **5** rather than thiol structure **6**. The absence of a doublet ($J \sim 2$ Hz) at 6.3–6.7 ppm for H(4) in the ^1H NMR spectrum indicates that R is *tert*-butyl and R′ is H in **5**. Structure **3** was confirmed by single-crystal X-ray analysis. Figure 1 shows a projection view of the molecule in the solid state, and Table I gives the crystal data. The oxazolethione **3** crystallizes with a planar (std dev 0.02) oxazoline ring. Comparison with the details of the structures of 3-methylbenzoxazoline-2-thione and benzoxazoline-2-thione reported by Groth[3] shows C=S distances and intraannular C–O, C–N, and C–C distances equivalent to those observed here within experimental error.

Treatment of the oxazolethione **3** with active MnO_2 gave the new bis(oxazolyl) disulfide **4** in high yield. ^1H and ^{13}C NMR spectra data support structure **4**. Most notably the C(2) peak of **3** that appeared at 178.6 ppm was shifted to

(1) Corey, E. J.; Brunelle, D. J. *Tetrahedron Lett.* **1976**, 3409.

(2) Cornwell, S. P.; Kaye, P. T.; Kent, A. G.; Meakins, G. D. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2340.

(3) Groth, P. *Acta Chem. Scand.* **1973**, *27*, 945.

0022-3263/88/1953-1113$01.50/0

Table I. Crystal Data for $C_7H_{11}NOS$, Oxazolethione 3

mol form	$C_7H_{11}NOS$
M_r	157.23
a	19.142 (7) Å
b	6.197 (3) Å
c	7.400 (3) Å
β	100.42 (3)°
V	863.3 (6) Å^3
$F(000)$	336
μ(Mo K$_\alpha$)	2.978 cm^{-1}
λ(Mo K$_\alpha$)	0.71069 Å
D_{calcd}	1.210 g cm^{-3}
Z	4
obsd refln	829
R	5.1%
space group	$P2_1/n$

155.4 ppm in 4, and its spin–lattice relaxation time was so long that a 10-s delay between acquisitions was required to detect the C(2) signal.

Formation of the oxazolethione was quite unexpected, for the procedure[1] is a standard method for 2-mercaptoimidazoles. In a separate experiment the residue from reaction of 1-bromopinacolone with ammonia was treated with cold aqueous KOH and extracted with ether. Recrystallization of the recovered solid from petroleum ether gave a crystalline product, mp 90–91 °C. ^{1}H and ^{13}C NMR spectra were consistent with 1-aminopinacolone as the major component in a mixture of compounds. Reaction of the crystalline mixture with KSCN and HCl as before also gave oxazolethione 3.

Experimental Section

IR spectra (KBr) were recorded with a Perkin-Elmer 681 spectrophotometer. ^{1}H NMR spectra at 300 MHz and ^{13}C NMR spectra at 75.43 MHz were recorded in $CDCl_3$ with a Varian XL-300 spectrometer. ^{13}C NMR spectra at 25.2 MHz were obtained with a Varian XL-100(15) instrument equipped with a Nicolet TT-100 PFT accessory. Mass spectral analyses were done with a CEC Model 21-110B high resolution double focusing mass spectrometer with a Data General DS-50S data system at 70 eV. Elemental analyses were carried out by Galbraith Laboratories (Knoxville, TN).

4-*tert*-Butyl-2(3*H*)-oxazolethione (3). To 500 mL of liquid ammonia in a two-neck 1-L round-bottom flask equipped with a cold finger at −78 °C was added 45 mL (0.33 mol) of 1-bromopinacolone (Fluka, 99% pure by GC). The reaction mixture was allowed to warm to −20 °C and stirred for 4 h. The excess ammonia evaporated slowly. Final traces of ammonia were removed by using a vacuum pump. The residual pale yellow solid was dissolved in 190 mL of ethanol, 210 mL (0.42 mol) of 2 M HCl was added, and 39.46 g (0.406 mol) of KSCN (Aldrich, 99+% pure) was added. The mixture was refluxed at 80 °C for 20 h under argon, cooled to room temperature, and added to ice water while being stirred well. The precipitate was filtered, washed with water, and air-dried to yield 33.3 g of solid. Flash chromatography of the solid over silica gel (Baker, 40-μm diameter) using a gradient mixture of ethyl acetate–petroleum ether as eluent gave 19.2 g (37% yield) of 4-*tert*-butyl-2(3*H*)-oxazolethione (3): mp 145–147 °C; IR 3300–2700 br, 3180, 3060, 2960, 1640, 1495, 1470, 1460, 1255, 1175, 1130, 1060, 980, 940, 935, 735, and 640 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 12.59 (1 H, br), 7.04 (1 H, s), and 1.30 (9 H, s); ^{13}C NMR ($CDCl_3$, 75.43 MHz) δ 178.60 s, 140.86 s, 130.78 d, 29.94 s, and 28.65 q; MS, m/z 157.0609 (M$^+$, 100%); calcd for $C_7H_{11}NOS$ 157.0561. Anal. Calcd for $C_7H_{11}NOS$: C, 53.47; H, 7.05; N, 8.91; O, 10.18; S, 20.39. Found: C, 53.40; H, 6.85; N, 8.89; O, 10.39; S, 20.67.

2,2′-Bis(4-*tert*-butyloxazolyl) Disulfide (4). To 16.93 g (0.108 mol) of 4-*tert*-butyl-2(3*H*)-oxazolethione (3) in 400 mL of toluene was added 18.89 g (0.217 mol) of active MnO_2 (Aldrich). The mixture was stirred at room temperature under argon for 25 h and filtered through a bed of silica gel. The filtrate was evaporated to give 14.1 g of a gummy residue. Flash chromatography over silica gel (Baker, ~40-μm diameter) using 2% ethyl acetate in petroleum ether as eluent gave 13.1 g (78% yield) of 2,2′-bis(4-*tert*-butyloxazolyl) disulfide (4): mp 68–70 °C; IR 3150, 3110, 2970, 2930, 2910, 2870, 1610 br w, 1570, 1465, 1450, 1365, 1360, 1210, 1175, 1140, 1080, 970, 945, 935, 805, 670, 665, and 605 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.47 (2 H, s) and 1.26 (18 H, s); ^{13}C NMR ($CDCl_3$, 25.2 MHz) δ 155.39 s, 153.07 s, 135.84 d, 31.18 s, and 29.03 q. MS, m/z 312.1011 (M$^+$, 24%); calcd for $C_{14}H_{20}N_2O_2S_2$ 312.0966. Anal. Calcd for $C_{14}H_{20}N_2O_2S_2$: C, 53.82; H, 6.45; N, 8.97; O, 10.24; S, 20.52. Found: C, 54.02; H, 6.37; N, 8.97; O, 10.00; S, 20.80.

X-ray Analysis of 4-*tert*-Butyl-2(3*H*)-oxazolethione (3). A crystal of 3 was mounted on a Syntex P3 automated diffractometer. Unit cell dimensions (Table I) were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2\theta > 15°$) during normal alignment procedures using molybdenum radiation ($\lambda = 0.71069$ Å). Data (2348 points) were collected at room temperature by using a variable scan rate, a θ–2θ scan mode, and a scan width of 1.2° below Kα_1 and 1.2° above Kα_2 to a maximum 2θ value of 60.0°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections, and as the intensities of these reflections showed less than 6% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. After removal of redundant and space group forbidden data, 829 points were considered observed [$I > 3.0\ \sigma(I)$]. The structure was solved by using MULTAN80[4] to locate heavy atom positions. Successive cycles of least-squares refinement followed by difference Fourier synthesis allowed location of the remainder of the non-hydrogen atoms. Refinement of scale factor, positional, and anisotropic thermal parameters for all non-hydrogen atoms was carried out to convergence. Hydrogen positions were apparent from a final difference Fourier and were refined in the final cycles of least squares along with their isotropic thermal parameters.[5] The final cycle of refinement – [functional minimized $\sum(|F_o| - |F_c|)^2$] led to a final agreement factor, $R = 5.1\%$, $R = \sum(||F_o| - |F_c||/\sum|F_o|) \times 100$. Anomalous dispersion corrections were made for S. The scattering factors were taken from Cromer and Mann.[6] Unit weights were used until the final cycles of refinement, when a weight = $1/\sigma F$ was introduced. $R_w = 6.9$.

Acknowledgment. We thank the U.S. Army Research Office of the support of contract DAAG-82-K-0133. The 300-MHz NMR spectrometer was supported in part by National Science Foundation Grant CHE-8106157.

Supplementary Material Available: Tables II–V listing positional parameters, thermal parameters, distances from the plane, and bond angles and distances for compound 3 (4 pages). Ordering information is given on any current masthead page. A listing of calculated and observed structure factors is availabile from W.T.F.

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3,4-Dihydrobenz[*f*]isoquinoline and 3,4-Dihydrobenz[*g*]isoquinoline

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Previous attempts to prepare the linear isoquinoline 2 by Bischler–Napieralski cyclization of 2-(2-formamidoylethyl)naphthalene (1) resulted only in the formation of 3,4-dihydrobenz[*h*]isoquinoline (3).[1] When blocking

