(m, 2 H), 4.7–6.0 (m, 3 H), 6.06 (dt, J = 3, 6 Hz, 1 H), 7.57 (dt, J = 3, 6 Hz, 1 H); HRMS, m/z 136.0882, calcd for $C_9H_{12}O$ 136.0888.

3-*tert*-Butyl-2-cyclopenten-1-one (4c): 88% yield; IR 1708 cm^{-1}; ^1H NMR δ 1.22 (s, 9 H), 2.3–2.7 (m, 4 H), 5.90 (t, J = 1.5 Hz, 1 H). Its spectra were consistent with those reported.[14]

3,5-Dimethyl-2-cyclopenten-1-one (5c): 91% yield; IR 1707 cm^{-1}; ^1H NMR δ 1.09 (s, 3 H), 2.10 (br s, 3 H), 2.2–2.8 (m, 3 H), 5.80 (br s, 1 H). Its spectra were consistent with those reported.[15]

5-Allyl-3,5-dimethyl-2-cyclopenten-1-one (6c): 85% yield; IR 1708 cm^{-1}; ^1H NMR δ 1.12 (s, 3 H), 2.13 (br s, 3 H), 2.1–2.5 (m, 4 H), 5.3–6.0 (m, 3 H), 5.87 (br s, 1 H); HRMS, m/z 150.1037, calcd for $C_{10}H_{14}O$ 150.1045.

2-Cyclohexen-1-one (7c): 45% yield; IR 1671 cm^{-1}; ^1H NMR δ 1.8–2.7 (m, 6 H), 5.90 (dt, J = 11 Hz, 1 H), 6.90 (dm, J = 11 Hz, 1 H). Its spectra were consistent with those reported.[13]

6-Allyl-4,4,6-trimethyl-2-cyclohexen-1-one (8c): 85% yield; IR 1670 cm^{-1}; ^1H NMR δ 1.11 (s, 3 H), 1.16 (2 s, 6 H), 1.61, 1.88 (AB, J = 15 Hz, 2 H), 2.27 (d, J = 7 Hz, 2 H), 4.7–6.0 (m, 3 H), 5.68 (d, J = 10 Hz, 1 H), 6.44 (d, J = 10 Hz, 1 H); HRMS, m/z 178.1352, calcd for $C_{12}H_{18}O$ 178.1358.

3-Methyl-2-cyclohexen-1-one (9c): 85% yield; IR 1668, 1626 cm^{-1}; ^1H NMR δ 1.93 (br s, 3 H), 2.0–2.7 (m, 6 H), 5.74 (narrow m, 1 H). Its spectra were consistent with those reported.[13]

3,5,5-Trimethyl-2-cyclohexen-1-one (10c): 83% yield; IR 1670, 1649 cm^{-1}; ^1H NMR δ 1.04 (s, 6 H), 1.94 (br s, 3 H), 2.18 (2 s, 4 H), 5.87 (br s, 1 H). Its spectra were consistent with those reported.[13]

5-*tert*-Butyl-3-methyl-2-cyclohexen-1-one (11c): 88% yield; IR 1669 cm^{-1}; ^1H NMR δ 0.90 (s, 9 H), 1.96 (br s, 3 H), 1.7–2.6 (m, 5 H), 5.85 (br s, 1 H); HRMS, m/z 166.1344, calcd for $C_{11}H_{18}O$ 166.1358.

3,6-Dimethyl-2-cyclohexen-1-one (12c): 93% yield; IR 1667 cm^{-1}; ^1H NMR δ 1.13 (d, J = 7 Hz, 3 H), 1.92 (br s, 3 H), 2.0–2.5 (m, 5 H), 5.82 (br s, 1 H). Its spectra were consistent with those reported.[16]

6-Isopropyl-3-methyl-2-cyclohexen-1-one (13c): 84% yield; IR 1667 cm^{-1}; ^1H NMR δ 0.85 (d, J = 7 Hz, 3 H), 0.92 (d, J = 7 Hz, 3 H), 0.92 (d, J = 7 Hz, 3 H), 1.88 (br s, 3 H), ca. 1.9–2.6 (m, 5 H), 5.70 (br s, 1 H). Its spectra were consistent with those reported.[17]

Acknowledgment. We thank the National Science Foundation for its generous support. FT-NMR and FT-IR spectra were run at the CUA Chemical Instrumentation Center. Mass spectra were run at the NIH/NIDDK Laboratory of Analytical Chemistry by Dr. Lewis Pannell and Noel Whittaker, to whom we are grateful. Several compounds used in this study were prepared by Ivor Zwane.

(14) Garbisch, E. W., Jr.; Sprecher, R. F. *J. Am. Chem. Soc.* **1969**, *91*, 6785.
(15) Santelli-Rouvier, C. *Tetrahedron* **1981**, *37*, 4195.
(16) Chapurlat, R.; Huet, J.; Dreux, J. *Bull. Soc. Chim. Fr.* **1967**, 2446.
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Formation of Acridine from the Reaction of Dibenz[*b*,*f*]azepine with Silver(I): Formation of an Aromatic Nitrenium Ion?

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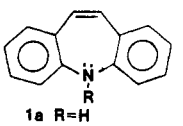
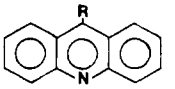
Dibenz[*b*,*f*]azepine (**1a**) represents a heterocyclic structure that is common to the tricyclic antidepressants and the anticonvulsant carbamazepine (**1b**). Compound **1a** has been identified as a metabolite in the biotransformation of **1b**.[1]



1a R=H
1b R=$CONH_2$



2a R=H
2b R=COH

While investigating some of the properties of **1a**, we discovered an interesting reaction of **1a** with silver trifluoroacetate.[2] Addition of 4 equiv of this silver salt to 1 equiv of **1a** results in a quantitative yield of acridine (**2a**), formic acid, and metallic silver.

Because of the pharmaceutical potential of the derivatives of **1a**, many reactions of this compound have been investigated. However, the ring contraction of **1a** is an uncommon reaction. The only other ring contraction directly from **1a** that we are aware of is observed upon reaction of **1a** with Fremy's salt.[3] This reaction produces acridine-9-aldehyde (**2b**) as a minor product.

It is also unusual that such a mild oxidizing agent as silver(I) is capable of reaction with **1a**. We suggest that the mechanism for this reaction proceeds as outlined in Scheme I. Loss of one electron from **1a** is followed by loss of a proton from the nitrogen and loss of a second electron to produce the dibenzazatropylium ion **3**. Ring contraction of **3** and subsequent reaction with two additional equivalents of silver(I) ultimately produces **2a** and formic acid. The underlying reason for the reaction of **1a** with such a mild oxidizing agent as silver(I) may be found in the structure of the nitrenium ion **3**.

Many investigators have postulated nitrenium ions as intermediates in numerous chemical reactions. Arylnitrenium ions have been generated by several different methods. However, the closest analogy to the oxidation of **1a** and the formation of **3** is the electrochemical oxidation of diarylamines. Serve observed the facile anodic oxidation of diarylamines **4** and postulated the formation of diarylnitrenium ion **7**.[4] The process allegedly proceeds (Scheme II) via a one-electron oxidation to the radical cation **5**, followed by loss of a proton to yield the radical **6** and loss of a second electron to the resonance-stabilized nitrenium ion **7**. Electron-releasing substituents, such as the methoxy group, facilitate the reaction by stabilizing **7**. The nitrenium ion **3** is formed by a similar mechanism and **3** has the added stability rendered by its aromatic character. However, observation of **3** under the reaction conditions is prohibited by the ease of the ring contraction and oxidation to acridine.

Experimental Section

Melting points were determined on a Mel-Temp capillary apparatus and are uncorrected. Dibenz[*b*,*f*]azepine (**1a**), authentic acridine (**2a**), and silver trifluoroacetate were all purchased from Aldrich Chemical Co., Milwaukee, WI, and were used without further purification. GC-MS were obtained on a Hewlett Packard Model 5995C equipped with a 12-m fused silica capillary column OV101; nuclear magnetic resonance spectra were recorded on a Varian T60 NMR spectrometer; HPLC were performed on a Perkin-Elmer Series 400 liquid chromatograph.

Formation of Acridine (2a). In 25 mL of methanol, 2.30 g (10.4 mmol) of silver trifluoroacetate was added to 0.50 g (2.6

(1) Csetenyi, J.; Baker, K. M.; Frigerio, A.; Morselli, P. L. *J. Pharm. Pharmacol.* **1973**, *25*, 340.
(2) Silver tetrafluoroborate or silver acetate may also be used, yielding the same results.
(3) (a) Haque, K. E.; Proctor, G. R. *J. Chem. Soc. D* **1968**, 1412. (b) Haque, K. E.; Hardie, K. M.; Proctor, G. R. *J. Chem. Soc., Perkin Trans. 1* **1972**, 539.
(4) Serve, D. *J. Am. Chem. Soc.* **1975**, *97*, 432.

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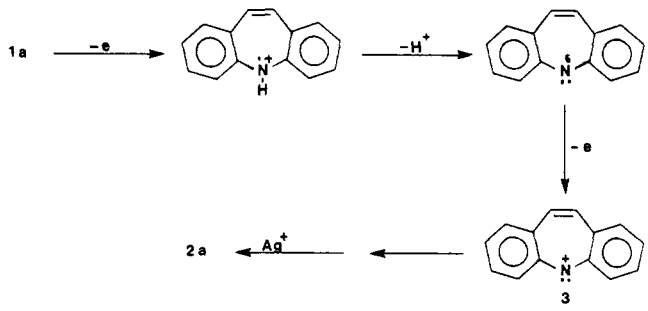
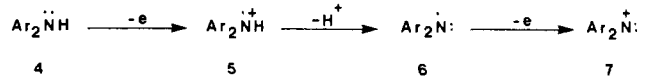
Scheme I



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.

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(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**).

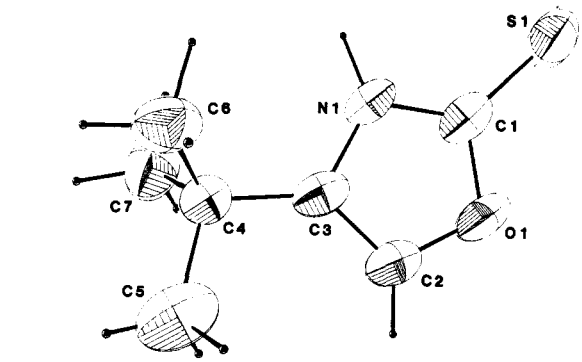
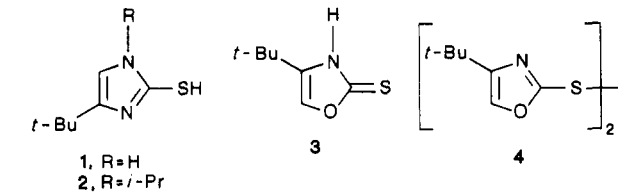
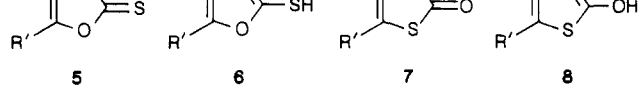


Figure 1. ORTEP drawing of oxazolethione **3**.



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.

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