solubilize the salt of 8. The mixture was heated at 55 °C for 4 h after which time the solution was basified ($NaHCO_3$ solid) and extracted with $CHCl_3$. The volatiles were removed and the residue acidified to ~pH 2 with 0.1 N HCl. The resulting solution was again stripped of volatiles to yield a crude solid, 8a as the HCl salt. This was purified as in footnote d, Table II.

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support and Ms. K. I. Skorey for the preparation of **2d**, **10**, and **11**.

Supplementary Material Available: Table of C, H, N analytical data, exact masses, and ^1H NMR data (2 pages). Ordering information is given on any current masthead page.

Synthetic Elaboration of Diosphenols. 3.† Replacement of Enolic Oxygen by Hydrogen

Anthony A. Ponaras,* Ömer Zaim, Yessica Pazo, and Lena Ohannesian

Department of Chemistry, The Catholic University of America, Washington, D.C. 20064

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In the course of applying the diosphenol Claisen rearrangement[1] to natural products synthesis, we desired to deoxygenate C-allylated diosphenols in the sense a → c (Figure 1). Reported sequences[2] for effecting this transformation involve a catalytic hydrogenation step incompatible with preservation of the allyl group. In our hands lithium/ammonia reduction of diosphenol methyl ethers gave predominantly α-methoxy ketones; similar reduction of diosphenol acetates gave complex mixtures. We therefore examined a different approach to activation of the enolic hydroxyl toward reductive fission.

Our previous work[3] showed that functionalization of diosphenols as dialkylthiocarbamates b activates the system toward reaction with bromide or chloride ion. The products of this reaction depend on the substitution pattern of the ring: when R = H, α-halo-α,β-unsaturated ketones are obtained cleanly;[3a] when R = alkyl, a variety of products is obtained.[3b] We now report that, *irrespective of substitution pattern*, diosphenol dialkylthiocarbamates are converted in high yield to c when treated with iodide ion in hot acetic acid. Figure 2 shows 13 enones prepared by this method (yields in parentheses) from the corresponding diosphenol dimethylthiocarbamates.

Since diosphenols may be C-alkylated via their dianions[4] (or, where allylic groups are concerned, via O-alkylation and Claisen rearrangement[1]), our reaction sequence allows the preparation of 3-alkyl-2-cycloalkenones from 1,2-diketones, *introducing the alkyl group as an electrophile.* This protocol complements other methods proceding from 1,3-diketones[5] or 3-unsubstituted enones[6] where the alkyl group is introduced as a nucleophile.

The replacement of enolic oxyygen by hydrogen may be rationalized by extension of our previous mechanistic postulates:[3] fused-cyclization followed by attack of iodide ion at the α-carbon leads to e which, via reductive elimination, gives c (Figure 3).

The insensitivity of the reduction process with iodide ion to the substitution pattern of the ring (cf. chloride ion, ref 3b) is probably the consequence of the greater nucleophilicity of iodide (reversion of d to b is not significant);

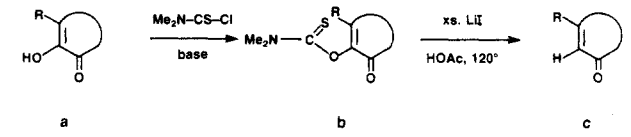

Figure 1.

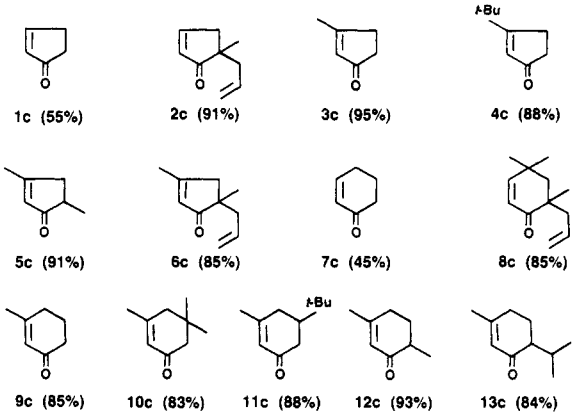

Figure 2.

the existence of other reduction mechanisms is also under present consideration. Diosphenol **2a** and its derived dimethylcarbamate or brosylate are *not* reduced by iodide ion under the standard conditions (1 h). If the brosylate is subjected to these conditions for 24 h some **2c** can be detected in the reaction mixture among several other products including starting material. We are continuing to explore the mechanism(s) and utility of these reactions.

Experimental Section

General Methods: see ref 3b.

Preparation of Diosphenol Dimethylthiocarbamates and Related Substances. General Procedure A. 6-Allyl-3,3,6-trimethyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclohexen-1-one (8b). A solution of 11.29 g (58 mmol) of 3-allyl-3,5,5-trimethyl-1,2-cyclohexanedione[1a] in 20 mL of THF was added dropwise at 0 °C, under nitrogen, to a magnetically stirred suspension of 3.34 g (70 mmol) of sodium hydride (50% dispersion in mineral oil) in 20 mL of THF. A solution of 8.36 g (70 mmol) of dimethylthiocarbamoyl chloride in 15 mL of THF was added and the reaction mixture was stirred overnight and then diluted with 180 mL of ether and washed successively with 180 mL of water, 180 mL of 1 M aqueous sodium hydroxide solution, and 180 mL of brine. The organic phase was dried over anhydrous magnesium sulfate and evaporated, giving 11.7 g of a solid whose NMR spectrum indicated that it was mainly the desired product. The crude product was chromatographed on 300 g of silica gel packed in a mixture of cyclohexane/ethyl acetate (3:1), giving 8.234 g (51%) of a white solid. Crystallization from pentane gave white crystals: mp 51–53 °C; IR 1677, 1645, 1633, 1525 cm^{-1}; ^1H NMR δ 1.22 (s, 3 H), 1.28 (s, 6 H), 1.82 (m, 2 H), 2.40 (d, J = 7 Hz, 2 H), 3.26 (s, 3 H), 3.38 (s, 3 H), 4.8–5.1 (dd, J = 3, 7 Hz, 1 H), 5.17 (br s, 1 H), 5.3–6.1 (m, 1 H), 6.18 (s, 1 H). Anal. Calcd for $C_{15}H_{23}NO_2S$: C, 64.03; H, 8.23. Found: C, 64.17; H, 8.32.

General Procedure B. 5-*tert*-Butyl-3-methyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclohexen-1-one (11b). A 2-mL portion of 10 M aqueous sodium hydroxide solution was added

† Part 2: see ref 3b.

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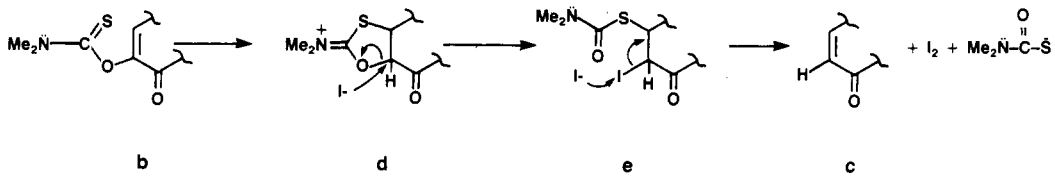

b d e c

Figure 3.

at room temperature under nitrogen to a magnetically stirred solution of 3.64 g (20 mmol) of 5-*tert*-butyl-3-methyl-1,2-cyclohexanedione[1b] in 15 mL of acetone and then 2.48 g (20 mmol) of solid dimethylthiocarbamoyl chloride was added in one portion. The mixture was stirred at room temperature for 1 h, heated to 60 °C for 10 min, cooled, and diluted with 60 mL of water. The resulting yellow precipitate was collected by suction filtration, washed with water, and dried under vacuum, to give 3.66 g (64%) of yellowish crystals whose NMR spectrum indicated that it was substantially pure. Sublimation afforded white crystals: mp 141–142 °C; IR 1679, 1658, 1538 cm^{-1}; ^1H NMR δ 0.92 (s, 9 H), 1.77 (br s, 3 H), 1.9–2.5 (m, 5 H), 3.22 (s, 3 H), 3.35 (s, 3 H). Anal. Calcd for $C_{14}H_{23}NO_2S$: C, 62.42; H, 8.59. Found: C, 62.24; H, 8.61.

General Procedure C. 5-Allyl-5-methyl-2-[(dimethylthiocarbamoyl)oxy]-2-penten-1-one (2b). A 10-mL portion of 1 M aqueous lithium hydroxide solution was added at room temperature to a magnetically stirred solution of 1.52 g (10 mmol) of 3-allyl-3-methyl-1,2-cyclopentanedione[1a] in 5 mL of chloroform and then a solution of 1.36 g (11 mmol) of dimethylthiocarbamoyl chloride in 5 mL of chloroform was added. After stirring for 2 h the chloroform phase was removed and the aqueous phase was extracted with 10 mL of chloroform. The combined organic extracts were washed with saturated sodium chloride solution, dried over anhydrous magnesium sulfate, and evaporated, giving 2.75 g of a solid. Crystallization from 13 mL of methanol/water (5:8) gave 1.53 g (64%) of white crystals: mp 71–72 °C; IR 1711, 1639, 1529 cm^{-1}; ^1H NMR δ 1.18 (s, 3 H), 2.25 (d, J = 6 Hz, 2 H), 2.51 (dd, J = 3.5, 8 Hz, 2 H), 3.28 (s, 3 H), 3.39 (s, 3 H), 4.8–5.05 (m, 1 H), 5.05–5.3 (m, 1 H), 7.14 (t, J = 3.5 Hz, 1 H). Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.02; H, 7.15. Found: C, 60.12; H, 7.09.

General Procedure D. 2-[(Dimethylthiocarbamoyl)oxy]-2-cyclopenten-1-one (1b). A 1.5-g portion (13 mmol) of thiophosgene was added at room temperature to a magnetically stirred solution of 0.98 g (10 mmol) of 1,2-cyclopentanedione[7] in 10 mL of methylene chloride and then 0.79 g (10 mmol) of dry pyridine was added dropwise. After being stirred for 30 min, the reaction mixture was diluted with 40 mL of hexane and filtered. The solvent was evaporated and the crude product (1.235 g) was chromatographed on 105 g of silica gel packed in a mixture of cyclohexane/ethyl acetate (1:1), giving 1.14 g (65%) of yellow crystals: ^1H NMR δ 2.4–2.9 (m, 4 H), 7.53 (t, J = 3 Hz, 1 H). A 1.52-g portion (13 mmol) of dimethyl(trimethylsilyl)amine was added to a solution of the above (1.14 g, 6.5 mmol) in 5 mL of chloroform and, after stirring 10 min at room temperature, the solvent was evaporated, leaving 0.74 g of a brown solid. Crystallization from 5 mL of a mixture of cyclohexane/ethyl acetate (3:1) gave 0.61 g (33% overall) of yellowish crystals: mp 99–100 °C; IR 1719, 1639, 1549 cm^{-1}; ^1H NMR δ 2.4–2.8 (m, 4 H), 3.30 (s, 3 H), 3.43 (s, 3 H), 7.22 (t, J = 2.5 Hz, 1 H). Anal. Calcd for $C_8H_{11}NO_2S$: C, 51.87; H, 5.99. Found: C, 51.84; H, 6.08.

The following dimethylthiocarbamates were made according to procedure B:

5-Allyl-3,5-dimethyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclopenten-1-one (6b): mp 47–48 °C; IR 1718, 1667, 1540 cm^{-1}; ^1H NMR δ 1.19 (s, 3 H), 1.98 (s, 3 H), 2.1–2.5 (m, 4 H), 3.31 (s, 3 H), 3.42 (s, 3 H), 5.3–5.6 (m, 3 H). (Parent dione: see ref 8). Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.15; H, 7.49. Found: C, 61.52; H, 7.54.

6-Isopropyl-3-methyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclohexen-1-one (13b): mp 70–71 °C; IR 1682, 1656 cm^{-1}; ^1H NMR δ 0.88 (d, J = 7 Hz, 3 H), 1.00 (d, J = 7 Hz, 3 H), 1.94 (br s, 3 H), 2.0–2.8 (m, 6 H), 3.45 (s, 3 H), 3.58 (s, 3 H). (Parent dione: see ref 9). Anal. Calcd for $C_{13}H_{21}NO_2S$: C, 61.14; H, 8.28. Found: C, 61.20; H, 8.25.

The following dimethylthiocarbamates were made according to procedure C:

3-Methyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclopenten-1-one (3b), 3-*tert*-butyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclopenten-1-one (4b), and 3,5-dimethyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclopenten-1-one (5b): see ref 3b.

2-[(Dimethylthiocarbamoyl)oxy]-2-cyclohexen-1-one (7b): mp 138–139 °C; IR 1687, 1643, 1549 cm^{-1}; ^1H NMR δ 1.7–2.3 (m, 2 H), 2.3–2.8 (m, 4 H), 3.21 (s, 3 H), 3.32 (s, 3 H), 6.42 (t, J = 4 Hz, 1 H). (Parent dione: see ref 7). Anal. Calcd for $C_9H_{13}NO_2S$: C, 54.25; H, 6.57. Found: C, 54.33; H, 6.53.

3-Methyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclohexen-1-one (9b): mp 96–97 °C; IR 1686, 1650, 1543 cm^{-1}; ^1H NMR δ 1.81 (s, 3 H), 1.95–2.65 (m, 6 H), 3.22 (s, 3 H), 3.32 (s, 3 H). (Parent dione: see ref 7). Anal. Calcd for $C_{10}H_{15}NO_2S$: C, 56.32; H, 7.08. Found: C, 56.15; H, 7.12.

3,5,5-Trimethyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclohexen-1-one (10b): mp 90.5–92 °C; IR 1686, 1655, 1544 cm^{-1}; ^1H NMR δ 1.14 (s, 6 H), 1.82 (s, 3 H), 2.33 (s, 2 H), 2.39 (s, 2 H), 3.26 (s, 3 H), 3.37 (s, 3 H). (Parent dione: see ref 11). Anal. Calcd for $C_{12}H_{19}NO_2S$: C, 59.73; H, 7.93. Found: C, 59.83; H, 8.01.

3,6-Dimethyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclohexen-1-one (12b): mp 54–55.5 °C; IR 1684, 1660, 1505 cm^{-1}; ^1H NMR δ 1.12 (d, J = 6 Hz, 3 H), 1.79 (br s, 3 H), 2.2–2.7 (m, 5 H), 3.18 (s, 3 H), 3.30 (s, 3 H). (Parent dione: see ref 12). Anal. Calcd for $C_{11}H_{17}NO_2S$: C, 58.13; H, 7.53. Found: C, 58.14; H, 7.52.

General Procedure for Making α,β-Unsaturated Ketones from Diosphenol Dimethylthiocarbamates. 3-Methyl-2-cyclopenten-1-one (3c). A 1.34-g portion (10 mmol) of lithium iodide and 0.402 g (3 mmol) of lithium acetate (scavenger for traces of HI) were added to a magnetically stirred boiling solution of 0.199 g (1 mmol) of 3-methyl-2-[(dimethylthiocarbamoyl)oxy]-2-cyclopenten-1-one **3b** in 5 mL of acetic acid. The color immediately turned dark red and within 15 min GC analysis showed that the reaction was complete. The reaction mixture was cooled and poured into 25 mL of 0.2 M aqueous sodium thiosulfate solution. The acetic acid was neutralized with solid potassium bicarbonate and then the mixture was extracted with three 15-mL portions of methylene chloride. The organic extract was washed with 25 mL of brine, dried over anhydrous magnesium sulfate, and evaporated, giving 0.101 g of a yellow liquid. Chromatography on 9 g of silica gel packed in hexanes gave 0.091 g (95%) of the title compound as a pale yellow liquid whose GC retention time and spectra were identical with an authentic sample (Aldrich).

In similar fashion, the following enones were prepared:

2-Cyclopenten-1-one (1c): 55% yield; IR 1708 cm^{-1}; ^1H NMR δ 2.4 (m, 2 H), 2.7 (m, 2 H), 6.16 (m, 1 H), 7.9 (m, 1 H). Its spectra were consistent with those reported.[13]

5-Allyl-5-methyl-2-cyclopenten-1-one (2c): 91% yield; IR 1708 cm^{-1}; ^1H NMR δ 1.10 (s, 3 H), 2.19 (d, J = 7 Hz, 2 H), 2.55

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(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.

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Formation of Acridine from the Reaction of Dibenz[*b*,*f*]azepine with Silver(I): Formation of an Aromatic Nitrenium Ion?

Michael C. Cann

Department of Chemistry, University of Scranton, Scranton, Pennsylvania 18510

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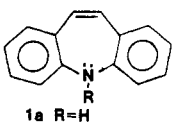
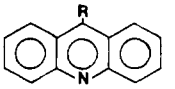
Dibenz[*b*,*f*]azepine (**1a**) represents a heterocyclic structure that is common to the tricyclic antidepressants and the anticonvulsant carbamazepine (**1b**). Compound **1a** has been identified as a metabolite in the biotransformation of **1b**.[1]



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

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