2-Amino-1-nitro-1-[(*o*-nitrophenyl)thio]propene (3a): mp 189–190 °C; yield 94%; IR ($CHCl_3$) 3470, 3280, 3170 cm^{-1} [ν(NH)]; NMR (Me_2SO-d_6) 10.1 (br, 1 H). 9.7 (br, 1 H), 8.4–7.1 (m, 4 H), 2.35 (s, 3 H).

2-(Methylamino)-1-nitro-1-[(*o*-nitrophenyl)thio]propene (3b): mp 186–187 °C; yield 99%; IR ($CHCl_3$) 3170 cm^{-1} [ν(NH)]; NMR 11.4 (br, 1 H), 8.4–7.0 (m, 4 H). 3.25 (d, J = 6 Hz, 3 H), 2.48 (s, 3 H).

2-(Benzylamino)-1-nitro-1-[(*o*-nitrophenyl)thio]propene (3c): mp 156–157 °C; yield 93%; IR ($CHCl_3$) 3170 cm^{-1} [ν(NH)]; NMR 11.3 (br, 1 H), 8.3–7.0 (m, 9 H), 4.73 (d, J = 6 Hz, 2 H), 2.48 (s, 3 H).

2-Anilino-1-nitro-1-[(*o*-nitrophenyl)thio]propene (3d): mp 164–165 °C; yield 91%; IR ($CHCl_3$) 3160 cm^{-1} [ν(NH)]; NMR 12.57 (br, 1 H), 8.4–7.0 (m, 9 H), 3.4 (s, 3 H).

1-Nitro-1-[(*o*-nitrophenyl)thio]-2-piperidinopropene (3e): mp 168–169 °C; yield 68%; NMR 8.4–7.1 (m, 4 H), 3.46 (m, 4 H), 2.65 (s, 3 H), 1.85 (m, 6 H).

1-Amino-2-nitro-2-[(*o*-nitrophenyl)thio]-1-phenylethylene (3f): mp 219–220 °C; yield 90%; IR ($CHCl_3$) 3460, 3300, 3150 cm^{-1} [ν(NH)]; NMR 10.2 (br, 1 H), 9.8 (br, 1 H), 8.4–7.1 (m, 9 H).

1-(Methylamino)-2-nitro-2-[(*o*-nitrophenyl)thio]-1-phenylethylene (3g): mp 163–164 °C; yield 91%; IR ($CHCl_3$) 3170 cm^{-1} [ν(NH)]; NMR 11.03 (br, 1 H), 8.1–7.0 (m, 9 H), 2.85 (d, J = 6 Hz, 3 H).

1-(Benzylamino)-2-nitro-2-[(*o*-nitrophenyl)thio]-1-phenylpropene (3h): mp 188–190 °C; yield 92%; IR ($CHCl_3$) 3170 cm^{-1} [ν(NH)]; NMR 11.13 (br, 1 H), 8.2–7.0 (m, 14 H), 4.38 (d, J = 6 Hz, 2 H).

1-Anilino-2-nitro-2-[(*o*-nitrophenyl)thio]-1-phenylethylene (3i): mp 197 °C; yield 69%; IR ($CHCl_3$) 3160 cm^{-1} [ν(NH)]; NMR 12.5 (br, 1 H), 8.3–7.0 (m, 14 H).

2-Nitro-2-[(*o*-nitrophenyl)thio]-1-phenyl-1-piperidinoethylene (3j): mp 136–137 °C; yield 83%; NMR 8.3–7.2 (m, 9 H), 3.3 (m, 4 H), 1.85 (m, 6 H).

Reaction of 1a–j with Thiocyanogen. To a solution of 1 (10 mmol) in dichloromethane (20 times mass of 1) was added with stirring at −15 °C a dichloromethane solution of thiocyanogen (10 mmol) which had previously prepared from lead thiocyanate and bromine at −15 °C, and then the mixture was stirred for 1.5 h at 0 °C or for 2–4 h at room temperature. The reaction mixture was washed with cold water and then dried with sodium sulfate. The solvent was evaporated in vacuo, and fractional precipitation of the residue from solvents afforded 4 and 5 or 6. The results of the reaction are shown in Table I.

2-Amino-1-nitro-1-thiocyanatopropene (4a): IR ($CHCl_3$) 3470, 3300, 3160 [ν(NH)], 2160 cm^{-1} [ν(CN)]; NMR (Me_2SO-d_6) 9.9 (br, 1 H), 9.3 (br, 1 H), 2.4 (s, 3 H).

2-(Methylamino)-1-nitro-1-thiocyanatopropene (4b): IR ($CHCl_3$) 3140 [ν(NH)], 2150 cm^{-1} [ν(CN)]; NMR 10.9 (br, 1 H), 3.27 (d, J = 6 Hz, 3 H), 2.58 (s, 3 H).

1-Amino-2-nitro-1-phenyl-2-thiocyanatoethylene (4f): IR ($CHCl_3$) 3460, 3300, 3160 [ν(NH)], 2160 cm^{-1} [ν(CN)]; NMR (Me_2SO-d_6) 10.1 (br, 1 H), 9.8 (br, 1 H), 7.5 (s, 5 H).

1-(Benzylamino)-2-nitro-1-phenyl-2-thiocyanatoethylene (4h): IR ($CHCl_3$) 3190 [ν(NH)], 2160 cm^{-1} [ν(CN)]; NMR 11.0 (br, 1 H), 7.6 (m, 10 H), 4.35 (d, J = 6 Hz, 2 H).

2-Nitro-1-phenyl-1-piperidino-2-thiocyanatoethylene (4j): IR ($CHCl_3$) 2150 cm^{-1} [ν(CN)]; NMR 7.6 (m, 5 H), 3.24 (m, 4 H), 1.85 (m, 6 H).

2-Imino-3,4-dimethyl-5-nitro-4-thiazoline (6b): IR ($CHCl_3$) 3330 cm^{-1} [ν(NH)]; NMR 5.8 (br, 1 H), 3.39 (s, 3 H), 2.71 (s, 3 H).

3-Benzyl-2-imino-4-methyl-5-nitro-4-thiazoline (6c): IR ($CHCl_3$) 3330 cm^{-1} [ν(NH)]; NMR 7.3 (s, 5 H), 7.1 (br, 1 H), 5.14 (s, 2 H), 2.6 (s, 3 H).

2-Imino-4-methyl-5-nitro-3-phenyl-4-thiazoline (6d): IR ($CHCl_3$) 3330 cm^{-1} [ν(NH)]; NMR 7.5 (m, 5 H), 7.1 (br, 1 H), 2.38 (s, 3 H). [ν(NH)]; NMR 7.5 (m 5 H), 7.1 (br, 1 H), 2.38 (s, 3H).

2-Imino-3-methyl-5-nitro-4-phenyl-4-thiazoline (6g): IR ($CHCl_3$) 3330 cm^{-1} [ν(NH)]; NMR 7.4 (m, 5 H), 7.05 (br, 1 H), 3.08 (s, 3 H).

3-Benzyl-2-imino-5-nitro-4-phenyl-4-thiazoline (6h): IR ($CHCl_3$) 3320 cm^{-1} [ν(NH)]; NMR 7.5 (m, 10 H), 6.9 (br, 1 H), 4.85 (s, 2 H).

2-Imino-5-nitro-3,4-diphenyl-4-thiazoline (6i): IR ($CHCl_3$) 3360 cm^{-1} [ν(NH)]; NMR 7.5 (m, 10 H), 6.7 (br, 1 H).

General Procedure for the Preparation of 5 or 6 by Cyclization of 4. The solution of 4 in dichloromethane (20 times mass of 4) containing 0.1% acetoc acid was stirred for 2 h at room temperature. After removal of the solvent, the residue was recrystallized to give 5 or 6 in quantitative yields.

Registry No. **1a**, 95512-60-0; **1b**, 95512-61-1; **1c**, 95382-91-5; **1d**, 95382-89-1; **1e**, 95512-62-2; **1f**, 73025-50-0; **1g**, 73025-51-1; **1h**, 95512-63-3; **1i**, 73025-54-4; **1j**, 95512-64-4; **2a** (X = Cl), 95512-65-5; **2a** (X = Br), 95512-66-6; **2a** (X = I), 95512-67-7; **2b** (X = Cl), 95512-68-8; **2b** (X = Br), 95512-69-9; **2b** (X = I), 95512-70-2; **2c** (X = Cl), 95512-71-3; **2c** (X = Br), 95512-72-4; **2c** (X = I), 95512-73-5; **2d** (X = Br), 95512-74-6; **2d** (X = I), 95512-75-7; **2f** (X = Cl), 95512-76-8; **2f** (X = Br), 95512-77-9; **2f** (X = I), 95512-78-0; **2g** (X = Cl), 95512-79-1; **2g** (X = Br), 95512-80-4; **2g** (X = I), 95512-81-5; **2h** (X = Cl), 95512-82-6; **2h** (X = Br), 95512-83-7; **2h** (X = I), 95512-84-8; **2i** (X = Cl), 95512-85-9; **2i** (X = Br), 95512-86-0; **2i** (X = I), 95512-87-1; **2j** (X = Cl), 95512-88-2; **2j** (X = Br), 95512-89-3; **2j** (X = I), 95512-90-6; **3a**, 95512-91-7; **3b**, 95512-92-8; **3c**, 95512-93-9; **3d**, 95512-94-0; **3f**, 95512-96-2; **3g**, 95512-97-3; **3h**, 95512-98-4; **3i**, 95512-99-5; **3j**, 95513-00-1; **4a**, 95513-01-2; **4b**, 95513-02-3; **4f**, 95513-03-4; **4h**, 95513-04-5; **4j**, 95513-05-6; **5a**, 56682-07-6; **5f**, 95513-06-7; **6b**, 95513-07-8; **6c**, 95513-08-9; **6d**, 95513-09-0; **6g**, 95513-10-3; **6h**, 95513-11-4; **6i**, 95513-12-5; thiocyanogen, 505-14-6; nitromethyl phenyl ketone, 614-21-1; ammonia, 7664-41-7; methylamine, 74-89-5; benzylamine, 100-46-9; aniline, 62-53-3; piperidine, 110-89-4; 2-nitrobenzenesulfonyl chloride, 7669-54-7; acetic acid, 64-19-7.

Acenaphthenedithione

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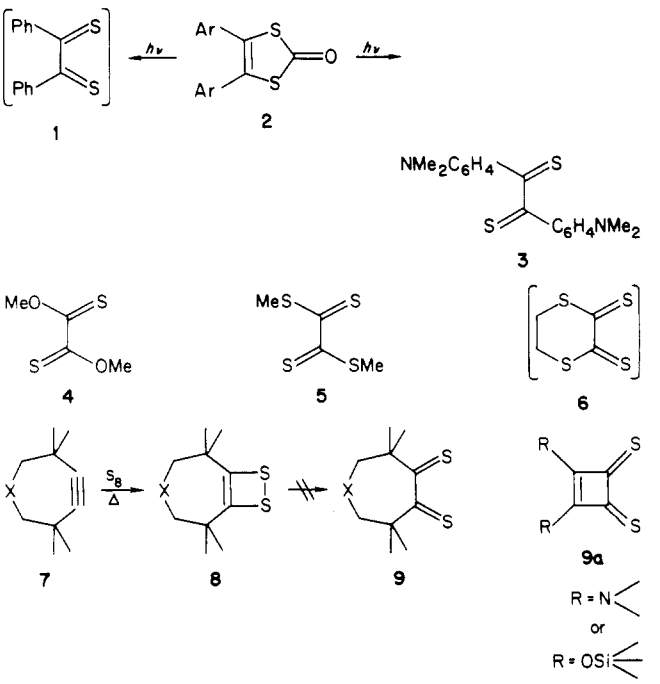
As compared to α-diketones, little is known concerning the chemistry of α-dithiones. Early attempts to synthesize dithiobenzil (1) led to inconclusive results.[1] Later, a study

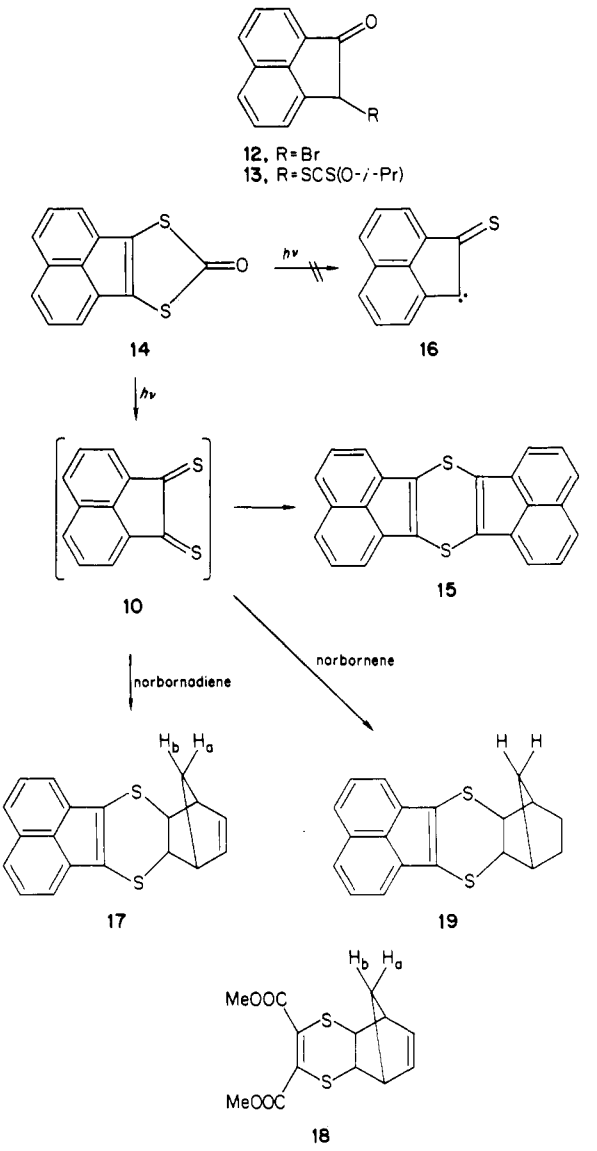


of the photolysis of diphenylvinylene dithiocarbonate (**2**, Ar = C_6H_5) indicated that dithiobenzil was produced as a transient intermediate as evidenced by its trapping, in low yield, as complexes with metal carbonyls.[2] A similar photolysis reaction led to the formation of the push–pull-stabilized, crystalline red *p,p'*-bis(dimethylamino)-dithiobenzil (**3**), the first isolable α-dithione.[2] More recently, several aliphatic α-dithiones have also been generated photochemically and characterized by trapping reactions.[3] While not true α-dithiones (α-dithioketone), dithionooxalate esters (i.e., **4**),[4] and tetrathiooxalate esters (i.e., **5**)[5] represent reactive but isolable compounds containing resonance-stabilized α-dithiocarbonyl systems. The oxalate esters are assumed to exist essentially in the presumably more stable trans configuration as shown, since attempts to prepare cyclic cisoid analogues such as **6** led only to sulfur and polymeric material.[6] The stabilized α-dithione **3** has also been assumed to prefer a transoid configuration.[2] Finally, the highly strained cycloalkynes **7** (X = S or SO_2) react with elemental sulfur in boiling DMF to give stable dithietes (**8**) rather than their cisoid α-dithione tautomers (**9**).[7a,b] Several push–pull-stabilized 1,2-dithione analogues (**9a**) of squaric acid have also been described.[7c,d]

In view of these results, we were interested in attempting the synthesis of acenaphthenedithione (**10**). The latter represents an aromatic α-dithione in which the two thiocarbonyl functions must assume a rigid cisoid and coplanar structure; in addition, formation of the corresponding ring-tautomeric dithiete **11** should be disfavored due to ring-strain considerations. Since dithione **3** as well as tetrathiooxalate **5** was prepared by photochemical decarbonylation,[2,5] we chose to explore a similar route to **10**.

2-Bromoacenaphthenone (**12**)[8] reacted with potassium *O*-isopropyl xanthate in acetonitrile solution to give the corresponding α-ketoxanthate **13**. α-Ketoxanthates have been converted to 1,3-dithiol-2-ones by 70% perchloric acid or 80% sulfuric acid.[9] In the case of **13**, cyclization to the dithiolone **14** was best accomplished by brief warming with 31% HBr in acetic acid.

Photolysis of **14** was carried out in a mixed-solvent system (acetonitrile/*i*-PrOH/cyclohexane) under nitrogen using a high-pressure mercury lamp and a Corex filter. In addition to a powdery orange polymer, the reaction afforded a reasonable yield (41%) of a red crystalline compound $C_{24}H_{12}S_2$. An X-ray crystallographic analysis proved this to be the 1,4-dithiine **15**.[13]



The simplest explanation for the formation of **15** seemed to be that it resulted from the dimerization of the thiocarbonyl carbene **16**, which could be formed from **14** either by the concerted loss of carbonyl sulfide or by a two-step loss of CO followed by sulfur. This type of thiocarbonyl carbene is usually trapped efficiently by CS_2 to give a cyclic trithiocarbonate.[10] In the case of **14**, however, irradiation in CH_2Cl_2 in the presence of CS_2 or other reagents such as dimethyl acetylenedicarboxylate, vinyl acetate, or cyclohexene afforded only the dithiine **15**.

In contrast, irradiation of **14** in the presence of a large excess of norbornadiene suppressed the formation of the dithiine **15** and gave instead, in good yield (62%), a single red crystalline compound which proved to be the (4 + 2) cycloaddition product of norbornadiene and acenaphthenedithione (**10**). This adduct was shown to be the exo isomer **17** on the basis of its NMR spectrum, which showed

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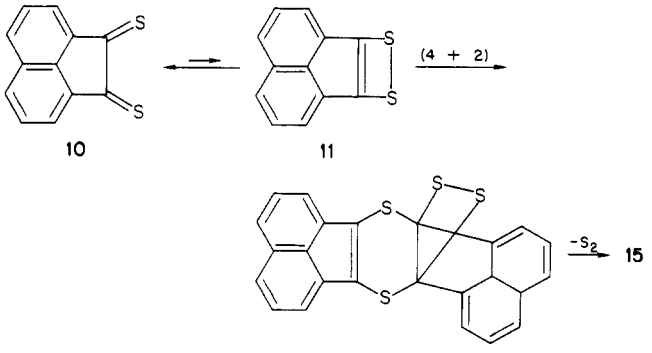
(13) Crystal Data. Compound **15**, $C_{24}H_{12}S_2$, fw = 364.49, orthorhombic, space group *Pbca*, a = 8.285 (3) Å, b = 13.651 (5) Å, c = 14.758 (5) Å, Z = 4, D_{calcd} = 1.452 g cm^{-3}, λ(Mo Kα) = 0.710 73 Å. Intensities for 1715 reflections in the range $0 < 2\theta \leq 50°$ were measured on an Enraf-Nonius CAD4 diffractometer by the ω–2θ scan technique. Of these, 848 unique reflections with $I > 3\sigma(I)$ were used in the structure determination. The structure was solved by the use of the MULTAN 11/82 program package supplied by Enraf-Nonius. Full-matrix least-squares refinement converged to R = 0.075 and R_w = 0.092. During least-squares refinement, hydrogen positions were refined but H thermal parameters were fixed at 5.0 Å^2.

diagnostic similarities with that of the known exo adduct (18) of dimethyl dithionooxalate with norbornadiene. In adduct 18, the methylene bridge protons H_b and H_a (J_{ab} = 9 Hz) are clearly separated at δ 2.69 and 1.65, respectively, due to the marked deshielding effect on H_b of the nearby sulfurs.[11] In adduct 17, an analogous deshielding effect is observed, since H_b and H_a appear at δ 2.89 and 1.83, respectively (J_{ab} = 9 Hz). In a similar manner, dithione 10 was efficiently trapped by norbornene to give the exo adduct 19.

In conclusion, photolysis of the dithiolone 14 generates acenaphthenedithione (10) as a highly reactive transient intermediate which could be trapped in situ by 4 + 2 additions to the strained olefins norbornadiene and norbornene. In the absence of a trapping agent, 10 is transformed fairly efficiently into the dithiine 15. We propose that this conversion proceeds by a (4 + 2) cycloaddition of dithione 10 to its strained dithiete tautomer 11, followed by loss of S_2 as shown below.



Experimental Section

General Methods. Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. ^1H NMR spectra were recorded on a Bruker 250-MHz FT spectrometer using $CDCl_3$ containing Me_4Si as the internal standard and are reported in δ units. Mass spectra were determined with a VG Micromass 7070H spectrometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Organic solutions were dried over Na_2SO_4.

***O*-Isopropyl *S*-(2-Oxoacenaphthenyl) Dithiocarbonate (13).** A solution of potassium *O*-isopropyl xanthate[12] (3.53 g) in acetonitrile (40 mL) was added to a solution of 2-bromoacenaphthenone[8] (12, 5.00 g) in acetonitrile (60 mL). After the mixture was stirred at room temperature for 2 h, the solvent was evaporated in vacuo and water was added. The precipitate was filtered, washed with water, dried, and crystallized from benzenehexane to give needles of xanthate 13: mp 127–129 °C (5.80 g, 96%). Anal. Calcd for $C_{16}H_{14}O_2S_2$: C, 63.55; H, 4.67. Found: C, 63.78; H, 4.85.

Acenaphtho[1,2-*d*][1,3]dithiol-2-one (14). A suspension of xanthate 13 (5.00 g) in 31% HBr/acetic acid (100 mL) was heated gently until all of the solid dissolved. Heating was continued for an additional 5 min, when the solution suddenly turned into a crystalline slurry. The precipitate was filtered and the solid was refluxed with methanol (100 mL) for 15 min. The cooled suspension was filtered, washed with methanol, and dried to give red-brown needles of dithiolone 14: mp 159–160 °C (2.88 g, 71%); NMR δ 7.54–7.62 (m, 4 H), 7.82 (dd, 2 H, J = 7.5, 1.3 Hz); mass spectrum, m/e 242 (M^+, 30%), 214 (M^+ - 28, 100%). Anal. Calcd for $C_{13}H_6OS_2$: C, 64.44; H, 2.50. Found: C, 64.43; H, 2.37.

Photolysis of Dithiolone 14. A solution of 14 (0.500 g) in a 2:1:1 mixture of acetonitrile, isopropyl alcohol, and cyclohexane (400 mL) was photolyzed (N_2) for 3 h with a 400-W high-pressure Hg vapor lamp covered by a Corex filter. The red solution and the solid which separated on the walls were combined, and after evaporation of the solvents, the residue was crystallized from chlorobenzene to give small red diamond-shape crystals of dithiine 15:[13] mp 262–264 °C (0.155 g, 41%); NMR δ 7.44–7.58 (m, Ar H); mass spectrum, m/e 364 (M^+, 25%), 332 (M^+ - 32, 100%). Anal. Calcd for $C_{24}H_{12}S_2$: C, 79.09; H, 3.32. Found: C, 78.93; H, 3.3.

Photolysis of Dithiolone 14 in the Presence of Norbornadiene. A solution of dithiolone 14 (0.53 g) and norbornadiene (3.7 g, excess) in degassed methylene chloride (750 mL) was photolyzed (N_2) for 40 min with a 450-W Hanovia lamp with a Pyrex filter. The solvent was evaporated and the residue was crystallized from hexane to give adduct 17: mp 123–124 °C (0.45 g, 62%); NMR δ 7.76–7.48 (m, 6 H, Ar), 6.24 (2 H, t, J = 1.7 Hz), 3.55 (2 H, d, J = 2.0 Hz), 3.05 (m, 2 H), 2.89 (d of t, J = 9, 1.8 Hz), 1.83 (d of t, J = 1.8 Hz); mass spectrum, m/e 306 (M^+, 18%), 240 (M^+ - 66, 100%), 214 (M^+ - 92, 8%), 208 (M^+ - 66 - 32, 13%), 170 (M^+ - 92 - 44, 20%). Anal. Calcd for $C_{19}H_{14}S_2$: C, 74.50; H, 4.61; S, 20.89. Found: C, 74.42; H, 4.67; S, 21.38.

Photolysis of Dithiolone 14 in the Presence of Norbornene. A solution of dithiolone 14 (0.48 g) and norbornene (3.7 g, excess) in degassed methylene chloride (450 mL) was photolyzed for 1 h with a 450-W Hanovia lamp with a Pyrex filter. The intense red solution was evaporated to dryness and the residue was crystallized several times from methanol/methylene chloride to yield adduct 19 as red plates: mp 137–138 °C (0.40 g; 59.8%); NMR δ 7.74–7.46 (m, 6 H, Ar), 3.35 (d, 2 H, J = 1.5 Hz), 2.57–2.49 (m, 3 H), 1.32–1.74 (m, 5 H); mass spectrum, m/e 308 (M^+, 90%), 214 (M^+ - 94, 100%), 170 (M^+ - 94 - 44, 50%). Anal. Calcd for $C_{19}H_{16}S_2$: C, 74.01; H, 5.23; S, 20.76. Found: C, 73.52; H, 5.23; S, 20.94.

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Registry No. 10, 95532-40-4; 12, 16269-27-5; 13, 95532-41-5; 14, 95532-42-6; 15, 95532-43-7; 17, 95532-44-8; 19, 95532-45-9; norbornadiene, 121-46-0; norbornene, 498-66-8; potassium *O*-isopropyl xanthate, 140-92-1.

Supplementary Material Available: Tables of positional and thermal parameters and their estimated standard deviations, bond distances, and bond angles (5 pages). Ordering information is given on any current masthead page.

Reduction of β-Keto Sulfoxides: A Highly Efficient Asymmetric Synthesis of Both Enantiomers of Allylic Alcohols

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Optically active β-keto sulfoxides are convenient intermediates for the synthesis of both enantiomers of methylcarbinols in very high enantiomeric excesses through reduction with $LiAlH_4$ or Dibal[1] (Scheme I).

The application of this process to α,β-unsaturated β-keto sulfoxides in order to obtain optically active allylic alcohols was not straightforward because of the difficulty first in synthesizing high yields of α,β-unsaturated β-keto sulfoxides and then in desulfurizing the resulting β-hydroxy sulfoxide without reduction of the double bond.

Optically active β-keto sulfoxides are generally obtained from carboxylic esters and (+)-(*R*)-methyl *p*-tolyl sulfoxide at −78 °C.[1-3] In the case of α,β-unsaturated esters a

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