white crystals; $^1$H NMR ($D_2O$–$Na_2CO_3$) $\delta$ 1.8–2.08 (2 H, m), 1.9 (6 H, s), 2.44–2.64 (2 H, m); IR (KBr) 2400–2700 (COOH), 1695, 1615 cm$^{-1}$ (C=O); MS, calcd for $C_{11}H_{12}O_4$ $m/e$ 208.0753, found $m/e$ 208.0737 ($M^+$).

***syn*-7-Methylquadricyclane-2,3-dicarboxylic acid (1o)**: white crystals; mp 218–222 °C (from dichloromethane and hexane); $^1$H NMR ($D_2O$–$Na_2CO_3$) $\delta$ 1.27 (3 H, d, $J$ = 6 Hz), 2.24 (2 H, d, $J$ = 5 Hz), 2.44 (2 H, d, $J$ = 5 Hz), 2.74 (1 H, q, $J$ = 6 Hz); IR (KBr) 2400–2650 (COOH), 1685, 1615 cm$^{-1}$ (C=O); MS, calcd for $C_{10}H_{10}O_4$ $m/e$ 194.0578, found $m/e$ 194.0578 ($M^+$).

***anti*-7-Methylquadricyclane-2,3-dicarboxylic acid (1p)**: white crystals; mp 160–163 °C (from ether); $^1$H NMR ($D_2O$–$Na_2CO_3$) $\delta$ 1.05 (3 H, d, $J$ = 7 Hz), 1.92 (2 H, d, $J$ = 5 Hz), 2.39 (2 H, d, $J$ = 5 Hz), 2.76 (1 H, q, $J$ = 7 Hz); IR (KBr) 2400–2700 (COOH), 1690, 1625 cm$^{-1}$ (C=O); MS, calcd for $C_{10}H_{10}O_4$ $m/e$ 194.0578, found $m/e$ 194.0581 ($M^+$).

**7,7-Dimethylquadricyclane-2,3-dicarboxylic acid (1q)**: white crystals; mp 237–239 °C (from dichloromethane and hexane); $^1$H NMR ($D_2O$–$Na_2CO_3$) $\delta$ 1.26 (3 H, s), 1.37 (3 H, s), 1.84 (2 H, d, $J$ = 5 Hz), 2.39 (2 H, d, $J$ = 5 Hz); IR (KBr) 2350–2700 (COOH), 1675, 1600 cm$^{-1}$ (C=O); MS, calcd for $C_{11}H_{12}O_4$ $m/e$ 208.0735, found $m/e$ 208.0734 ($M^+$).

**Dimethyl 1-methylquadricyclane-2,3-dicarboxylate (3b)**: colorless oil; bp 105 °C (0.15 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 1.29 (3 H, s), 2.06–2.54 (5 H, m), 3.66 (3 H, s), 3.74 (3 H, s); IR (neat) 1715 cm$^{-1}$ (C=O); MS, calcd for $C_{12}H_{14}O_4$ $m/e$ 222.0891, found $m/e$ 222.0892 ($M^+$).

**Dimethyl 5-methylquadricyclane-2,3-dicarboxylate (3c)**: colorless oil; bp 110 °C (0.15 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 1.41 (3 H, s), 2.08–2.37 (5 H, m), 3.66 (3 H, s), 3.68 (3 H, s); IR (neat) 1725, 1705 cm$^{-1}$ (C=O); MS, calcd for $C_{12}H_{14}O_4$ $m/e$ 222.0891, found $m/e$ 222.0889 ($M^+$).

**Dimethyl *syn*-7-methylquadricyclane-2,3-dicarboxylate (3d)**: colorless oil; bp 102–105 °C (0.16 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 1.29 (3 H, d, $J$ = 7 Hz), 2.10–2.21 (2 H, m), 2.49 (2 H, d, $J$ = 5 Hz), 2.69 (1 H, q, $J$ = 7 Hz), 3.76 (6 H, s); IR (neat) 1705 cm$^{-1}$ (C=O); MS, calcd for $C_{12}H_{14}O_4$ $m/e$ 222.0891, found $m/e$ 222.0891 ($M^+$).

**Dimethyl *anti*-7-methylquadricyclane-2,3-dicarboxylate (3e)**: colorless oil; bp 110 °C (0.2 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 1.08 (3 H, d, $J$ = 6 Hz), 2.12–2.26 (2 H, m), 2.54 (2 H, d, $J$ = 4 Hz), 2.85 (1 H, q, $J$ = 6 Hz), 3.70 (6 H, s); IR (neat) 1720 cm$^{-1}$ (C=O); MS, calcd for $C_{12}H_{14}O_4$ $m/e$ 222.0891, found $m/e$ 222.0890 ($M^+$).

**Dimethyl 7,7-dimethylquadricyclane-2,3-dicarboxylate (3f)**: white crystals; bp 95 °C (0.2 mmHg); $^1$H NMR ($CDCl_3$) $\delta$ 1.21 (3 H, s), 1.30 (3 H, s), 1.97 (2 H, d, $J$ = 5 Hz), 2.50 (2 H, d, $J$ = 5 Hz), 3.69 (6 H, s); IR (neat) 1725, 1710 cm$^{-1}$ (C=O); MS, calcd for $C_{13}H_{16}O_4$ $m/e$ 236.1048, found $m/e$ 236.1053 ($M^+$).

**Co-TPP.** According to the method described by A. D. Adler et al.,[23] the reaction of $H_2$-TPP[24] and cobalt acetate ($Co(OAc)_2$) in dimethylformamide (DMF) gave Co-TPP. Chromatography over silica gel with dichloromethane and hexane as eluants and recrystallization from dichloromethane and methanol gave an analytically pure sample: reddish purple crystals; mp >300 °C; $^1$H NMR ($CDCl_3$) $\delta$ 9.72 (4 H, m), 9.92 (8 H, m), 13.1 (8 H, br), 15.9 (8 H, br); UV ($C_6H_6$) $\lambda_{max}$ 413 ($\epsilon$ 271 000), 529 nm (16 700). Anal. Calcd for $C_{44}H_{28}N_4Co$: C, 78.68; H, 4.20; N, 8.34. Found: C, 78.42; H, 4.03; N, 8.31.

**Co-TPP(*o*-Me).** In a manner similar to the synthesis of Co-TPP, the reaction of $H_2$-TPP(*o*-Me)[25] and $Co(OAc)_2$ in DMF gave Co-TPP(*o*-Me) as a mixture of atropisomers: purple plates; mp >300 °C; $^1$H NMR ($CDCl_3$) $\delta$ 2.4, 3.2, 3.9, and 4.6 (12 H, br, *o*-$CH_3$), 9.2–9.9 (12 H, m, meta and para H), 11.7, 12.3, 12.9, and 13.5 (4 H, br, ortho H), 15.4 (8 H, br, pyrrole H); UV ($C_6H_6$) $\lambda_{max}$ 412 ($\epsilon$ 253 000), 528 nm (15 400). Anal. Calcd for $C_{48}H_{36}N_4Co$: C, 79.22; H, 4.99; N, 7.70. Found: C, 79.18; H, 5.00; N, 7.70.

**Co-TPP(*p*-Me).** In a manner similar to the synthesis of Co-TPP, the reaction of $H_2$-TPP(*p*-Me)[24] and $Co(OAc)_2$ in DMF gave Co-TPP(*p*-Me): purple needles; mp >300 °C; $^1$H NMR ($CDCl_3$) $\delta$ 4.14 (12 H, s), 9.73 (8 H, m), 13.0 (8 H, br), 15.9 (8 H, br); UV ($C_6H_6$) $\lambda_{max}$ 414.5 ($\epsilon$ 272 000), 530 nm (16 500). Anal. Calcd for $C_{48}H_{36}N_4Co$: C, 79.22; H, 4.99; N, 7.70. Found: C, 79.08; H, 4.84; N, 7.68.

**Co-TMP.** In a manner similar to the synthesis of Co-TPP, the reaction of $H_2$-TMP[26] and $Co(OAc)_2$ in DMF gave Co-TMP: reddish purple crystals; mp >300 °C; $^1$H NMR ($CDCl_3$) $\delta$ 1.52 (24 H, s), 3.92 (12 H, s), 9.18 (8 H, s), 15.2 (8 H, br); UV ($C_6H_6$) $\lambda_{max}$ 412.5 ($\epsilon$ 260 000), 528.5 nm (16 500). Anal. Calcd for $C_{56}H_{52}N_4Co$: C, 80.07; H, 6.24; N, 6.67. Found: C, 80.06; H, 6.34; N, 6.75.

**Measurement of Second-Order Rate Constants.** According to the literature,[3a] the rate constants were determined by means of $^1$H NMR ([1] = 0.1 M, in 0.5 M $Na_2CO_3$–$D_2O$, at 25 °C; [3] = 0.1 M, in $C_6D_6$, at 25 °C).

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# $S_{RN}1$ Reactions of Halocyclopropanes with Benzenethiolate Ion

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Ultraviolet irradiation of *gem*-dibromocyclopropanes **1** with benzenethiolate ion in liquid ammonia or in $Me_2SO$ solution gave dithioacetals **2** and, in some cases, cyclopropyl phenyl sulfides **3**. The reactions did not proceed in the dark and they were inhibited by *m*-dinitrobenzene, di-*tert*-butyl nitroxide, and oxygen. The bromocyclopropane **6a** underwent a similar, but slower, reaction. Treatment of the bromochlorocyclopropane **7b** led to replacement of only the bromine, while the dichlorocyclopropane **9b** was inert under the reaction conditions. The results appear consistent with a radical chain mechanism.

Nucleophilic substitution of *gem*-dihalocyclopropanes normally involves an elimination–addition sequence and in many cases the nucleophile enters *cine* to the leaving group.[1] Attempted substitution by the $S_N1$ mechanism usually leads to fissure of the ring,[2,3] whereas substitution by the $S_N2$ mechanism is considered geometrically unfavorable.[5,6]

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(2) Aksenov, V. S.; Terent'eva, G. A.; Savinykh, Yv. V. *Usp. Khim.* **1980**, *49*, 1039.
(3) Certain stabilizing substituents allow substitution without ring opening.[4]
(4) van der Vecht, J. R.; Steinberg, H.; de Boer, Th. J. *Recl. Trav. Chem. Pays-Bas* **1977**, *96*, 313.

0022-3263/86/1951-0606$01.50/0 

**Table I. Reaction of 7,7-Dibromobicyclo[4.1.0]heptane with Benzenethiolate Ion in Liquid Ammonia**

| entry | [1a], M | [$PhS^-$], M | time, h | lamps, nm | 1a remaining, % | 2a, % |
|---|---|---|---|---|---|---|
| 1 | 0.025 | 0.15 | 4 | 350 | 25 | 43 |
| 2 | 0.025 | 0.15 | 0.5 | 350 | 64 | 10 |
| 3 | 0.05 | 0.15 | 4 | 350 | 67 | 17 |
| 4 | 0.025 | 0.15 | 4 | none | 98 | 0 |
| 5 | 0.025 | 0.15 | 8 | 350 | 8 | 55 |
| 6 | 0.05 | 0.15 | 2 | 350 | 78 | 11 |
| 7 | 0.05 | 0.15 | 2 | 254[a] | 65 | 6 |
| 8 | 0.025[b] | 0.15 | 4 | 350 | 41 | *e* |
| 9 | 0.025[c] | 0.15 | 4 | 350 | 50 | *e* |
| 10 | 0.025[d] | 0.15 | 4 | 350 | 83 | 15 |

[a] The irradiation was conducted in a silica flask. [b] 2,2,6,6-Tetramethylpiperidinooxy (0.0013 M) was also present. [c] The reaction was conducted under an atmosphere of oxygen. [d] *m*-Dinitrobenzene (0.0025 M) was also present. [e] Not determined.

**Table II. Irradiation of 1,1-Dibromo-2,2,3,3-tetramethylcyclopropane for 4 h with Benzenethiolate Ion in Various Solvents**

| | | | | | yield, % | | |
|---|---|---|---|---|---|---|---|
| entry | [1b], M | [$PhS^-$], M | solvent | 1b remaining, % | 2b | 4b | 6b |
| 1 | 0.025 | 0.15 | liquid ammonia | 52 | 17 | 13 | 7 |
| 2 | 0.025 | 0.15 | THF/liquid ammonia (1:3) | 35 | 6 | 11 | 20 |
| 3 | 0.025 | 0.15 | Bu-*t*-OH/liquid ammonia (1:3) | 43 | 1 | 13 | 7 |
| 4 | 0.025 | 0.15 | Bu-*t*-$NH_2$/liquid ammonia (1:3) | 64 | 2 | 1 | 8 |
| 5 | 0.025 | 0.15 | $Me_2SO$ | 11 | 29 | 2 | 18 |
| 6 | 0.05 | 0.30 | $Me_2SO$ | 27 | 40 | 1 | 17 |
| 7 | 0.10 | 0.60 | $Me_2SO$ | 38 | 47 | 2 | 5 |
| 8[a] | 0.10 | 0.60 | $Me_2SO$ | 19 | 54 | 5 | 14 |

[a] The irradiation time for this experiment was 15 h.

I have previously reported in preliminary form that *gem*-dibromocyclopropanes react with several nucleophiles under irradiation to form the products of ipso substitution, apparently by an elaborated $S_{RN}1$ pathway.[7,8] The $S_{RN}1$ mechanism is a radical chain process which has been reported for certain substitutions of aliphatic,[9] aromatic,[10,11] vinyl,[12] adamantyl,[13,14] and tryptycenyl halides.[14] In generalized form, the propagation steps are outlined in Scheme I.

**Scheme I**

$$[RX]^{-\cdot} \rightarrow R\cdot + X^-$$

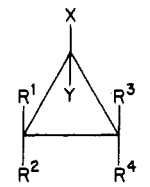
$$R\cdot + Y^- \rightarrow [RY]^{-\cdot}$$

$$[RY]^{-\cdot} + RX \rightarrow RY + [RX]^{-\cdot}$$

Initiation can be effected by the addition of alkali metals, by irradiation with photons, by electrochemical means, or, in some cases, thermally. Such procedures are believed either to lead directly to R· or to result in the halocompound RX accepting an electron to form $[RX]^{-\cdot}$.[11] These species can then enter the propagation cycle of Scheme I.

I now report the details of an investigation of the reaction between benzenethiolate ion and various halocyclopropanes under conditions expected to promote $S_{RN}1$ substitution.

**Chart I**




**1**, X=Y=Br
**2**, X=Y=SPh
**3**, X=Br; Y=SPh; or X=SPh; Y=Br
**4**, X=H; Y=SPh
**5**, X=SPh; Y=H
**6**, X=H; Y=Br; or X=Br; Y=H
**7**, X=Br; Y=Cl
**8**, X=SPh; Y=Cl
**9**, X=Cl; Y=Cl
**10**, X=Cl; Y=H
**11**, X=Br; Y=$SCH_3$

**a**, $R^1$, $R^3=(CH_2)_4$; $R^2=R^4=H$
**b**, $R^1=R^2=R^3=R^4=CH_3$
**c**, $R^1=CH_3(CH_2)_3$; $R^2=R^3=R^4=H$
**d**, $R^1=Ph$; $R^2=R^3=R^4=H$
**e**, $R^1$, $R^3=(CH_2)_6$; $R^2=R^4=H$
**f**, $R^1=R^2=R^3=R^4=H$
**g**, $R^1=CO_2CH_3$; $R^2=CH_3$; $R^3=R^4=H$
**h**, $R^1=CN$; $R^2=CH_3$; $R^3=R^4=H$
**i**, $R^1=CN$; $R^2=CH_3$; $R^3=SPh$; $R^4=H$
**j**, $R^1=R^2=CH_3$; $R^3=R^4=H$

## Results

Initially, exploratory experiments were carried out with 7,7-dibromobicyclo[4.1.0]heptane (**1a**) (see Chart I) in liquid ammonia. Table I summarizes the results. After 4 h of irradiation with 16 "350-nm" lamps (entry 1), substitution of both bromines of **1a** had occurred to give the dithioacetal **2a** in moderate yield. Some starting material remained, but no other products could be isolated. In particular, the product of monosubstitution **3a** was not found in the reaction mixture, even when the irradiation was brief so that the conversion of **1a** was low (entry 2). No products derived from the cyclopropyl–allyl radical rearrangement were detected. The reaction was less successful when the concentration of **1a** was higher and the excess of benzenethiolate ion correspondingly lower (entry 3). This may, however, be a consequence of the limited solubility of **1a** in the reaction mixture. Substitution did not occur in the dark; after 4 h of reaction time (entry 4), only starting material and a small quantity of diphenyl disulfide was recovered. Longer irradiation time improved the yield of **2a** only slightly (compare entries 1 and 5). A comparison of entries 6 and 7 indicates that irradiation with lamps emitting maximally at 350 nm yielded more **2a** than irradiation with those emitting maximally at 254

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(14) Palacios, S. M.; Santiago, A. N.; Rossi, R. A. *J. Org. Chem.* **1984**, *49*, 4609.

**Table III. Reaction of Other Substrates with Benzenethiolate Ion in $Me_2SO$[a]**

| substrate | 1 remaining, % | yield, % 2 | 4 | 5 |
|---|---|---|---|---|
| 1c | 10 | 43 | 11 | 19 |
| 1d | 36 | 28 | 0 | 18 |
| 1e | 26 | 38 | 14 | 4 |
| 1f | 25 | 34 | 10 | |
| 1g | 0 | 12 | 21 | 17 |
| 1h | 9[b] | 22 | 0 | 0 |
| 1h[c] | 15 | 47 | 0 | 0 |
| 6a | 65 | 0 | 27 | 0 |
| 7b | 31[d] | 0 | 0 | 0 |
| 9b | 99 | 0 | 0 | 0 |

[a] All reactions were carried out for 4 h under irradiation with 350-nm lamps. [b] **4i** (26%) was also isolated. [c] This reaction was conducted in liquid ammonia. [d] **8b** (26%) and **10b** (32%) were isolated.

nm, even though more starting material was consumed in the latter case.

The reaction rate was retarded by the addition of 2,2,6,6-tetramethylpiperidinooxy (5 mol % relative to **1a**) and *m*-dinitrobenzene (10 mol % relative to **1a**) and by an atmosphere of oxygen (compare entries 1 and 8–10). Such inhibition and the observation that substitution did not proceed in the dark have been taken in other cases[11] as support for a chain sequence involving radical/radical–anion intermediates.

Initial experiments with 1,1-dibromo-2,2,3,3-tetramethylcyclopropane (**1b**) were less successful. They are summarized in Table II. In liquid ammonia, the reaction was very slow and gave, in addition to the expected dithioacetal **2b**, the reduced monosubstituted product **4b** and the monobromide **6b** in small yield (entry 1). In order to determine whether the slowness of reaction was due to the low solubility of **1b** in liquid ammonia, several cosolvents were tried (entries 2–4). Such procedures offered no improvement in the yield of **2b**, and, in the case of THF cosolvent (entry 2), they led to a substantial increase in the amount of monobromide **6b** formed. $Me_2SO$, which has been used successfully as a solvent for many $S_{RN}1$ reactions,[11,15] gave a homogeneous solution with **1b** and potassium benzenethiolate. The substitution was more successful in this solvent and acceptable yields of **2b** were obtained when the reaction was conducted in relatively concentrated solution (compare entries 5–8).

When the dibromide **1a** was irradiated with benzenethiolate ion in $Me_2SO$ solvent, the dithioacetal **2a** (42%) was obtained. Some starting material (20%) was also recovered. The monosulfide **4a** was not detected. This result is similar to that obtained in liquid ammonia.

Several other dibromides were also irradiated with potassium benzenethiolate in $Me_2SO$ solution, and the results are summarized in Table III.

Reaction of **1c** with benzenethiolate afforded, as the major product, the dithioacetal **2c**, which was accompanied by the isomeric monosulfides **4c** and **5c**. A similar experiment, except that the reaction mixture was protected from light, returned the starting material (93%) unchanged; the substitution products were not detected.

The dibromide **1d**, when irradiated with benzenethiolate, afforded the dithioacetal **2d** in modest yield, accompanied by the phenyl cyclopropyl sulfide **5d**. As with the other entries in Table III, and in contrast to the reactions with **1b**, the monobromide was not found in the product mixtures. The reaction was carefully examined in the absence of irradiation, since it was envisaged that with **1d** an elimination–addition[1] mechanism of substitution might be facilitated by conjugative stabilization of the intermediate olefinic bond with the phenyl group. Nevertheless, in the dark, the reaction returned only starting material (99%), showing that elimination–addition was not favored under the reaction conditions. There was some inhibition of the photostimulated reaction by di-*tert*-butyl nitroxide; in the presence of 5 mol % relative to **1d**, the amount of starting material remaining increased from 36% (without nitroxide) to 56%. The dibromides **1e** and **1f** also underwent a photostimulated reaction, affording the dithioacetals **2e** and **2f** as the major products accompanied by some of the monosubstituted cyclopropyl phenyl sulfides. In both cases, some starting material remained.

The cyclopropane **1g** was completely consumed after 4 h of irradiation. The major products, however, were the cyclopropyl phenyl sulfides **4g** and **5g**. A small amount of the disubstituted dithioacetal **2g** was also obtained. Further recognizable products could not be isolated. The reaction did not proceed to any significant extent in the dark; after 4 h, **2g** could not be detected and the starting material (90%) was recovered.

Compound **1h** did not react with benzenethiolate in the dark in $Me_2SO$. On irradiation, however, in addition to a modest yield of the expected disubstituted compound **2h**, the product of *cine* substitution **4i** was also obtained. The expected dithioacetal **2h** was the only isolable product when the reaction was repeated in liquid ammonia, although a considerable amount of the starting material was unaccounted for.

The monobromide **6a** (as a mixture of cis and trans isomers; ratio 3.8:1) also underwent photostimulated replacement, but the reaction was much slower than that for the dibromides. After 4 h, only 35% of **6a** was consumed, and **4a** was formed in 27% yield. It was uncontaminated by the cis isomer **5a**. The cis isomer of **6a** appeared to react preferentially, since the cis:trans ratio of **6a** decreased to 2.9:1 after the reaction. The reaction returned only starting material in the dark.

The bromochlorocyclopropane **7b** underwent replacement of only the bromine. After 4 h of irradiation, the products were the monosubstituted **8b** and the reduced compound **10b**.

The dichloride **9b** was unaffected by irradiation with benzenethiolate even in the presence of the radical initiator azobisisobutyronitrile or in the presence of iodobenzene (100 mol %).[16]

## Discussion

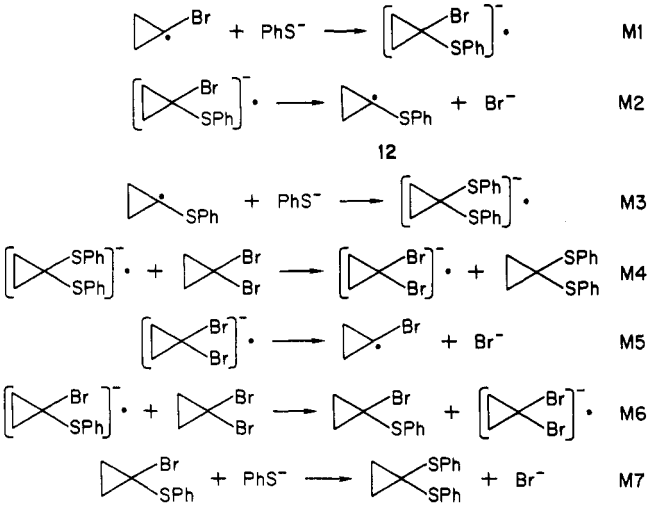
A radical chain mechanism is consistent with the observation that there is no substitution in the dark and that the photostimulated reaction is retarded by radical inhibitors and the electron scavenger, *m*-dinitrobenzene. Such a substitution is visualized as occuring via an elaborated $S_{RN}1$ chain mechanism, for which possible propagation steps (M1–M5) are sketched in Scheme II. Steps M1 and M3 involve the colligation of a radical and a nucleophile and reflect the electrophilicity and high reactivity of the cyclopropyl radical.[17] Significantly, there were no products found to arise from ring opening of the intermediate cyclopropyl radicals. This is in accord with the believed high activation barrier to the cyclopropyl–allyl

(15) Bunnett, J. F.; Scamehorn, R. G.; Traber, R. P. *J. Org. Chem.* **1976**, *41*, 3677.

(16) A reactive substrate such as iodobenzene is frequently employed to initiate a slower $S_{RN}1$ reaction. This phenomenon is known as entrainment.

(17) Walborsky, H. M. *Tetrahedron* **1981**, *37*, 1625.

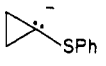
**Scheme II**




radical interconversion.[17] Additionally, such steps would be likely to lead to chain termination, since it is unlikely that the resultant allyl radical would be sufficiently reactive to propagate the reaction cycle. Steps M2 and M5 are fragmentation steps, whereas M4 involves single-electron transfer; the electron-accepting ability of *gem*-dibromocyclopropanes has precedent.[18]

Although there is strong evidence to suggest that the first bromine in a *gem*-dibromide is replaced by a homolytic mechanism, the pathway of replacement of the second bromine is less clear. de Boer and co-workers have shown that halocyclopropyl sulfides, e.g., **11j**, undergo heterolytic nucleophilic substitution with little rupture of the cyclopropane ring.[19] This is believed to be due to stabilization of the intermediate carbonium ion by sulfur. Thus, **3b** was prepared and was treated with potassium benzenethiolate in $Me_2SO$, under similar conditions to the photostimulated reactions, except that the mixture was protected from light. The dithioacetal **2b** (79%) was formed. The reaction was not inhibited by di-*tert*-butyl nitroxide and appeared to be of ionic character. In liquid ammonia, however, a similar attempted replacement failed to produce more than a trace of **2b**. It is possible, therefore, that in $Me_2SO$ at least some of the **2b** formed in the photostimulated reactions arises from replacement of the second bromine by a heterolytic mechanism. Accordingly, steps M6 and M7 are included in Scheme II. It is doubted, however, whether steps M6 and M7 make a significant contribution to the reaction in liquid ammonia.

The intermediates of Scheme II also accommodate the formation of the monosulfides **4** and **5**. Electron transfer from benzenethiolate ion to the 1-(phenylthio)cyclopropyl radical **12**, formed either as shown in Scheme II or by cleavage[20,21] of the dithioacetal radical anion $[2]^{-\cdot}$, would lead to the anion **13** which is likely to be protonated readily under the reaction conditions. An alternative pathway



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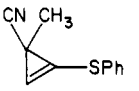
to the monosulfides, especially in the reactions carried out in $Me_2SO$, might involve the abstraction of hydrogen atoms from the solvent.[22] The monobromide **6b**, formed in the reactions involving **1b**, is likely to be formed by a similar process.

An analogous pathway with fewer propagation steps is envisaged for the substitution of the monobromide **6a** and the bromochlorocyclopropane **7b**. In the case of **7b**, the monosubstituted radical anion $[8b]^{-\cdot}$ evidently does not fragment, but instead loses an electron to afford **8b**. The compound **8b** does not appear to react further with benzenethiolate ion. The lack of reactivity of the dichloride **9b** may reflect the poorer electron-accepting properties of **9b** or the lower frangibility[23] of the radical anion $[9b]^{-\cdot}$.

The product of *cine* substitution **4i** was isolated from the reaction of benzenethiolate ion with **1h** and is likely to be formed in an elimination–addition sequence.[1] Since **4i** was not formed in the absence of irradiation, it is thought to arise from **3h**, via **14**. It is noteworthy that



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compound **4i**, however, was formed only when the reaction was carried out in $Me_2SO$ and not in liquid ammonia. Perhaps, the lower reaction temperature in the latter solvent suppressed the elimination–addition pathway. It is not known, however, why **1h** is unique among the *gem*-dibromocyclopropanes studied in giving *cine* substitution.

## Experimental Section

**General Methods.** Analytical GC was carried out on a Perkin-Elmer 990 gas chromatograph equipped with a flame ionization detector. The column used was a 55 m × 0.5 mm SP2100 SCOT capillary, temperature programmed between 80 and 240 °C. $^1H$ NMR spectra were recorded at 60 MHz unless stated otherwise on a Jeol JNM-PMX 60 spectrometer. 300-MHz NMR spectra were determined on a Bruker CXP-300 spectrometer and $^{13}C$ NMR spectra on a Bruker WP-80 DS instrument. Mass spectra were determined at 70 eV in electron impact mode on an AEI MS-3074 spectrometer equipped with a peak-matching facility. IR spectra were generally recorded as liquid films on a Perkin-Elmer 397 spectrophotometer. Elemental analyses were carried out by Amdel, Melbourne, and melting points were determined on a Kofler hot stage apparatus. "350-nm" lamps refer to fluorescent tubes (R.P.R. 3500A) made by the Southern New England Ultraviolet Company for inclusion in a Rayonet photochemical reactor.

**Starting Materials.** *gem*-Dihalocyclopropanes were prepared by phase-transfer methods as previously described.[24-29] 1,1-Dibromocyclopropane was prepared by a Hunsdieker–Cristol reaction.[30] Ammonia was distilled from sodium prior to use, and $Me_2SO$ was distilled from calcium hydride and stored over 4A molecular sieves under an atmosphere of $N_2$. Potassium *tert*-butoxide was used as received from EGA-Chemie. Benzenethiol (Aldrich) was redistilled before use.

**General Procedure for the Reaction of Dibromocyclopropanes with Benzenethiolate in Liquid Ammonia.** The following example is representative. Ammonia was distilled from sodium into a 100-mL two-necked Pyrex flask, which had been flushed with nitrogen and equipped with a dry ice condenser and

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stirring bar, until the solution volume was 40 mL. An atmosphere of nitrogen was maintained throughout the experiment. Benzenethiol (661 mg, 6 mmol) and 7,7-dibromobicyclo[4.1.0]heptane (**1a**) (254 mg, 1 mmol) were successively added by syringe. The mixture was irradiated for 4 h, with stirring, with 16 350-nm lamps in a Rayonet photochemical reactor. Frost was removed from the outside of the flask hourly. After the irradiation, chilled (−40 °C) ether (40 mL) was added, and the ammonia was allowed to evaporate as the apparatus warmed to room temperature over several hours. Water (40 mL) was then added, the mixture was stirred, and the organic phase was separated, washed successively with 10% aqueous sodium hydroxide (2 × 30 mL) and water (2 × 30 mL), and dried ($MgSO_4$). A fraction (10%) of the solution was removed and analyzed for starting material by GC after the addition of an internal standard (**1c**). The solvent was removed from the remaining solution, and the residue was subjected to flash chromatography on silica gel (light petroleum) to afford, after an initial fraction of diphenyl disulfide (136 mg), 7,7-bis(phenylthio)bicyclo[4.1.0]heptane (**2a**) (120 mg, 43%): mp 59–60 °C (from MeOH, low temperature) (lit.[31] 58–59 °C); $^{13}C$ NMR δ 20.6 (t), 21.0 (t), 27.7 (d), 39.8 (s), 125.5 (d), 126.2 (d), 127.7 (d), 128.9 (d), 129.1 (d), 135.4 (s), 136.8 (s); MS, *m/z* (relative intensity) 312 ($M^+$, 12), 203 (100). The IR and $^1H$ NMR spectra were in agreement with those previously reported.[31]

**General Procedure for the Reaction of Dibromocyclopropanes with Benzenethiolate in $Me_2SO$.** The following preparation of **2b** is representative. Benzenethiol (661 mg, 6 mmol) was added to a solution of potassium *tert*-butoxide (673 mg, 6 mmol) in $Me_2SO$ (10 ml) under $N_2$. After 5 min, 1,1-dibromo-2,2,3,3-tetramethylcyclopropane (**1b**) (256 mg, 1 mmol) was added and the mixture was irradiated, with stirring, with 16 350-nm lamps in a Rayonet photochemical reactor. After 4 h, the mixture was poured into a mixture of saturated sodium chloride solution and water (1:1, 50 mL) and extracted with ether (2 × 30 mL). The combined ether phases were washed successively with water and 10% sodium hydroxide solution. After a further water washing, the organic phase was dried ($MgSO_4$). A fraction (10%) of the solution was removed and analyzed for starting materials by GC after the addition of an internal standard (**1a**). After removal of the solvent from the remaining portion, it was subjected to flash chromatography on silica gel (light petroleum) to afford a small fraction containing diphenyl disulfide and then 1,1-bis(phenylthio)-2,2,3,3-tetramethylcyclopropane (**2b**) (44%): mp 123–125 °C (from petroleum ether); IR ($CCl_4$) 3010, 3000, 1570, 1470, 680 $cm^{-1}$; $^{13}C$ NMR δ 20.2 (q), 32.3 (s), 48.5 (s), 125.3 (d), 128.1 (d), 128.6 (d), 136.8 (s); $^1H$ NMR δ 1.40 (s, 12 H), 7.1 (br s, 10 H); MS, *m/z* (relative intensity) 314 ($M^+$, 1), 205 (18), 196 (33), 153 (14), 149 (20), 121 (100), 119 (50), 95 (41), 77 (44), 57 (50). Anal. Calcd for $C_{19}H_{22}S_2$: C, 72.59; H, 7.05. Found: C, 72.79; H, 7.15.

**Reaction of 7,7-Dibromobicyclo[4.1.0]heptane (1a) with Benzenethiolate Ion in $Me_2SO$.** This reaction was carried out for 4 h as described above. Examination of the crude reaction mixture by TLC (alumina, light petroleum) against authentic[32] **4a** and **5a** showed that the monosulfides were not present. Subjection of the mixture to flash chromatography (silica gel, light petroleum) afforded 7,7-bis(phenylthio)bicyclo[4.1.0]heptane (**2a**) (117 mg, 42%).

**Reaction of 2-Butyl-1,1-dibromocyclopropane (1c) with Benzenethiolate Ion in $Me_2SO$.** This reaction was carried out for 4 h as described above. Flash chromatography on silica gel (light petroleum) afforded an initial fraction (68 mg) containing a mixture of diphenyl disulfide and *cis*- and *trans*-2-butyl(phenylthio)cyclopropane in the ratio 49:51:30 as determined by GC comparison with authentic samples[33] and confirmed by $^1H$ NMR spectroscopy. This was followed by 1,1-bis(phenylthio)-2-butylcyclopropane (**2c**) (121 mg, 43%) as an oil: IR 1570, 1465, 1425, 1010, 675 $cm^{-1}$; $^{13}C$ NMR δ 14.0 (q), 22.4 (t), 25.9 (t), 30.3 (t), 31.4 (t), 33.0 (d), 37.6 (s), 126.3 (d), 126.9 (d), 128.9 (d), 129.5 (d), 130.6 (d), 135.9 (s), 136.1 (s); $^1H$ NMR δ 0.6–2.0 (m, 12 H), 6.9–7.6 (m, 10 H); MS, *m/z* (relative intensity) 314 ($M^+$, 14), 257 (13), 205 (67), 149 (47), 147 (47), 135 (43), 123 (41), 121 (47), 110 (57), 109 (43), 95 (100), 91 (80), 77 (60); exact mass *m/z* 314.1156, calcd for $C_{19}H_{22}S_2$ *m/z* 314.1162. Anal. Calcd for $C_{19}H_{22}S_2$: C, 72.59; H, 7.05. Found: C, 72.36; H, 6.96.

**Reaction of 1,1-Dibromo-2-phenylcyclopropane (1d) with Benzenethiolate Ion in $Me_2SO$.** Flash chromatography (light petroleum) of the crude reaction mixture gave, in order of elution: the starting material (36%), *cis*-2-phenyl-1-(phenylthio)cyclopropane (**5d**) (28%), identified by its GC retention time, $^{13}C$ NMR spectrum, and MS, which were identical with those of an authentic sample,[32] and 1,1-bis(phenylthio)-2-phenylcyclopropane (**2d**) (28%): mp 55–56 °C (from light petroleum); IR 3050, 1580, 1470, 1430, 1110, 1020, 720, 680 $cm^{-1}$; $^{13}C$ NMR δ 25.1 (t), 36.8 (d), 41.2 (s), 126.8 (d), 127.2 (d), 127.4 (d), 128.1 (d), 128.7 (d), 129.0 (d), 129.3 (d), 130.7 (d), 131.2 (d), 135.2 (s), 135.7 (s), 136.1 (s); $^1H$ NMR (300 MHz) δ 1.8–2.0 (m, 2 H), 2.96 ("t", *J* = 8 Hz, 1 H), 7.1–7.5 (m, 15 H); MS, *m/z* (relative intensity) 334 ($M^+$, 6), 226 (11), 225 (17), 224 (11), 167 (52), 147 (24), 121 (28), 117 (83), 115 (100), 91 (43); exact mass *m/z* 334.0843, calcd for $C_{21}H_{18}S_2$ *m/z* 334.0850.

**Reaction of 9,9-Dibromobicyclo[6.1.0]nonane (1e) with Benzenethiolate Ion in $Me_2SO$.** Flash chromatography (light petroleum) afforded a mixture (51 mg) comprising diphenyl disulfide, *cis*-9-(phenylthio)bicyclo[6.1.0]nonane (**5e**), and *trans*-9-(phenylthio)bicyclo[6.1.0]nonane (**4e**) in the ratio 27:17:56 (by GC comparison with authentic samples[32] and confirmed by $^1H$ NMR spectral analysis). These were followed by 9,9-bis(phenylthio)bicyclo[6.1.0]nonane (**2e**) (115 mg, 38%): mp 97–98 °C (from petroleum ether); IR 3050, 2900, 2840, 1575, 1475, 1430, 1010, 680 $cm^{-1}$; $^{13}C$ NMR δ 23.9 (t), 26.4 (t), 28.8 (t), 34.3 (d), 38.8 (s), 125.8 (d), 126.2 (d), 128.7 (d), 128.9 (d), 129.0 (d), 135.9 (s), 136.6 (s); $^1H$ NMR δ 1.1–2.2 (m, 14 H), 7.0–7.5 (m, 10 H): MS (20 eV), *m/z* (relative intensity) 340 ($M^+$, 11), 231 (20), 149 (24), 134 (24), 105 (100); exact mass *m/z* 340.1319, calcd for $C_{21}H_{24}S_2$ *m/z* 340.1306.

**Reaction of 1,1-Dibromocyclopropane (1f) with Benzenethiolate Ion in $Me_2SO$.** Subjection of the crude reaction mixture to flash chromatography (light petroleum) afforded 1,1-bis(phenylthio)cyclopropane (**2f**) (80 mg, 34%) as an oil, which had identical spectral characteristics and GC retention time with those of a sample prepared by the method of Cohen.[34] 1-(Phenylthio)cyclopropane (**4f**) was identified by GC "spiking" with an authenic sample[35] and was quantified after the addition of an internal standard (thioanisole).

**Reaction of Methyl 2,2-Dibromo-1-methylcyclopropanecarboxylate (1g) with Benzenethiolate Ion in $Me_2SO$.** Subjection of the crude reaction mixture to flash chromatography (3% ether/light petroleum) afforded diphenyl disulfide (109 mg) and methyl *c*-2-(phenylthio)-1-methyl-*r*-1-cyclopropanecarboxylate (**4g**) as an oil: IR 1710 $cm^{-1}$; $^{13}C$ NMR δ 14.2 (q), 22.7 (t), 26.3 (s), 29.1 (d), 52.4 (q), 125.7 (d), 127.2 (d), 129.2 (d), 137.4 (s), 202.7 (s); $^1H$ NMR δ 0.83 (dd, *J* = 5, 6 Hz, 1 H), 1.41 (s, 3 H), 1.80 (dd, *J* = 5, 9 Hz, 1 H), 2.91 (dd, *J* = 6, 9 Hz, 1 H), 3.70 (s, 3 H), 7.17 (s, 5 H); MS, *m/z* (relative intensity) 222 ($M^+$, 58), 190 (40), 163 (71), 113 (100); exact mass *m/z* 222.0710, calcd for $C_{12}H_{14}O_2S$ *m/z* 222.0715. A subsequent fraction (79 mg) was shown by $^1H$ NMR spectroscopy to contain methyl *t*-2-(phenylthio)-1-methyl-*r*-1-cyclopropanecarboxylate (**5g**) and methyl 2,2-bis(phenylthio)-1-methylcyclopropanecarboxylate (**2g**) in the ratio 53:47. These could be purified by repeated flash chromatography (30% $CH_2Cl_2$/light petroleum). Methyl 2,2-bis(phenylthio)-1-methylcyclopropanecarboxylate was eluted as an oil: IR 1710, 1040 $cm^{-1}$; $^{13}C$ NMR δ 18.6, 27.7, 39.5, 42.4, 52.5, 126.3, 127.5, 128.9, 129.1, 131.6, 135.1, 171.6; $^1H$ NMR δ 1.23 (d, *J* = 5.5 Hz, 1 H), 1.65 (s, 3 H), 2.00 (d, *J* = 5.5 Hz, 1 H), 3.75 (s, 3 H), 7.0–7.5 (m, 10 H); MS, *m/z* (relative intensity) 330 ($M^+$, 14), 221 (58), 193 (78), 161 (100); exact mass *m/z* 330.0758, calcd for $C_{18}H_{18}O_2S_2$ *m/z* 330.0748. Methyl *t*-2-(phenylthio)-1-methyl-*r*-1-cyclopropanecarboxylate was also an oil: IR 1720, 1040 $cm^{-1}$; $^1H$ NMR δ 1.20 (dd, *J* = 5, 9 Hz, 1 H), 1.48 (s, 3 H), 1.65 (dd, *J* = 5, 6 Hz, 1 H), 2.38 (d, *J* = 6, 9 Hz, 1 H), 3.57 (s, 3 H), 7.17 (s, 5 H); MS, *m/z* (relative intensity) 222 ($M^+$, 77), 190 (48), 163 (73), 113 (100); exact mass *m/z* 222.0720, calcd for $C_{12}H_{14}O_2S$ *m/z* 222.0715.

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**Reaction of 2,2-Dibromo-1-methylcyclopropanecarbonitrile (1h) with Benzenethiolate Ion in $Me_2SO$.** The product of the reaction was chromatographed on silica gel (5% ether/light petroleum). A sample of *c*-2,*t*-3-bis(phenylthio)-1-methyl-*r*-1-cyclopropanecarbonitrile (68 mg) was first eluted. This could not be obtained completely pure even after repeated chromatography, and it remained an oil: IR 2320, 1585, 1480, 1440, 1090, 1025, 690 $cm^{-1}$; $^{13}C$ NMR $\delta$ 16.4 (q), 22.6 (s), 36.6 (d), 36.0 (d), 120.0 (s), 126.9 (d), 127.4 (d), 128.2 (d), 129.4 (d), 129.5 (d), 129.8 (d), 133.5 (s), 134.0 (s); $^1H$ NMR $\delta$ 1.57 (s, 3 H), 2.45 and 2.97 (AB q, $J_{AB}$ = 5.6 Hz, 2 H), 6.8–7.5 (m, 10 H); MS, *m/z* (relative intensity) 297 ($M^+$, 13), 188 (100), 161 (31), 110 (51), 109 (35); exact mass *m/z* 297.0650, calcd for $C_{17}H_{15}NS_2$ *m/z* 297.0646. The next fraction contained crude 2,2-bis(phenylthio)-1-methylcyclopropanecarbonitrile (**2h**) (88 mg) which was rechromatographed to afford the pure compound (60 mg, 22%) as an oil: IR 2320, 1585, 1480, 1425, 1025, 690 $cm^{-1}$; $^{13}C$ NMR $\delta$ 19.5 (q), 25.1 (s), 30.8 (t), 44.3 (s), 120.9 (s), 127.5 (d), 128.3 (d), 129.2 (d), 129.3 (d), 130.3 (d), 132.3 (d), 133.4 (s), 134.9 (s); $^1H$ NMR $\delta$ 1.40 and 1.90 (AB q, $J_{AB}$ = 6.5 Hz, 2 H), 1.75 (s, 3 H), 7.2–7.6 (m, 10 H); MS, *m/z* (relative intensity) 297 ($M^+$, 100), 188 (58), 130 (45), 121 (46), 109 (21), 77 (56); exact mass *m/z* 297.0645, calcd for $C_{17}H_{15}NS_2$ *m/z* 297.0646. The reaction was repeated in liquid ammonia, and the crude reaction mixture was chromatographed to give the starting material (32 mg, 15%) and **2h** (126 mg, 47%), identical with the sample prepared previously.

**Reaction of 7-Bromobicyclo[4.1.0]heptane (6a) with Benzenethiolate Ion in Ammonia.** A mixture of *cis*- and *trans*-7-bromobicyclo[4.1.0]heptane[18] (**6a**) (ratio 79:21) was irradiated with benzenethiolate ion in liquid ammonia in the usual way. After chromatography (light petroleum), *trans*-7-(phenylthio)bicyclo[4.1.0]heptane (**4a**) (50 mg, 27%) was isolated as an oil, which had identical spectral characteristics and GC retention time with those of the minor isomer formed on phase-transfer-catalyzed addition of (phenylthio)carbene to cyclohexene.[32] The stereochemistry was further confirmed by the presence of a triplet, $J$ = 4 Hz, at $\delta$ 1.80 in the $^1H$ NMR spectrum (300 MHz), consistent with trans coupling.

**Reaction of 1-Bromo-1-chloro-2,2,3,3-tetramethylcyclopropane (7b) with Benzenethiolate Ion in Ammonia.** After analysis of the reaction mixture for starting material and **10b** by GC, the remainder was distilled to afford 1-chloro-1-(phenylthio)-2,2,3,3-tetramethylcyclopropane (**8b**) (56 mg, 31%): bp 130 °C [block] (0.3 mm); mp 36–42 °C; IR 3050, 2975, 2925, 2900, 1570, 1460, 1425, 1360, 675 $cm^{-1}$; $^{13}C$ NMR $\delta$ 19.7 (q), 20.1 (q), 31.0 (s), 65.6 (s), 125.6 (d), 127.2 (d), 128.9 (d), 135.8 (s); $^1H$ NMR $\delta$ 1.28 (s, 6 H), 1.34 (s, 6 H), 7.0–7.6 (m, 5 H); MS, *m/z* (relative intensity) 242 ($M^+$, 13), 240 ($M^+$, 36), 227 (10), 225 (26), 204 (36), 133 (34), 131 (100), 95 (69), 81 (41), 77 (52), 67 (66), 55 (83); exact mass *m/z* 240.0734, calcd for $C_{13}H_{17}S^{35}Cl$ *m/z* 240.0740. It was identical in all respects with a sample prepared by another method.[36]

**1-Bromo-1-(phenylthio)-2,2,3,3-tetramethylcyclopropane (3b).** A solution of *n*-butyllithium (6.25 mL, 1.6 M, 10 mmol) in THF was added to a suspension of 1,1-dibromo-2,2,3,3-tetramethylcyclopropane (**1b**) (2.56 g, 10 mmol) in THF (30 mL) at −78 °C. The mixture was stirred at −78 °C for 45 min. After this period, a solution of diphenyl disulfide (1.75 g, 8 mmol) in THF (15 mL) was added dropwise; the resultant solution was stirred for 30 min and then slowly allowed to warm to room temperature. The solution was poured into water (100 mL) and extracted thrice with ether. The combined organic phases were washed successively with sodium hydroxide solution and water and dried ($MgSO_4$). The solvent was removed under reduced pressure to afford an oil (3.2 g), which crystallized on standing and was purified by sublimation [30–50 °C (0.005 mm)] to give 1-bromo-1-(phenylthio)-2,2,3,3-tetramethylcyclopropane (**3b**) (1.8 g, 63%), mp 62–66 °C, which was stored in the dark at −15 °C: $^1H$ NMR $\delta$ 1.27 (s, 6 H), 1.38 (s, 6 H), 7.0–7.2 (m, 5 H); MS, *m/z* (relative intensity) 286 ($M^+$, 21), 284 ($M^+$, 21), 206 (94), 150 (34), 95 (100); exact mass *m/z* 284.0245, calcd for $C_{13}H_{17}{}^{79}BrS$ *m/z* 284.0234.

**Reaction of 1-Bromo-1-(phenylthio)-2,2,3,3-tetramethylcyclopropane (3b) with Benzenethiolate Ion. 3b** (55 mg, 0.19 mmol) was added to a stirred solution prepared from potassium *tert*-butoxide (123 mg, 1.1 mmol) and benzenethiol (121 mg, 1.1 mmol) in $Me_2SO$ (1.9 mL). The resultant mixture was protected from light and placed in a working Rayonet apparatus for 4 h. The mixture was then diluted with water and worked up in the usual way to afford, after chromatography on silica gel (light petroleum), 1,1-bis(phenylthio)-2,2,3,3-tetramethylcyclopropane (**2b**) (48 mg, 79%), which was identical by $^1H$ NMR and mixed mp with the sample of **2b** prepared above.

A similar experiment carried out in the presence of 50 mol % di-*tert*-butyl nitroxide (relative to **3b**) returned **2b** (73%) after chromatography.

The reaction was repeated (without the addition of nitroxide) in liquid ammonia (40 mL). After chromatography, **2b** (2 mg, 0.6%) was isolated. An earlier fraction (266 mg) was a mixture; the $^1H$ NMR spectrum was consistent with it containing impure 2,4-dimethyl-3-(phenylthio)-1,3-pentadiene and diphenyl disulfide. $^1H$ NMR $\delta$ 1.80 (s, 3 H), 1.95 (s, 3 H), 2.07 (s, 3 H), 4.67 (br, 1 H), 4.97 (br, 1 H), 7.0–7.6 (m, 12 H).

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