Table III. Analytical Data for New Compounds

| | |
|---|---|
| 1b | high-resolution mass spectrum,[a] $m/z$ 246.0720 ($C_{11}H_{15}FO_3S$ requires 246.0726) |
| 1c | anal.[b] calcd for $C_{12}H_{17}O_4S$: C, 55.82; H, 7.02. Found: C, 56.03; H, 6.98 |
| 3 | high-resolution mass spectrum,[a] $m/z$ 284.1441 ($C_{15}H_{24}O_3S$ requires 284.1446) |
| 5b | solvolysis equivalent,[c] 269 ± 2 ($C_{14}H_{18}O_3S$ requires 266.1) |

[a] By Dr. Woodfin Ligon, General Electric Research and Development Center, Schenectady, NY. [b] Instranal Laboratory, Inc., Rensselaer, NY. [c] Weighed samples were heated with measured amounts of sodium acetate in acetic acid and then back-titrated with standard perchloric acid in acetic acid solution.

**2-*tert*-Butylnaphthalene** was prepared after the manner of Crawford and Glesmann[14] and purified by preparative GC: NMR ($CDCl_3$) δ 1.4 (s, 9 H), 7.2–7.8 (m, 7 H).

**Reaction of Sulfonate Esters with Arene Anion Radicals.** The general procedure was to place measured quantities of sulfonate ester (0.1–0.2 mmol) and internal standard (usually an alkane of suitable molecular weight) in a 10-mL vial equipped with glass covered stirring bar and septum cap. To this was added ca. 5 mL of dry solvent, and the system was thoroughly flushed with dry $N_2$ or Ar. Anion radical solution (0.2–0.4 M) was then added dropwise via syringe until the intense color of the reagent persisted. The contents of the vial were stirred and cooled (if noted in Table I) during this period. After being stirred for an additional 10 min, the reaction mixture was treated with a few drops of water and dried with a small amount of magnesium sulfate. Analysis by GC was then carried out directly on this solution. Various data for the new compounds are given in Table III.

**Acknowledgment.** This research was supported in part by Grant No. 77-3241A from the Air Force Office of Scientific Research. We thank Dr. Ann Ligon for experimental assistance and consultation.

**Registry No. 1a**, 2346-07-8; **1b**, 81390-32-1; **1c**, 81390-33-2; **2**, 21816-03-5; **3**, 60697-64-5; **4**, 25966-61-4; **5a**, 4455-09-8; **5b**, 32376-95-7; **8**, 5906-87-6; naphthalene radical ion (1−) sodium salt, 3481-12-7; anthracene radical ion (1−) sodium salt, 12261-48-2; acenaphthylene radical ion (1−) sodium salt, 81390-34-3; neopentyl alcohol, 75-84-3; β,β-dimethylbenzenethanol, 2173-69-5; 2,2-dimethylhexanol, 2370-13-0; 3,3-dimethyl-2-butanol, 464-07-3; benzenemethanol, 100-51-6; *endo*-bicyclo[2.2.1]hept-5-en-2-ol, 694-97-3; *exo*-bicyclo[2.2.1]hept-5-en-2-ol, 2890-98-4; 1-*tert*-butyldihydronaphthalene, 81390-35-4; 2-*tert*-butyldihydronaphthalene, 81390-36-5; cumene, 98-82-8; naphthalene, 91-20-3; anthracene, 120-12-7; acenaphthylene, 208-96-8.

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[14] H. M. Crawford and M. C. Glesmann, *J. Am. Chem. Soc.* **76**, 1108 (1954).

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# Synthesis of α-Phenylthio Aldehydes and Alkylation of 2-(Phenylthio)octanal Enolate

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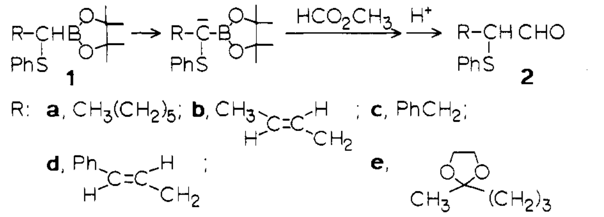
*Received October 14, 1981*

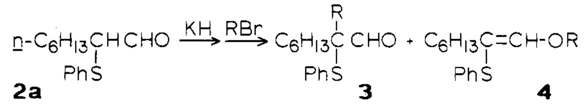
The preparation and α-lithiation of α-(phenylthio)alkaneboronic esters (1) and their condensation with carboxylic esters to provide a regiospecific synthesis of α-phenylthio ketones has been reported.[1] We have now extended this chemistry to formate esters and have found that α-phenylthio aldehydes (2) are readily prepared in good yields, as summarized in Table I. To demonstrate the potential utility of 2 as synthetic intermediates, we have studied the α-deprotonation of α-(phenylthio)octanal (**2a**) and the alkylation of the resulting enolate by allyl and other reactive halides, as summarized in Table II.



α-Phenylthio aldehydes have been made previously from aldehyde enolates by Seebach and Teschner,[2] and reactions of α-thio aldehydes have been described by Duhamel and co-workers.[3]

Two reports of direct alkylation of aldehydes have appeared. Isobutyraldehyde has been C alkylated with benzyl chloride in the presence of sodium hydroxide and a phase-transfer catalyst.[4] A more general reaction is the generation of aldehyde enolates with potassium hydride in tetrahydrofuran (THF) and their alkylation with allylic or benzyl halides.[5] The latter approach proved applicable to an α-phenylthio aldehyde.

Addition of 2-(phenylthio)octanal (**2a**) to a suspension of potassium hydride in THF at room temperature resulted in hydrogen evolution and formation of the enolate within a few minutes. It was verified that conversion to enolate is complete by quenching a sample with $D_2O$, which led to recovered octanal that lacked any measurable absorption by the α proton at δ 3.4 and had a singlet in place of the usual CHO doublet at δ 9.2. Addition of allyl bromide or a similarly reactive halide led to a mixture of C alkylation and O alkylation products **3** and **4**, respectively, as summarized in Table II. When a mixture of cyclohexane and benzene was used in place of THF as solvent, formation of the enolate was slower but the proportion of C alkylation product (**3**) became much more favorable (Table II). In contrast, addition of an equivalent of dicyclohexyl-18-crown-6 resulted in exclusive O alkylation of **2a** to **4c** by phenyl bromide in THF.



R: **3** and **4** **a**, $CH_2{=}CHCH_2$-; **b**, E-$CH_3CH{=}CHCH_2$-; **c**, $(CH_3)_2C{=}CHCH_2$-; **d**, $PhCH_2$-; **e**, $CH_3$-

In contrast to the highly successful results with allylic halides, a single attempted reaction of the potassium enolate of **2a** with a typical primary halide, *n*-propyl iodide, yielded no alkylation product whatever, as indicated by TLC and NMR analysis of the reaction mixture. Although primary alkyl iodides have been reported to alkylate simple aldehyde enolates,[5] they gave lower yields and more O alkylation than allylic bromides, and this precedent did not encourage us to pursue the matter further.

## Experimental Section

Reactions involving carbanions were run under argon in oven-dried glassware, with transfer of reagents by syringe.

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[1] Matteson, D. S.; Arne, K. *J. Am. Chem. Soc.* **1978**, *100*, 1325–1326. Matteson, D. S.; Arne, K.; *Organometallics* **1982**, *1*, 280–288.

[2] Seebach, D.; Teschner, M. *Chem. Ber.* **1976**, *109*, 1601–1616.

[3] Duhamel, P.; Duhamel, L.; Chauvin, J. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1972**, *274*, 1233–1236.

[4] Sjöberg, K. *Aldrichimica Acta* **1980**, *13*, 55–58.

[5] Groenwegen, P.; Kallenberg, H.; van der Gen, A. *Tetrahedron Lett.* **1978**, 491–494.

0022-3263/82/1947-2479$01.25/0

**Table I. α-Phenylthio Aldehydes (2) from Pinacol α-(Phenylthio)alkaneboronates**

| R of $RCH(SPh)BO_2C_2(CH_3)_4$ (**1**) and RCH(SPh)CHO (**2**) | yield of **2**, % | $^1H$ NMR of RCH(SPh)CHO, δ [a] | | | |
|---|---|---|---|---|---|
| | | CHSPh | CHO | $SC_6H_5$ | R |
| $CH_3(CH_2)_5$ (a) | 61, 85[b] | 3.38 | 9.18 | 7.2 | 0.87 (3), 1.3 (10) |
| $CH_3CH{=}CHCH_2{-}$ (b) | 68[c] | 3.68 | 9.67 | 7.4 | 1.8 (3), 2.5 (2), 5.7 (2) |
| $PhCH_2{-}$ (c) | 86 | 3.75 | 9.53 | 7.4 | 3.00 (2), 7.4 (5) |
| $PhCH{=}CH{-}CH_2{-}$ (d) | 71 | 3.58 | 9.60 | 7.4 | 2.6 (2), 6.4 (2), 7.4 (5) |
| $C_2H_4O_2C(CH_3){-}(CH_2)_3{-}$ (e) | 57 | 3.60 | 9.60 | 7.4 | 1.5 (9), 3.95 (4) |

[a] In $CCl_4$, internal $Me_4Si$ reference. Peaks had expected multiplicities and integrals. [b] Improved yield when 1 equiv of $Me_2NCH_2NMe_2$ was used in preparation of α-lithio boronic ester. [c] Ethyl formate was used. This compound was not fully purified.

**Table II. Alkylation of the Potassium Enolate of 2-(Phenylthio)octanal**

| halide, RX | solvent | yield of **3**, %[a] | yield of **4**, %[a] |
|---|---|---|---|
| $CH_2{=}CHCH_2Br$ | THF | 43 | 24 |
| $CH_2{=}CHCH_2Br$ | HC[b] | 76 | 12 |
| $CH_3CH{=}CHCH_2Br$[c] | HC | 84 | 0 |
| $(CH_3)_2C{=}CHCH_2Br$ | THF | 59 | 28 |
| $(CH_3)_2C{=}CHCH_2Br$ | THF[d] | 0 | ~100[e] |
| $(CH_3)_2C{=}CHCH_2Br$ | HC | 81 | 0 |
| $PhCH_2Br$ | HC | 89 | 0 |
| $CH_3I$ | THF | ~50[e] | ~50[e,f] |

[a] Isolated by preparative TLC, except as noted. [b] Cyclohexane/benzene. [c] 2 equiv used. [d] With 1 equiv of dicyclohexyl-18-crown-6. [e] Estimated proportion by $^1H$ NMR spectroscopy. [f] Mixture (~2:1) of geometric isomers.

Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. Butyllithium was titrated with 2-propanol, with 1,10-phenanthroline as indicator. A Varian EM-360 spectrometer was used to measure 60-MHz proton NMR spectra, a JEOL MH-100 for 100-MHz spectra, with internal tetramethylsilane as reference. Infrared spectra were measured with a Beckman IR-5 instrument. Microanalyses were by Galbraith Laboratories, Knoxville, TN.

**Boronic Esters (1).** These were prepared by the method previously described.[1] Pinacol 1-(phenylthio)-2-phenylethane-1-boronate (**1c**)[1] and the ethylene ketal of pinacol 1-(phenylthio)-5-hexanone-1-boronate (**1e**)[6] have been reported previously. Properties of three new members of this series follow.

**Pinacol 1-(Phenylthio)heptane-1-boronate (1a)** (from 1-bromohexane): 75%; bp 138–140 °C (0.2 torr); NMR ($CCl_4$) δ 1.3 (m, 25, $CH_2$ + $CH_3$), 2.6 (t, 1, CH), 7.35 (m, 5, $C_6H_5$). Anal. Calcd for $C_{19}H_{31}BO_2S$: C, 68.26; H, 9.35; B, 3.23; S, 9.59. Found: C, 68.38; H, 9.37; B, 3.20; S, 9.69.

**Pinacol 1-(Phenylthio)-3-pentene-1-boronate (1b)** (from crotyl bromide): 57%; bp 93 °C (0.025 torr); NMR ($CCl_4$) δ 1.2 (s, 12, $CCH_3$), 1.75 (d, 3, $C{=}CCH_3$), 2.4 (m, 3, $CH_2CH$), 5.55 (m, 2, $CH{=}CH$), 7.4 (m, 5, $C_6H_5$). Anal. Calcd for $C_{17}H_{25}BO_2S$: C, 67.11; H, 8.28; B, 3.55; S, 10.54. Found: C, 67.03; H, 8.17; B, 3.25; S, 10.72.

**Pinacol 1-(Phenylthio)-4-phenyl-3-butene-1-boronate (1d)** (from pinacol lithio(phenylthio)methaneboronate[1] and cinnamyl chloride): 60%; bp 160–170 °C (0.025 torr); NMR ($CCl_4$) δ 1.2 (s, 12, $CCH_3$), 2.65 (m, 3, $CH_2CH$), 6.45 (m, 2 $CH{=}CH$), 7.35 (m, 10, $C_6H_5$). Anal. Calcd for $C_{22}H_{27}BO_2S$: C, 72.13; H, 7.43; B, 2.95; S, 8.75. Found: C, 72.17; H, 7.45; B, 2.76; S, 8.74.

**General Preparation of α-Phenylthio Aldehydes (2).** To a stirred solution of 11 mmol of diisopropylamine in 50 mL of THF at 0 °C was added 10 mmol of *n*-butyllithium (2 M in hexane) followed by 10 mmol of the selected pinacol 1-(phenylthio)alkane-1-boronate in 20 mL of THF. After 4–6 h at 0 °C, 10 mmol of methyl formate was added, and the mixture was stirred 3–10 h at 20 °C. Acidification with 10% aqueous phosphoric acid was followed by extraction with ether, drying over magnesium sulfate, concentration, chromatography on a silica gel column with petroleum ether/benzene, and distillation. Yield and NMR spectral data are recorded in Table I, and other data follow.

**2-(Phenylthio)octanal (2a)**: simple distillation, bp 103–106 °C (0.07 torr); IR (neat) 1715 $cm^{-1}$ (C=O). Anal. Calcd for $C_{14}H_{20}OS$: C, 71.14; H, 8.53; S, 13.56. Found: C, 70.89; H, 8.26; S, 13.57.

**2-(Phenylthio)-4-hexenal (2b)**: simple distillation, bp 87–90 °C (0.2 torr); IR (neat) 1715 $cm^{-1}$ (C=O). Anal. Calcd for $C_{12}H_{14}OS$: C, 69.86; H, 6.84; S, 15.54. Found: C, 68.34; H, 6.64; S, 15.01.

**2-(Phenylthio)-3-phenylpropanal (2c)**: distilled bulb to bulb at 130–135 °C (0.5 torr); IR (neat) 1710 $cm^{-1}$ (C=O). Anal. Calcd for $C_{15}H_{14}OS$: C, 74.34; H, 5.82; S, 13.23. Found: C, 74.31; H, 5.96; S, 12.97.

**2-(Phenylthio)-5-phenyl-4-pentenal (2d).** Distilled bulb to bulb at 130–140 °C (0.1 torr); IR (neat) 1710 $cm^{-1}$ (C=O). Anal. Calcd for $C_{17}H_{16}OS$: C, 76.08; H, 6.01; S, 11.95. Found: C, 75.78; H, 6.24; S, 12.14.

**6-Ethylene Ketal of 6-Oxo-2-(phenylthio)heptan-1-al (2e)**: simple distillation, bp 135–145 °C (0.2 torr); IR (neat) 1710 $cm^{-1}$. Anal. Calcd for $C_{15}H_{20}O_3S$: C, 64.26; H, 7.19; S, 11.44. Found: C, 64.00; H, 6.93; S, 11.22.

**Alkylation of 2-(Phenylthio)octanal (2a).** A portion of potassium hydride (1–5 mmol) was washed free of oil with pentane, dried under vacuum, and weighed under argon. In the experiments that produced mixtures of O- and C-alkylation products, THF (4 mL/mmol) was added, followed by 0.9 equiv of 2-(phenylthio)octanal (**2a**) in some THF. In experiments that led to nearly exclusive C alkylation, cyclohexane (10 mL/mmol) was added to the potassium hydride, followed by the **2a** in benzene (3–5 mL/mmol). The mixture was stirred 5 min if in THF, 45 min if in cyclohexane/benzene, during which time hydrogen evolution occurred. An equivalent of the allylic or benzyl halide was added, stirring was continued an additional 5 min for reactions in THF or overnight for reactions in cyclohexane/benzene, and the mixture was treated with water and extracted with ether. The products were separated by preparative TLC.

**2-Allyl-2-(phenylthio)octanal (3a).** (From **2a** and allyl bromide in THF or, preferably, cyclohexane/benzene): $R_f$ 0.75 on silica with 2:1 benzene/petroleum ether; NMR ($CCl_4$) δ 1.5 (m, 13, $C_6H_{13}$), 2.35 (d, 2, $C{=}CCH_2$), 5.2 (m, 3, $CH{=}CH_2$), 7.45 (m, 5, $C_6H_5$), 9.45 (s, 1, CHO). Anal. Calcd for $C_{17}H_{24}OS$: C, 73.86; H, 8.75; S, 11.60. Found: 73.62; H, 9.00; S, 11.34.

**1-(Allyloxy)-2-(phenylthio)-1-octene (4a)** (from **2a** and allyl bromide in the THF): $R_f$ 0.9 on silica with 2:1 benzene/petroleum ether; NMR ($CCl_4$) δ 0.9–1.4 (m, 11, $C_5H_{11}$), 2.25 (t, 2, $CH_2CH_2C{=}C$), 4.39 (d, 2, $OCH_2$), 5.2–6.0 (m, 3, $CH{=}CH_2$), 6.62 (s, 1, $C{=}CHOR$), 7.5 (m, 5, $C_6H_5$).

**2-(2-Buten-1-yl)-2-(phenylthio)octanal (3b)** (from **2a** and crotyl bromide in cyclohexane/benzene) $R_f$ ~0.7 in 1:6 ether/petroleum ether; NMR ($CDCl_3$) δ 0.87 (m, 3, $CH_3$), 1.2–1.5 (m, 10, $(CH_2)_5$), 1.67 (d, $J$ = 4 Hz, $C{=}CHCH_3$), 2.27 (m, 2, $CH_2C{=}C$), 5.4 (m, 2, $CH{=}CH$), 7.23 (s, 5, $C_6H_5$), 9.22 (s, 1, CHO), 9.41 (s, 0.1–0.15, CHO impurity). Anal. Calcd for $C_{18}H_{26}OS$: C, 74.43; H, 9.02; S, 11.04. Found: C, 74.44; H, 9.14; S, 10.82.

**2-(3-Methyl-2-buten-1-yl)-2-(phenylthio)octanal (3c)** (from **2a** and 1-bromo-3-methyl-2-butene in THF or, preferably, cyclohexane/benzene): $R_f$ 0.45 on silica in 2:1 benzene/petroleum ether; NMR ($CCl_4$) δ 0.9 (m, 3, $CH_3$), 1.3 (m, 10, $CH_2$), 1.62 (s, 3, $C{=}CCH_3$), 1.77 (s, 3, $C{=}CCH_3$), 2.25 (m, 2, $C{=}CCH_2$), 5.2 (m, 1, $C{=}CH$), 7.35 (m, 5, $C_6H_5$), 9.35 (s, 1, CHO); IR (neat) 1715 $cm^{-1}$. Anal. Calcd for $C_{19}H_{28}OS$: C, 74.95; H, 9.27; S, 10.53. Found: C, 74.99; H, 9.43; S, 10.38.

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(6) Mendoza, A.; Matteson, D. S. *J. Organomet. Chem.* **1978**, *156*, 149–157.

*J. Org. Chem.* **1982**, *47*, 2481–2483 **2481**

**1-(3-Methyl-2-buten-1-yloxy)-2-(phenylthio)-1-octene (4c)** (from **2a** and 1-bromo-3-methyl-2-butene in THF, preferably with 1 equiv of dicyclohexyl-18-crown-6): $R_f$ 0.75 on silica in 2:1 benzene/petroleum ether; NMR ($CCl_4$) $\delta$ 0.9 (m, 3, $CH_3$), 1.3 (m, 8, $CH_2$), 1.77 (s, 3, $CH_3$), 1.85 (s, 3, $CH_3$), 2.25 (m, 2, $C{=}CCH_2$), 4.37 (d, 2, $OCH_2$), 5.4 (m, 1, $C{=}CHCH_2$), 6.52 (s, 1, $C{=}CHOR$), 7.17 (m, 5, $C_6H_5$); IR (neat) 1580, 1630 $cm^{-1}$ ($C{=}C$). Anal. Calcd for $C_{19}H_{28}OS$: C, 74.95; H, 9.27; S, 10.53. Found: C, 75.05; H, 9.07; S, 10.67.

**2-Benzyl-2-(phenylthio)octanal (3d)** (from **2a** and benzyl bromide in cyclohexane/benzene): $R_f$ 0.7 in 1:3 ether/petroleum ether; NMR ($CDCl_3$) $\delta$ 0.85 (m, 3, $CH_3$), 1.2–1.4 (m, 10, $(CH_2)_5$), 2.97, 3.01 (s, s, 2, $PhCH_2$), 7.15, 7.25 (s, s, 10, $C_6H_5$), 9.38 (s, 1, CHO). Anal. Calcd for $C_{21}H_{26}OS$: C, 77.25; H, 8.03; S, 9.82. Found: C, 77.15; H, 8.31; S, 9.60.

**2-Methyl-2-(phenylthio)octanal (3e) and 1-Methoxy-2-(phenylthio)-1-octene (4e)** (from **2a** and methyl iodide in THF, isomer mixture not separated): NMR ($CCl_4$) $\delta$ 0.88 (m, 3, $CH_3$, **3e** + **4e**), 1.17 (s, $C{-}CH_3$, **3e**), 1.3 (m, $CH_2$, **3e** + **4e**), 2.0 (m, ~1, $C{=}CCH_2$, **4e**), 3.56, 3.61 (s, s, ~1, ~0.5, **4e**, *E* and *Z*), 6.24, 6.38 (s, s, ~0.35, ~0.15, **4e**, *E* and *Z*), 7.08 (m, ~2.5, $C_6H_5$, **4e**), 7.20 (s, ~2.5, $C_6H_5$, **3e**), 9.15 (s, ~0.5, CHO, **3e**).

**Acknowledgment.** We thank the National Science Foundation for support, Grant No. CHE77-11283.

**Registry No. 1a**, 81447-38-3; **1b**, 81447-39-4; **1c**, 66080-30-6; **1d**, 81447-40-7; **1e**, 67808-83-7; **2a**, 81447-41-8; **2b**, 81447-42-9; **2c**, 55064-98-7; **2d**, 81456-91-9; **2e**, 81447-43-0; **3a**, 81447-44-1; **3b**, 81447-45-2; **3c**, 81456-92-0; **3d**, 81447-46-3; **3e**, 81447-47-4; **4a**, 81447-48-5; **4c**, 81447-49-6; (*E*)-**4e**, 81447-50-9; (*Z*)-**4e**, 81447-51-0; allyl bromide, 106-95-6; (*E*)-crotyl bromide, 29576-14-5; 1-bromo-3-methyl-2-butene, 870-63-3; benzyl bromide, 100-39-0; methyl iodide, 74-88-4.

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# Oxidation of Ionol by Silver(I)

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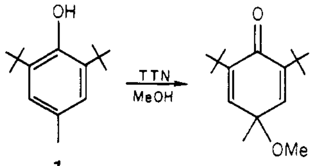
Silver(I) salts have long served the organic chemist as versatile, yet mild, one-electron oxidizing agents.[1] $\epsilon^\circ_{red}$ for $Ag^+$ (aq) is +0.80 V. Several years ago we began investigating the reaction of Ag(I) with alkoxide ions in hopes of studying the chemistry of silver alkoxides. We found[2] that Ag(I) does indeed react instantaneously and irreversibly with all alkoxides studied, but the silver alkoxides proved highly unstable at 25 °C (though somewhat more stable at −78 °C). For example, reactions of Ag(I) with methoxide in methanol or ethoxide in ethanol at 25 °C gave metallic silver in quantitative yield. Oxidation products deriving from the alkoxy fragment eluded identification, though the obvious ones (aldehydes, etc.) were specifically excluded. When the solvent in the above reactions was changed to THF or when the oxide was phenoxide or *tert*-butoxide, the reactions proved even less tractable.[2] Our frustration at being unable to identify the products from the (presumed) alkoxy radicals has led us to investigate the Ag(I) oxidation of oxides which would give either persistent free radicals or products characteristic of these intermediates. BHT (2,6-di-*tert*-butyl-4-methylphenol, ionol, **1**) is just such a compound.

The literature reports hundreds of studies of the reaction of **1** with a wide variety of oxidizing agents. Although $Ag_2O$ has been used to convert catechols to quinones[3] and oxidize 2,6-dimethylphenol,[4] we were unable to find reports on the oxidation of **1** with Ag(I). These are, nonetheless, recent reports of related oxidations of **1**. For example, while **1** reacts with $KMnO_4$ to give over a dozen products,[5] it reacts cleanly with thallium(III) nitrate to give **2**.[6] Most relevant to our work is the oxidation of **1** with DDQ, which is summarized in Scheme I.[7] Compounds **4** and **6** were isolated, the former being somewhat unstable; evidence for the intermediacy of **5** came from its ultraviolet spectrum ($\lambda_{max}$ 284 nm, log $\epsilon$ 4.45) and the formation of **6**. Support for the involvement of phenoxy radical **3** came from the solid-state ESR spectrum of **4**, which exhibited a four-line pattern.



**1** **2**

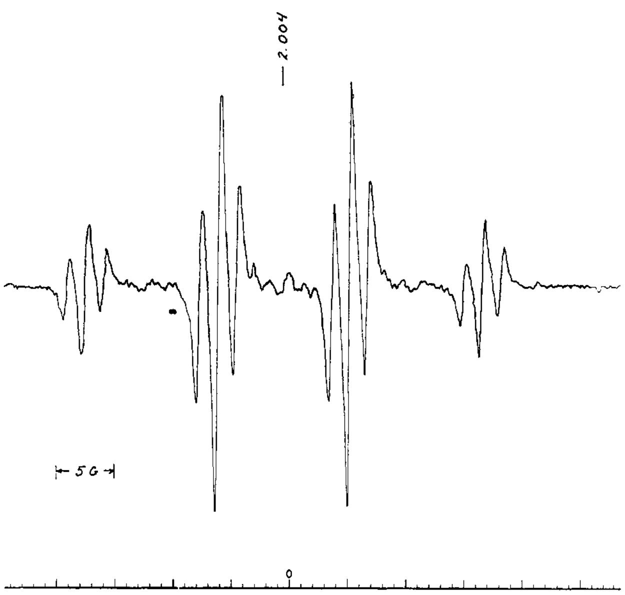


**Figure 1.** ESR spectrum of the supernatant from the oxidation of the conjugate base of **1** with Ag(I).

## Results

A methanol solution containing equimolar amounts of **1** and Ag(I) was essentially stable at room temperature. After the solution was left standing for 17 days, a perceptible silver mirror had formed, but this constituted less than 5% of the silver present.[8] In sharp contrast, when **1** was first converted to its conjugated base, it reacted instantaneously with 1 mol equiv of Ag(I) to give a grayish-black precipitate and a nearly colorless supernatant. The precipitate proved to be Ag, formed in quantitative yield. Examination of the supernatant by ESR spectros-

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(1) L. F. Fieser and M. Fieser, "Reagents for Organic Synthesis", Wiley, New York, 1967, and later volumes in the series.

(2) R. S. Macomber, J. C. Ford, and J. H. Wenzel, *Synth. React. Inorg. Met.-Org. Chem.*, 7(2) 111 (1977).

(3) See, for example, R. Wellstatter and A. Pfannensteil, *Ber. Dtsch. Chem. Ges.*, **37**, 4744 (1904).

(4) B. O. Lindgren, *Acta. Chem. Scand.*, **14**, 1203 (1960); the major product (15%) was 2,6-dimethyl-4-(2,6-dimethylphenoxy)phenol.

(5) B. M. Benjamin, V. R. Raaen, E. W. Hagaman, and L. L. Brown, *J. Org. Chem.*, **43**, 2986 (1978).

(6) A. Mckillop, D. H. Perry, M. Edwards, S. Antus, L. Farkas, M. Nogradi, and E. C. Taylor *J. Org. Chem.*, **41**, 282 (1976).

(7) H.-D. Becker, *J. Org. Chem.*, **30**, 982 (1965).

(8) We have found that photolysis of this solution gives a much more rapid deposition of silver metal. The details of these experiments, as related to some earlier work,[9] will be reported later.

(9) R. S. Macomber, S. Carr, P. Boudjouk, and C. Kapfer, *J. Org. Chem.*, **45**, 356 (1980).

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