New Procedure for the Transformation of Alcohols to Alkyl Halides via Xanthate Esters and Free-Radical Intermediates[1]

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O-Alkyl *S*-methyl xanthates have been used to convert alcohols to alkyl halides via free-radical pathways. The xanthate esters were readily prepared in high yields and were converted in 8–80% yields to the corresponding alkyl halides by (a) photolysis with 254-nm light in carbon tetrachloride or bromotrichloromethane and (b) by treatment with Cu(I)–Cu(II) halide in acetonitrile. The photochemical transformation gave low yields with highly aliphatic compounds due to carbon tetrachloride-mediated free-radical halogenation reactions. The transformation promoted by Cu(I)–Cu(II) halide competed with an electron-transfer oxidation process. The reaction could not be induced with AIBN or benzoyl peroxide or by treatment with molybdenum pentachloride. Mechanistic implications are discussed.

The conversion of alcohols to alkyl halides is an important one in organic chemistry. In general these are carried out via heterolytic displacement reactions.[2] Such processes have practical limitations in that problems associated with unreactivity due to steric or geometric constraints in direct displacement (S_N2) processes or with carbenium ion rearrangements in S_N1 processes often arise. Jensen and Moder[3] recognized the possibility of avoiding certain of these problems by utilizing homolytic pathways. They obtained alkyl halides in 5–59% yields by thermolysis of alkyl *tert*-butyl monoperoxyoxalates in carbon tetrachloride or bromotrichloromethane. Free-radical processes have several advantages over heterolytic displacement reactions in that steric factors are minimal, saturated alkyl radicals do not rearrange at moderate temperatures[4] (except for appropriately located hydrogen shifts), and phenylalkyl, vinylalkyl (nonallylic) and cyclopropylalkyl radicals rearrange only slowly,[4-8] compared with analogous carbenium ions. Further, radicals often rearrange to give regiochemistries or stereochemistries which differ from that of the corresponding cationic processes.[9,10]

Several years ago, Barton and McCombie[11] described a method for the conversion of alcohols to hydrocarbons via the reduction of *O*-alkyl *S*-methyl xanthates by tri-*n*-butyltin or triphenyltin hydride with free-radical initiation. Their proposed mechanism included chain-propagation steps involving (a) attack by trialkyltin radical on the xanthate ester to give trialkyltin methylmercaptide and (alkyloxy)thionocarbonyl radical, (b) loss of carbon oxysulfide from the latter radical to give an alkyl radical, and (c) hydrogen transfer from tin hydride to the alkyl radical to give hydrocarbon and tin radical. This mechanism was corroborated by work in our laboratory.[9]

We envisaged a modification of the Barton–McCombie procedure by use of carbon tetrachloride or bromotrichloromethane as the solvent instead of the tin hydride, in the hope that this would lead to alkyl halide by the chain process of Scheme I.

Scheme I

$$\text{initiator} + CCl_3X \longrightarrow CCl_3\cdot \quad (1)$$

$$CCl_3\cdot + ROC(S)SCH_3 \rightarrow RO\dot{C}{=}S + CCl_3SCH_3 \quad (2)$$

$$RO\dot{C}{=}S \rightarrow R\cdot + COS \quad (3)$$

$$R\cdot + CCl_3X \rightarrow RX + CCl_3\cdot \quad (4)$$

As the steps in eq 1, 3, and 4 are known,[3,11] the only unknown step is that represented by eq 2, that is, the attack of trichloromethyl radical on the xanthate ester, in which carbon–sulfur bonds are both formed and broken. We found no data upon which we could predict whether eq 2 was thermodynamically favorable, but we thought that if this were not the case (as in fact developed), we might utilize photochemical xanthate ester decomposition (a nonchain process) or a redox chain carrier system to substitute for the steps in eq 2 and 4.

Preparation of Xanthate Esters. The *O*-alkyl *S*-methyl xanthate esters were prepared readily[12] in high yields (68–100%) by treating the alcohols in tetrahydrofuran with sodium hydride or with *n*-butyllithium, carbon disulfide, and methyl iodide in sequence. The esters were stable to ordinary laboratory conditions, except for the *O*-benzhydryl and *O*-benzyl derivatives which rearranged to the dithiolcarbonate esters (Schönberg rearrangement[13]) readily. The benzhydryl compound rearranged at room temperature and the benzyl ester upon heating, in accord with the idea that the Schönberg rearrangement is a carbenium ion process. In view of the fugacity of the benzhydryl xanthate, it was not used in the further work.

(1) This work was described at the First International Kyoto Conference on New Aspects of Organic Chemistry in Kyoto, Japan, Dec 4–7, 1979.

(2) For recent reviews of such reactions see, among others: (a) Appel, R. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 801. (b) Cristol, S. J.; Strom, R. M.; Stull, D. S. *J. Org. Chem.* **1978**, *43*, 1150. (c) Brown, G. W. In "The Chemistry of the Hydroxyl Group"; Patai, S., Ed.; Wiley-Interscience: New York, 1971; Part I, Chapter 11.

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Table I. Irradiation of Xanthate Esters in CCl_4 or CCl_3Br with 254-nm Light

alcohol	halide formed	% yield[a]
2-octanol	Cl	15[b]
$(CH_3)_3CCH(OH)CH_3$	Cl	8[b]
$PhCH_2OH$	Cl	59,[b] 69[b]
$PhCH_2OH$	Br	69[b]
$PhCH_2CH_2OH$	Cl	37,[b] 57[c]
borneol	Br	fair[c]
1-OH	Br	80[c]
2-OH	3-Cl	80[c,d]
cholesterol	Cl	poor[c]

[a] Yield of halide from the xanthate ester. [b] Gas chromatographic analysis. [c] ^1H NMR. [d] Endo/exo ratio of 3:2.

Xanthate Ester Reactions. Two of the xanthate esters were heated in carbon tetrachloride or bromotrichloromethane at reflux, with azobis(isobutyronitrile) (AIBN) or benzoyl peroxide being added over a period of 17 h. Certain of these were heated in benzene solution at reflux with *N*-chlorosuccinimide or *N*-chloro-*N*-cyclohexylbenzenesulfonamide as halogen donors and AIBN or benzoyl peroxide as potential initiators. In all cases no significant reactions occurred, save for partial Schönberg rearrangement of the benzyl xanthate ester.

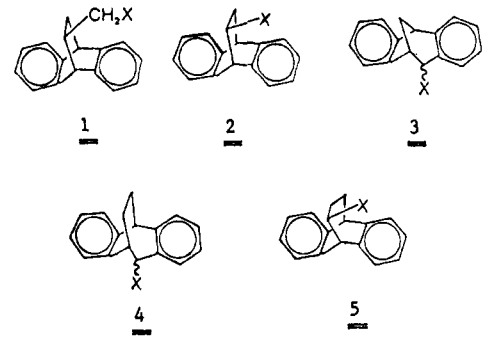
It was clear from these results that the envisaged chain reaction path of eq 1–4 with $CCl_3\cdot$ or with the other chain carriers was not realized, presumably due to the unfavorable nature of the step in eq 2. We therefore turned to alternative methods.

One of the methods attempted was photochemical. The envisaged reaction is shown in eq 5, with initial photo-

$$ROC(S)SCH_3 + CCl_3X \rightarrow RX + COS + CCl_3 - CCl_3 + CH_3SSCH_3 \text{ or } CCl_3SCH_3 \quad (5)$$

chemical cleavage of the thiocarbonyl–*S*-methyl bond, giving products from a nonchain process. The xanthate esters have molar extinction coefficients of about 10^3–10^4 M^{-1} cm^{-1} at both 300 and 254 nm. Irradiation of the xanthate esters at 300 nm gave no apparent reaction. On the other hand, irradiations of xanthate esters in carbon tetrachloride or in bromotrichloromethane led to slow disappearance of reactants, accompanied by formation of alkyl halide in poor to good (8–80%) yields (see Table I). The lower yields were associated with highly aliphatic compounds. We attribute this to photochemical initiation of carbon tetrahalide mediated free-radical halogenation reactions, which lead to highly halogenated products. This was confirmed by the identification of large amounts of chloroform from such reactions. Thus the reactions with the xanthate esters of 2-octanol, pinacolyl alcohol, borneol, and cholesterol were unsatisfactory, having yields considerably lower than those reported[3] for analogous compounds by the Jensen–Moder procedure. On the other hand, Jensen and Moder reported a yield of about 5% for benzyl chloride, as compared with our yields of 60–70% for the benzyl halides. The xanthate of 7-(hydroxymethyl)dibenzobicyclo[2.2.2]octadiene (1-OH; see Chart I), which is representative of a very unreactive[14] system, both in S_N1 and S_N2 reactions, gave an excellent yield of 1-Br. This represents a very useful procedure for such compounds. The xanthate of 7-hydroxydibenzobicyclo[2.2.2]octadiene (2-OH) gave no 2-Cl but a high yield of both epimers of the rearranged [3.2.1] chloride 3-Cl. The 2· radical is known[10] to rearrange fairly rapidly to the 3· radical, and apparently this rearrangement is faster than chlorine atom transfer from carbon tetrachloride to 2· radical.

Chart I



This photochemical reaction cannot be a chain process.[15] We ascribe this, as above, to the failure of the trichloromethyl radical to carry the chain in the step of eq 2. Two possibilities suggest themselves as likely for the photochemical reaction. The first of these is given in Scheme II, in which it is assumed that the tetrahalomethane is the

Scheme II

$$CCl_3X \xrightarrow{h\nu} CCl_3\cdot + X\cdot \quad (6)$$

$$X\cdot + ROC(S)SCH_3 \rightarrow RO\dot{C}{=}S + CH_3SX \quad (7)$$

$$RO\dot{C}S \rightarrow R\cdot + COS \quad (3)$$

$$R\cdot + CCl_3X \rightarrow RX + CCl_3\cdot \quad (4)$$

$$2CCl_3\cdot \rightarrow CCl_3CCl_3 \quad (8)$$

initiating chromophore, consistent with the observation that 254-nm light, but not 300-nm light, is effective. The second path, represented by Scheme III, contains the as-

Scheme III

$$ROC(S)SCH_3 \xrightarrow{h\nu} [ROC(S)SCH_3]^* \quad (9)$$

$$[ROC(S)SCH_3]^* \rightarrow RO\dot{C}S + CH_3S\cdot \quad (10)$$

$$RO\dot{C}S \rightarrow R\cdot + COS \quad (3)$$

$$R\cdot + CCl_3X \rightarrow RX + CCl_3\cdot \quad (4)$$

sumption that the lowest excited state of the xanthate ester is unreactive and decays to starting material, while an upper excited state decays, at least in part, by bond homolysis. In this regard, Okawara and co-workers[16] have shown that *O*-ethyl *S*-benzyl xanthate is photolabile when irradiated in ethanol or hexane in a silica cell with a high-pressure mercury lamp, while Barton and co-workers[17] have shown that it is stable when irradiated through Pyrex. These facts are consistent with the idea of an upper excited state in the xanthate photolyses, in accord with Scheme III, but we have no data presently available which allow us to make a definitive choice between Scheme II and Scheme III.

In view of the limited success of the photochemical

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(15) While quantum yield measurements were not made, our qualitative observations indicate quantum yields below 0.2.

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Table II. Redox Conversion of Xanthate Esters to the Corresponding Alkyl Halides with Copper(I)-Copper(II) Halides

xanthate ester	reaction conditions	alkyl halide	% yield of RX[a]
$PhCH_2$	CH_3CN, $CuBr_2$, 5.7 h, room temp	$PhCH_2Br$	63
$PhCH_2$	EtOAc, $CuBr_2$, 27 h, room temp	$PhCH_2Br$	50
$PhCH_2$	DMF, $CuBr_2$, 97 h, room temp	$PhCH_2Br$	37
$PhCH_2$	CH_3CN, $CuCl_2$, CuCl, 96 h, room temp	$PhCH_2Cl$	60
1	CH_3CN, $CuBr_2$, 52 h at room temp + 63 h at 82 °C	1-Br	58
1	CH_3CN, $CuBr_2$, 69 h, reflux	1-Br	37[b]

[a] Dimethyl disulfide was produced in every reaction. [b] A 30% yield of amide 4 and a 10% yield of thiocarbonate 1 were obtained.

method and the failure of the carbon- or nitrogen-centered radical-mediated chain reaction, we undertook a study of some redox-mediated processes. The copper(I)–copper(II) halide system[18] was chosen, as the reduced form seemed likely to attack the thiol sulfur atom and copper(II) halides are known[18] to supply halogen atoms to alkyl radicals. When *O*-benzyl *S*-methyl xanthate was stirred in acetonitrile with cupric bromide, the xanthate ester disappeared in less than 6 h, and benzyl bromide was obtained in 63% isolated yield. Dimethyl disulfide and benzyl methyl thioether were also formed. These results are consistent with Scheme IV.

Scheme IV

$$ROC(S)SCH_3 + CuBr \rightarrow RO\dot{C}S + CuBrSCH_3 \quad (11)$$

$$RO\dot{C}S \rightarrow R\cdot + COS \quad (3)$$

$$R\cdot + CuBr_2 \rightarrow RBr + CuBr \quad (12)$$

$$CuBrSCH_3 \rightarrow CuBr + CH_3S\cdot \quad (13)$$

$$2CH_3S\cdot \rightarrow CH_3SSCH_3 \quad (14)$$

$$R\cdot + CH_3S\cdot \rightarrow RSCH_3 \quad (15)$$

When *O*-benzyl *S*-methyl xanthate was treated with copper(I) and copper(II) chloride at room temperature, benzyl chloride was obtained in 60% yield, but the reaction time was 96 h. Treatment of 1-xanthate with cupric bromide in acetonitrile at room temperature for 52 h resulted in an incomplete reaction, and therefore the reaction was completed by heating at reflux for 63 h. This gave a 58% yield of 1-Br. When 1-xanthate was heated with cupric bromide in acetonitrile for 62 h at reflux, 37% of 1-Br, 8% 1-$OC(O)SCH_3$, and 30% of the amides 4-$NHCOCH_3$ were produced. 1-Br was stable to reaction conditions. As the radical 1· does not rearrange, it is clear that at elevated temperatures cupric bromide reacts not only by ligand exchange but also by electron-transfer oxidation to give the carbenium ion 1^+ which is known[14] to rearrange to give kinetically controlled products from the cation 4^+ (of which capture by acetonitrile, followed by hydration, gives 4-$NHCOCH_3$). Amides were also produced when the xanthate esters of 2-OH, borneol, and 2-octanol were treated with cupric bromide in refluxing acetonitrile. Jenkins and Kochi[18c] showed that oxidation to carbenium ions did not compete with ligand transfer from cupric chloride or bromide in acetonitrile with the primary radicals produced from 2,2-dimethylbutyryl peroxide or from β-phenylpropionyl peroxide at 0 °C but that oxidation does compete when radicals which give more stable cations are involved. Our results are consistent with theirs. Although the reactions with the benzyl xanthate ester and cupric bromide went in the solvents dimethylformamide and ethyl acetate, yields of benzyl bromide were poorer than in acetonitrile (Table II).

At the suggestion of Professor Kochi, we used molybdenum pentachloride, which is soluble in benzene and which gives some tetrachloride in refluxing benzene.[19] The benzyl xanthate ester gave diphenylmethane as the principal product of reaction with molybdenum chloride in benzene at room temperature. The xanthate ester of 1-OH gave a mixture of unidentified products under these conditions and a 90% yield of 5-Cl in the presence of *N*-chlorosuccinimide (4 derivatives are known to rearrange readily to 5 derivatives[20]). These results are consistent with electron-transfer oxidation of radicals by molybdenum(V) to give carbenium ions rather than the desired ligand transfer.

Conclusion. While, in certain cases, the conversion of *O*-alkyl *S*-methyl xanthates to alkyl halides by photolysis in carbon tetrachloride or bromotrichloromethane or by treatment with cupric bromide may be attractive, these are not generally useful techniques.

Experimental Section

All melting points were determined with a Thomas-Hoover apparatus and were corrected. Boiling points were determined by the micro boiling point method. ^1H NMR spectra were obtained with the use of a Varian Associates EM-390 instrument. Chemical shifts are reported in parts per million relative to tetramethylsilane. Mass spectra were obtained with a Varian MAT CH-5 spectrometer. Infrared spectra were obtained with the use of a Perkin-Elmer 337 grating infrared spectrophotometer. Gas chromatographic results were obtained on a Hewlett-Packard 5754 B gas chromatograph (flame-ionization detector) linked to a Hewlett-Packard 3380S integrator with the use of either a 3% Carbowax 1540 on 160/120-mesh Chromosorb G ($^1/_8$ in. × 5 m; column A) or a 5% Carbowax 20 M on 80/100-mesh Chromosorb G DMGS column (column B). Elemental analyses were performed by Galbraith Laboratories, Inc. Ultraviolet spectra were obtained with a Beckman Model 25 UV–vis or Cary 17 spectrophotometer. Irradiations with 254- and 300-nm light were carried out in a Srinivasan-Griffin photochemical reactor, hereafter referred to as a "Rayonet".

The tetrahydrofuran (THF) was Fisher reagent grade and was freshly distilled from lithium aluminum hydride. The benzene was reagent grade and was freshly distilled from calcium hydride. Irradiations in carbon tetrachloride (CCl_4) were performed with Fisher spectrograde CCl_4. All other solvents were reagent grade and they were used without further purification. All of the alcohols which were used in xanthate ester preparations were either commercially available or had been previously synthesized in this laboratory.[2b,14,21]

Preparation of Xanthate Esters. General Procedures.[12a] **Method A.** The alcohol (15.8 mmol) was added to an oil-free dispersion of sodium hydride (23.7 mmol) in THF (60 mL) under a nitrogen atmosphere. The mixture was heated at reflux until hydrogen evolution ceased (2–4 h) and was then cooled to 0 °C, and carbon disulfide (23.7 mmol) was slowly added. The ice bath

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(21) Cristol, S. J.; Parungo, F. P.; Schwarzenbach, K. *J. Am. Chem. Soc.* **1965**, *87*, 2879.

was allowed to melt, and the mixture was then stirred at room temperature until no alkoxide remained (2 days). Methyl iodide (23.7 mmol) was added at 0 °C. This temperature was maintained until the reaction was complete (4 h). The reaction mixture was then diluted with diethyl ether and washed with water, 1 M HCl, and saturated sodium chloride. The ethereal solution was dried over magnesium sulfate and evaporated in vacuo to yield the crude *O*-alkyl *S*-methyl xanthate.

Method B. The alcohol (20 mmol) was dissolved in THF (40 mL) in a flask which was equipped with a nitrogen atmosphere. The solution was cooled to 0 °C, and *n*-butyllithium (20 mmol) was added. The mixture was stirred for 0.5 h at 0 °C (or at room temperature) followed by the addition of carbon disulfide (21 mmol). This mixture was stirred at room temperature for 4 h before it was cooled to 0 °C, and the methyl iodide (21 mmol) was added. The final mixture was stirred at 0 °C until the reaction was complete (4 h). The workup was similar to that of procedure A.

Preparation of *O*-[(Dibenzobicyclo[2.2.2]octadien-7-yl)-methyl] *S*-Methyl Xanthate (1, x = OC(S)SCH$_3$). The corresponding alcohol (1-OH;[14] 2.23 g, 9.5 mmol) was converted into crude **1** by method A. Recrystallization from petroleum ether followed by recrystallization from ethanol gave small needles of **1** which were off-white: 2.86 g (92%); mp 120.0–122.5 °C; ^{1}H NMR ($CDCl_3$) δ 7.46–7.10 (m, 8 H, Ar H), 4.36 (m, 3 H, H-1, H-4, H-9′), 3.91 (dd, J_{gem} = 11 Hz, $J_{9,7}$ = 9 Hz, H-9), 2.57 (s, 3 H, SCH_3), 2.56 (m, 1 H, H-7), 2.02 (m, 1 H, H-8$_{anti}$), 1.20 (dm, J_{gem} = 11 Hz, H-8$_{syn}$); mass spectrum, *m/e* (relative intensity) 326 (0.5, M$^+$), 219 (16), 178 (100). Anal. Calcd for $C_{19}H_{18}OS_2$: C, 69.90; H, 5.56. Found: C, 69.91; H, 5.60.

Preparation of *O*-(5,7-Dibenzobicyclo[2.2.2]octa-5,7-dien-2-yl) *S*-Methyl Xanthate (2). The corresponding alcohol[21] (890 mg, 4 mmol) was converted into crude **2** (1.32 g of orange paste) by method A. Chromatography on four 20 cm × 20 cm × 2 mm silica gel thin-layer chromatography (TLC) plates with 50% methylene chloride in hexanes as the eluant gave a yellow solid, 850 mg (68%). Two recrystallizations from diethyl ether gave **2** as off-white crystals: mp 124.5–126.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.20 (m, 8 H, Ar H), 5.76 (dt, $J_{2,1}$ = 7 Hz, $J_{2,3}$ = 3 Hz, H-2), 4.69 (d, $J_{1,2}$ = 7 Hz, H-1), 4.26 (t, $J_{4,3}$ = 2 Hz, H-4), 2.56–2.30 (m, 1 H, H-3$_{anti}$), 2.26 (s, 3 H, SCH_3), 1.65 (dt, J_{gem} = 13 Hz, $J_{3,2}$ = $J_{3,4}$ = 3 Hz, H-3$_{syn}$); mass spectrum, *m/e* (relative intensity) 312 (2, M$^+$), 205 (100), 179 (57). Anal. Calcd for $C_{18}H_{16}OS_2$: C, 69.19; H, 5.16. Found: C, 69.37; H, 5.20.

Preparation of *O*-Benzyl *S*-Methyl Xanthate.[12a,b] Benzyl alcohol (21.6 g, 0.2 mol) was converted into the crude xanthate ester by method A. The xanthate ester was eluted from a silica gel column with 20% methylene chloride in hexanes and 25% methylene chloride in hexanes to yield 39.6 g (100%) of yellow liquid: bp 160 °C (640 mm) (lit.[12b] mp 29 °C); ^{1}H NMR ($CDCl_3$) δ 7.38 (s, 5 H, Ar H), 5.60 (s, 2 H, CH_2O), 2.50 (s, 3 H, SCH_3); mass spectrum, *m/e* (relative intensity) 198 (4, M$^+$), 138 (7), 91 (100).

Preparation of *O*-Cholesteryl *S*-Methyl Xanthate.[12a] Cholesterol (3.86 g, 10 mmol) was converted into the crude xanthate ester (4.87 g) by method B. The xanthate ester was decolorized with charcoal in ethyl acetate, recrystallized once from ethyl acetate, and recrystallized twice from hexanes to yield white crystals: mp 126.5–128.5 °C (lit.[16d] 127.5–128 °C); ^{1}H NMR ($CDCl_3$) δ 5.43 (m, 1 H, CHO), 2.53 (s, 3 H, SCH_3), 2.10–0.67 (remaining cholesteryl protons, 44 H); mass spectrum, *m/e* (relative intensity) 476 (<1, M$^+$), 369 (100), 354 (9), 260 (7).

Preparation of *O*-Benzhydryl *S*-Methyl Xanthate.[12c] Benzhydrol (9.2 g, 50 mmol) was converted into the xanthate ester by method B (with the exception that the temperature was maintained at 0 °C during the entire process). The crude xanthate ester was a red viscous liquid (lit.[12c] uncongealing yellow liquid): ^{1}H NMR ($CDCl_3$) δ 7.72 (s,1 H, CHO), 7.31 (m, 10 H, ArH), 2.47 (s, 3 H, SCH_3); IR (Nujol) 1940–1740 (w, overtones), 1630 (w), 1575 (w, C=C stretch), 1490 (m, CH bending), 1200 and 1050 cm^{-1} (s, C—O stretch).

Upon being allowed to stand, the xanthate ester rearranged to the dithiocarbonate isomer which was eluted from a silica gel column with 33% hexanes in methylene chloride to yield an orange solid. This solid was recrystallized twice from hexanes to yield yellowish white crystals of the dithiocarbonate in 60% yield from benzhydrol: mp 66.5–68.0 °C; ^{1}H NMR ($CDCl_3$) δ 7.32 (m, 10 H, Ar H), 6.09 (s, 1 H, CHO), 2.32 (s, 3 H, SCH_3); IR (Nujol) 1950–1740 (w, overtones), 1630 (s, C=O stretch), 1575 (m, C=C stretch), 1490 (s, CH bending), 1100–700 cm^{-1} (six major absorptions); mass spectrum, *m/e* (relative intensity) 273 (2, M$^+$), 199 (6), 167 (100).

Preparation of *O*-Bornyl *S*-Methyl Xanthate. Borneol (2.4 g, 15.8 mmol) was converted into the crude xanthate ester (4.0 g) by method A. The crude xanthate ester was eluted from a silica gel column with 14% ethyl acetate in hexanes and recrystallized from ethanol to yield colorless needles: 3.5 g (90%); mp 55.0–56.0 °C; ^{1}H NMR ($CDCl_3$) δ 5.66–5.43 (m, 1 H, CHO), 2.58 (s, 3 H, SCH_3), 2.18–1.05 (unresolved m, 16 H); mass spectrum, *m/e* (relative intensity) 244 (2, M$^+$), 137 (89), 81 (100). Anal. Calcd for $C_{12}H_{20}OS_2$: C, 58.97; H, 8.25. Found: C, 59.03; H, 8.32.

Preparation of *O*-2-Octyl *S*-Methyl Xanthate.[12a] 2-Octanol (2.61 g, 20 mmol) was converted into the crude xanthate ester (4.6 g) by method A. The crude xanthate ester was eluted from a silica gel column with 17% ethyl acetate in hexanes to yield a yellow liquid: 4.25 g (96%); bp 153 °C (640 mm) (lit.[12d] decomposes); ^{1}H NMR ($CDCl_3$) δ 5.72 (sextet, 1 H, CHO), 2.55 (s, 3 H, SCH_3), 1.90–1.56 (m, 2 H, CH_2), 1.46–1.10 (unresolved m, 11 H), 0.87 (t, 3 H, CH_3); mass spectrum, *m/e* (relative intensity) 220 (7, M$^+$), 159 (12), 113 (13), 112 (52), 108 (12), 71 (83), 58 (100), 43 (71).

Preparation of *O*-Phenylethyl *S*-Methyl Xanthate. β-Phenylethyl alcohol (2.1 g, 17 mmol) was converted into the crude xanthate ester by method A. The crude xanthate ester was eluted from a silica gel column with 50% methylene chloride in hexanes to yield a yellow liquid: 3.5 g (96%); bp 190–195 °C (640 mm); ^{1}H NMR ($CDCl_3$) δ 7.27 (m, 5 H, Ar H), 4.77 (t, 2 H, CH_2O), 3.07 (t, 2 H, $PhCH_2$), 2.50 (s, 3 H, SCH_3); mass spectrum, *m/e* (relative intensity) 212 (0.1, M$^+$), 105 (67), 104 (100).

Preparation of *O*-Pinacolyl *S*-Methyl Xanthate.[12e] Pinacolyl alcohol (1.9 g, 19 mmol) was converted into the crude xanthate ester (3.4 g, 93%) by method A. The crude xanthate ester was eluted from a silica gel column with 50% methylene chloride in hexanes to yield a yellow liquid: 3.0 g (82%); bp 160 °C (640 mm) [lit.[12e] bp 100 °C (12 mm)]; ^{1}H NMR ($CDCl_3$) δ 5.53 (q, 1 H, CHO), 2.52 (s, 3 H, SCH_3), 1.25 (d, 3 H, CH_3), 0.93 (s, 9 H, $C(CH_3)_3$); mass spectrum, *m/e* (relative intensity) 192 (9, M$^+$), 85 (70), 43 (100).

Treatment of Xanthate Esters with AIBN or Benzoyl Peroxide in CCl_4. Typical Procedure. The xanthate ester (1 equiv) and AIBN or benzoyl peroxide (0.2 equiv) were heated at reflux under nitrogen in spectrograde CCl_4 for 17 h. Additional AIBN or benzoyl peroxide (0.2 equiv) was added after 17 h, and the solution was heated at reflux for an additional 8 h. The ^{1}H NMR spectrum showed only starting materials.

Treatment of Xanthate Esters with AIBN or Benzoyl Peroxide and NCS or *N*-Chloro-*N*-cyclohexylbenzenesulfonamide[22] in Benzene. Typical Procedure. *O*-Benzyl *S*-methyl xanthate (1.0 equiv), NCS or *N*-chloro-*N*-cyclohexylbenzenesulfonamide (1.0 equiv), and AIBN or benzoyl peroxide (0.2 equiv) were heated at reflux in benzene under a nitrogen atmosphere. Additional AIBN or benzoyl peroxide was added periodically up to 24 h of refluxing. The solutions were heated at reflux for 24–48 h. The ^{1}H NMR spectrum of the products revealed that no reaction took place except for partial Schönberg rearrangement of *O*-benzyl *S*-methyl xanthate.

Irradiation of *O*-Alkyl *S*-Methyl Xanthates with 254-nm Light. Solutions of the xanthate esters (0.1–0.3 M) in CCl_4 or CCl_3Br were deoxygenated by bubbling nitrogen gas through the solution for 15 min. The solutions in quartz NMR tubes (which were sealed with rubber septums) were irradiated with 254-nm light in a Rayonet equipped with a merry-go-round apparatus. The reactions were monitored by ^{1}H NMR spectroscopy. Typical reaction times ranged from 10 to 70 h. The products were characterized by gas chromatography or ^{1}H NMR. (Larger scale reactions were irradiated at 254 nm in a quartz tube in a Rayonet, and the products were isolated by distillation or liquid chromatography and identified by ^{1}H NMR and mass spectrometry.)

Copper(I)–Copper(II) Bromide Conversion of *O*-Benzyl

(22) Theilacker, W.; Wessel, W. *Justus Liebigs Ann. Chem.* **1967**, *703*, 34.

S-Methyl Xanthate into Benzyl Bromide. Typical Procedure. O-Benzyl S-methyl xanthate (3.0 g, 15.2 mmol) and oven-dried copper(II) bromide (3.7 g, 16.6 mmol) were placed in acetonitrile (40 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature until the reaction was complete (5.7 h). The solvent was removed in vacuo. The remaining green slurry was diluted with diethyl ether, extracted with water, dried over magnesium sulfate, and concentrated in vacuo. The concentrate was distilled under vacuum to yield benzyl bromide (1.67 g, 63%) and dimethyl disulfide (0.5 g, 70%). The benzyl bromide was characterized by the following data: ^{1}H NMR ($CDCl_3$) δ 7.39 (m, 5 H, Ar H), 4.46 (s, 2 H, CH_2). When the product and benzyl bromide were coinjected onto column A, a single peak was formed on the GC trace. The dimethyl disulfide was characterized by the following data: ^{1}H NMR ($CDCl_3$) δ 2.46 (s, CH_3); mass spectrum, m/e (relative intensity) 94 (M^+), 47 (100).

Copper(I)–Copper(II) Bromide Conversion of Xanthate Ester 1 into 1-Br.[23] Typical Procedure. Xanthate ester 1 (652 mg, 2.0 mmol) and copper(II) bromide (588 mg, 2.6 mmol) were placed in acetonitrile (15 mL) under a nitrogen atmosphere. The mixture was stirred at room temperature for 52 h and at reflux (82 °C) for 63 h. The solvent was removed in vacuo to yield a residue which was mixed with diethyl ether, extracted with water, and dried over magnesium sulfate. The solvent was evaporated in vacuo to yield a crude solid which was eluted from a silica gel column with hexanes. Upon the removal of the hexanes in vacuo an off-white solid resulted (344 mg, 58%) which had the same ^{1}H NMR spectrum as 1-Br:[23] ^{1}H NMR ($CDCl_3$) δ 7.45–7.05 (m, 8 H, Ar H), 4.46 (d, $J_{1,7}$ = 3 Hz, H-1), 4.23 (t, $J_{4,8}$ = 3 Hz, H-4), 3.15–2.67 (septet, 2 H, H-9), 2.55–2.18 (m, 1 H, H-7), 2.05 (td, J_{gem} = 12 Hz, H-8$_{anti}$),1.17 (ddd, J_{gem} = 12 Hz, $J_{8,4} = J_{8,7}$ = 3 Hz, H-8 syn).

When the same reaction was run at reflux for 69 h, two side products were isolated (by TLC) in addition to the desired product 1-Br. Amide 4[24] was isolated in 30% yield: ^{1}H NMR ($CDCl_3$) δ 7.25 (m, 8 H, Ar H), 5.45 (br m, 1 H, H-4), 3.93 (t, 1 H, H-1), 3.60 (m, 1 H, H-5), 2.37–1.97 (m, 2 H, H-6), 1.90 (s, 3 H, CH_3), 1.47–1.06 (m, 2 H, H-7); mass spectrum, m/e 277 (M^+), 219, 178 (base). Thiocarbonate 1-OC(O)SCH_3 was isolated in 8% yield: ^{1}H NMR ($CDCl_3$) δ 7.36–7.06 (m, 8 H, Ar H), 4.27 (m, 2 H, H-1, H-4), 3.91 (dd, J_{gem} = 10 Hz, $J_{9,7}$ = 6 Hz, H-9′), 3.53 (dd, J_{gem} = 10 Hz, $J_{9,7}$ = 9 Hz, H-9), 2.30 (s, 3 H, SCH_3), 1.93 (td, $J_{7,1}$ = 3 Hz, $J_{7,8}$ = 10 Hz, H-7), 1.25–0.80 (m, 2 H, H-8); mass spectrum, m/e 310 (M^+), 219, 178 (base).

Copper(I)–Copper(II) Chloride Conversion of O-Benzyl S-Methyl Xanthate into Benzyl Chloride. O-Benzyl S-methyl xanthate (3.00 g, 15.2 mmol), copper(II) chloride (2.24 g, 16.7 mmol), and copper(I) chloride (0.15 g, 1.5 mmol) were placed in acetonitrile (40 mL) under a nitrogen atmosphere. The heterogeneous mixture was stirred at room temperature until no xanthate ester remained (96 h). This homogeneous reaction mixture was diluted with diethyl ether and extracted with saturated sodium chloride and water. The ethereal solution was dried over magnesium sulfate and evaporated in vacuo to yield an orange liquid (2.63 g). The orange liquid was eluted from a silica gel column with 50% methylene chloride in hexanes to yield benzyl chloride (1.157 g, 60%): ^{1}H NMR ($CDCl_3$) δ 7.41 (m, 5 H, Ar H), 4.56 (s, 2 H, CH_2Cl); mass spectrum, m/e 128 (M + 2), 126 (M^+), 91 (base). Dimethyl disulfide was formed quantitatively (710 mg): ^{1}H NMR ($CDCl_3$) δ 2.47 (s, CH_3S).

Treatment of O-Benzyl S-Methyl Xanthate with Molybdenum Pentachloride ($MoCl_5$). Molybdenum pentachloride (2.53 g, 9.2 mmol) was transferred under a blanket of nitrogen gas to a flask. O-Benzyl S-methyl xanthate (657 mg, 3.3 mmol) in dry benzene (80 mL) was added, and the mixture was stirred at room temperature until no xanthate ester remained (66 h). The mixture was filtered and extracted with water. The water was extracted with diethyl ether. The organic phases were combined, and the majority of the solvent was removed by vacuum distillation. The distilland was transferred to a micro vacuum distillation apparatus and distilled to yield diphenylmethane: ^{1}H NMR ($CDCl_3$) δ 7.26 (m, 10 H, Ar H), 3.96 (s, 2 H, CH_2); mass spectrum, m/e (relative intensity) 168 (82, M^+), 91 (100).

Treatment of Xanthate Ester 1 with $MoCl_5$ and NCS. $MoCl_5$ (553 mg, 2.0 mmol) was transferred under a blanket of nitrogen gas to a flask. NCS (670 mg, 5.0 mmol) and 1 (328 mg, 1.0 mmol) in dry benzene (50 mL) were added, and the resulting heterogeneous mixture was stirred at room temperature until no 1 remained (18 h). The crude reaction mixture was filtered and diluted with diethyl ether. The ethereal solution was extracted with water and saturated sodium chloride, dried over magnesium sulfate, and evaporated in vacuo to yield the crude product (638 mg). The crude product was purified on two silica gel TLC plates (20 cm × 20 cm × 2 mm) with 50% methylene chloride in hexanes as the eluant to yield 5:[24] 230 mg (90%); ^{1}H NMR ($CDCl_3$) δ 7.50–7.10 (m, 8 H, Ar H), 4.25 (s, 1 H, H-1), 4.20 (m, 1 H, H-4), 4.00 (dd, J = 2 Hz, J = 5 Hz, H-7), 2.10–1.10 (m, 4 H, H-8, H-9); mass spectrum, m/e (relative intensity) 256 (6, M + 2), 254 (38, M^+), 219 (9), 191 (64), 178 (100).

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Registry No. 1-OH, 6624-25-5; 1-OC(S)SCH_3, 79593-54-7; 1-Br, 42166-01-8; 1-OC(O)SCH_3, 79593-58-1; 2-OH, 1521-59-1; 2-OC(S)SCH_3, 79134-80-8; *endo*-3-Cl, 79646-01-8; *exo*-3-Cl, 2198-07-4; 4-$NHCOCH_3$, 79593-55-8; 5-Cl, 79593-56-9; O-benzyl S-methyl xanthate, 28925-45-3; benzyl alcohol, 100-51-6; O-cholesteryl S-methyl xanthate, 53496-46-1; cholesterol, 57-88-5; O-benzhydryl S-methyl xanthate, 28981-21-7; benzhydrol, 91-01-0; S-benzhydryl S-methyl dithiocarbonate, 79593-57-0; O-barnyl S-methyl xanthate, 79646-02-9; barneol, 507-70-0; O-2-octyl S-methyl xanthate, 35812-27-2; 2-octanol, 123-96-6; O-phenylethyl S-methyl xanthate, 70061-62-0; β-phenylethyl alcohol, 60-12-8; O-pinacolyl S-methyl xanthate, 72535-90-1; pinacolyl alcohol, 464-07-3; benzyl bromide, 100-39-0; benzyl chloride, 100-44-7; 2-chlorooctane, 628-61-5; pinacolyl chloride, 5750-00-5; phenethyl chloride, 622-24-2; barnyl chloride, 464-41-5.

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