2.7 kcal/mol). This quencher behaves somewhat differently than adamantylideneadamantane in that a reduced A factor accounts for at least 20-fold decrease in k_{ir}. A reduced A factor due to steric hindrance has also been observed in *cis*-1,2-di-*tert*-butylethylene.[2]

The allylic character of the tertiary C–H bonds presumably contributes little to their reactivity in TIE, since the molecular geometry would minimize any allylic resonance stabilization of the carbon-centered radical. On the other hand, formation of a planar tertiary radical would be accompanied by some reduction in unfavorable CH_3/CH_3 interactions. A good model for this reaction is not available, although the rate constants, A factor, and activation energy determined are not at odds with abstraction of a tertiary hydrogen. Our results are thus consistent with quenching via tertiary hydrogen abstraction or via exciplex formation. If more TIE were available, product studies and flash absorption studies would yield further information on the reaction intermediates.

Conclusion

We have studied the triplet state quenching of an aromatic ketone by tetraisopropylethylene. It is substantially less reactive than other tetrasubstituted alkenes. The rate and activation parameters can be explained either by an exciplex quenching mechanism or by tertiary hydrogen abstraction. Which ever mechanism dominates, it is clear that the steric hindrance of four isopropyl groups on a double bond causes a decrease in its reaction rate with the excited ketone to be at least 1000 times slower than tetramethylethylene and 100 times slower than adamantylideneadamantane.

Experimental Section

TIE was a gift from Professor Y. Okamoto of the Polytechnic Institute of New York. Sets of six solutions were prepared containing 1.5×10^{-3} M 4-(methoxycarbonyl)benzophenone in carefully purified CCl_4[4] and concentrations of TIE ranging from zero to 1×10^{-2} M. Aliquots (2 mL) in 13 mm o.d. Pyrex tubes were degassed on a vacuum line by five successive freeze–pump–thaw cycles and sealed under vacuum. Samples were excited with 10-ns pulses from a nitrogen laser. Emission was detected at right angles, as previously described,[4] with the transient signal digitized with a Biomation Model 8100 wave form recorder. Data were fit to a single exponential form and lifetimes were plotted according to eq 1 to obtain rate constants.

Acknowledgment. We thank NSERC Canada for its support of this work and Professor Y. Okamoto of the Polytechnic Institute of New York for a generous sample of TIE.

Registry No. 1, 6158-54-9; TIE, 7090-88-2; tetramethylethylene, 563-79-1; adamantylidene adamantane, 30541-56-1.

Deoxygenation of Sulfoxides with Boron Bromide Reagents

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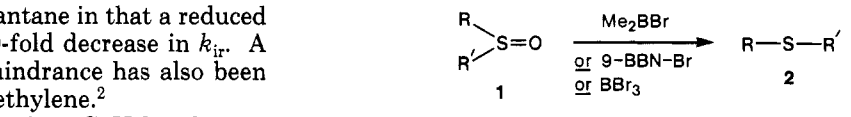
Received April 17, 1984

The growing importance of organosulfur compounds in organic synthesis has recently stimulated the development of numerous useful methods for the deoxygenation of sulfoxides to sulfides.[1] For example, hydrogen halides have been used for this purpose although their usefulness is somewhat restricted with acid-sensitive substrates.[2] Other methods have successfully utilized strong oxygenophiles such as trivalent phosphorus in order to activate the oxygen–sulfur bond.[3] However, in most cases the reaction requires the use of elevated reaction temperatures and/or prolonged reaction times. Reduction by hydrides ($LiAlH_4$–$TiCl_4$[4]; $NaBH_4$–$CoCl_2$[5]) has attracted some attention, but their strong reducing character represents a limitation. Acylating agents alone or in combination with reducing agents such as I^- have been used successfully, but the reactivity of these agents with a number of functionalities imposes certain limitations on their usefulness.[6]

Scheme I



Recently, trimethylsilyl halides (Me_3SiI, Me_3SiBr) have been reported to reduce dialkyl sulfoxides to sulfides rapidly at room temperature.[7] Deoxygenation of dibenzyl sulfoxides, however, resulted in a mixture of halogenated dibenzyl sulfides. This problem was very effectively solved by the use of (trichloromethyl)silane in the presence of sodium iodide at room temperature.[8]

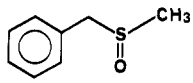
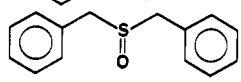
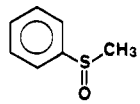
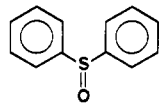
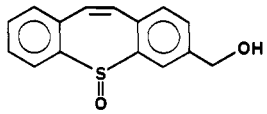
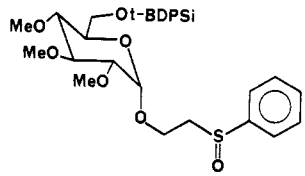
Among boron reagents, dichloroborane is the only discrete boron derivative which, to our knowledge, has been used successfully for the deoxygenation of sulfoxides.[9] Although dichloroborane reacts readily with dialkyl sulfoxides, the reduction of diaryl sulfoxides requires much longer reaction times, thus reducing somewhat the general usefulness of this reagent.

Recently we reported that dimethylboron bromide efficiently cleaves cyclic and acyclic acetals and ketals including MEM ((2-methoxyethoxy)methyl), MOM (methoxymethyl), and MTM (methylthiomethyl) ethers at −78 °C, as well as a variety of alkyl methyl, aryl methyl, cyclic, and THP ethers at room temperature.[10] Attracted by the powerful oxygenophilic character of this reagent, coupled with our interest in sulfur chemistry,[11] we decided to investigate its reactivity with sulfoxides. As a result we are gratified to report herein that dimethylboron bromide, 9-borabicyclo[3.3.1]nonyl bromide (9-BBN-Br) and boron

(1) For a review, see: Drabowicz, J.; Numata, T.; Oae, S. *Org. Prep. Proc. Int.* **1977**, *9*, 63.
(2) Landini, D.; Modena, G.; Montanari, F.; Scorrano, G. *J. Am. Chem. Soc.* **1970**, *92*, 7168 and references cited therein.
(3) (a) Denis, J. N.; Krief, A. *J. Chem. Soc., Chem. Commun.* **1980**, 544. (b) Suzuki, H.; Sato, N.; Osuka, A. *Chem. Lett.* **1980**, 143. (c) Wakisaka, M.; Hatanaka, M.; Nitta, H.; Hatamura, M.; Ishimaru, T. *Synthesis* **1980**, 67. (d) Still, I. W. J.; Reed, J. N.; Turnbull, K. *Tetrahedron Lett.* **1979**, 1481 and references cited therein.
(4) Drabowicz, J.; Mikolajczyk, M. *Synthesis* **1976**, 527.
(5) (a) Chung, S.; Han, G. *Synth. Commun.* **1982**, *12*, 903. See also: (b) Kano, S.; Tanaka, Y.; Sugino, E.; Hibino, S. *Synthesis* **1980**, 695. (c) Durst, H. D.; Zubrick, J. W.; Kieczykowski, G. R. *Tetrahedron Lett.* **1974**, 1777.
(6) (a) Numata, T.; Oae, S. *Chem. Ind. (London)* **1973**, 277. (b) Drabowicz, J.; Oae, S. *Synthesis* **1977**, 404. (c) Olah, G. A.; Malhotra, R.; Narang, S. C. *Synthesis* **1979**, 58.
(7) (a) Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *Synthesis* **1979**, 61. (b) Olah, G. A.; Gupta, B. G. B.; Narang, S. C. *Ibid.* **1977**, 583.
(8) Olah, G. A.; Husain, A.; Singh, B. P.; Mehrotra, A. K. *J. Org. Chem.* **1983**, *48*, 3667.
(9) Brown, H. C.; Ravindran, N. *Synthesis* **1973**, 42.
(10) (a) Guindon, Y.; Morton, H. E.; Yoakim, C. *Tetrahedron Lett.* **1983**, *24*, 3969. (b) Guindon, Y.; Yoakim, C.; Morton, H. E. *Ibid.* **1983**, *24*, 2969. (c) Guindon, Y.; Morton, H. E.; Yoakim, C. *J. Org. Chem.*, in press.
(11) (a) Guindon, Y.; Frenette, R.; Fortin, R.; Rokach, J. *J. Org. Chem.* **1983**, *48*, 1357. (b) Guindon, Y.; Young, R. N.; Frenette, R. *Synth. Commun.* **1981**, *11*, 391.

0022-3263/84/1949-4538$01.50/0

Table I. Deoxygenation of Sulfoxides 1 with Boron Bromide Reagents[a]

Entry	Substrate	Yield (%)[b] of Sulfide (2)[c] with: Me_2BBr[d]	9-BBN-Br[d]	BBr_3[e]
1	n-C_4H_9—S(=O)—C_4H_9-n	93	95	90
2	s-C_4H_9—S(=O)—C_4H_9-s	88	—	83
3		92	90	98
4		96	92	91
5		91	96	88
6		94[f]	96	83[g]
7		93[h]	—	39[i]
8		91	91	87

[a] Unless otherwise stated all reactions were carried out at −23 °C for 30 min and 0 °C for 10 min using concentrations of 0.2 M in the sulfoxide 1. [b] Isolated yields. [c] Known products were identified by comparison with authentic samples. New compounds gave spectral data in accord with their assigned structure as well as satisfactory combustion analysis. [d] 2.5 equiv of reagent was used. [e] 1.0 mol of reagent was used per mol of sulfoxide 1. [f] This product was isolated in 92% and 90% yield, respectively, when CH_3CN or acetone was used as the reaction solvent. [g] This reaction was carried out at −23 °C for 30 min and room temperature for 4 h. [h] This reaction was carried out at room temperature for 18 h using 3.5 equiv of reagent and cyclohexene (5 equiv) as the bromine scavenger. [i] This reaction was carried out at room temperature for 30 h using 1.5 equiv of BBr_3 in the presence of cyclohexene (5 equiv). A 27% yield of the corresponding bromide was also isolated.

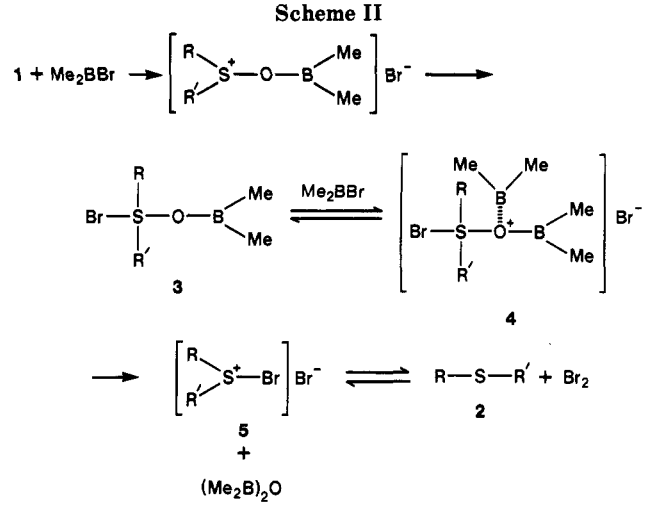
tribromide rapidly deoxygenate a wide range of sulfoxides under very mild conditions (see Scheme I).

Results and Discussion

Treatment of sulfoxides with 2.5 equiv of dimethylboron bromide in CH_2Cl_2 at −23 °C for $^1/_2$ h and at 0 °C for 10 min resulted in complete reduction of the sulfoxides to the corresponding sulfides in excellent yield (see Table I). Bromine is produced during the reaction and must be removed in order to avoid its possible secondary reactions with starting materials or products. This removal was easily effected by saturating the reaction mixtures with propene, prior to introduction of the reagent. The resulting 1,2-dibromopropane is easily removed during product isolation.

Significantly, under these conditions, the reaction is very rapid and equally applicable to dialkyl, aryl alkyl, and diaryl sulfoxides. In no cases were Pummerer-type products detected. The absence of halogenated byproducts in the reduction of aryl and benzyl sulfoxides underscores the utility of this method. It should be noted that either

Scheme II



acetone or acetonitrile can be substituted for CH_2Cl_2 as the reaction solvent.

Under identical experimental conditions, 9-borabicyclo[3.3.1]nonyl bromide works equally well, rapidly deoxygenating both dialkyl and diaryl sulfoxides. The reaction of boron tribromide with sulfoxides was also studied. In the case of dialkyl and aryl alkyl sulfoxides (entries 1–5 and 8) it represents a useful and interesting alternative to the previous reagents. However, longer reaction times and lower yields were noted with diaryl sulfoxides (entries 6 and 7).

A reasonable mechanism for these reactions can be envisaged as illustrated in Scheme II.

The proposed bromoalkoxysulfurane intermediate **3** is in agreement with the work of Martin[12] and Johnson[13] who have obtained good evidence that such species do exist in solution. Martin's[14] observation that the exchange of alkoxy ligands in dialkoxysulfuranes is acid catalyzed leads to the suggestion that a second molecule of dimethylboron bromide may coordinate with the oxygen of **3** leading successively to species such as **4** and **5**. The latter is known to be in equilibrium with the corresponding sulfide and elemental bromine,[15] and under our reaction conditions this equilibrium will be driven to the right by reaction of the bromine with propylene. It is also noteworthy that the deoxygenation reactions are much less efficient in the absence of a bromine scavenger, in accord with the reversible nature of the last step.[16]

We have experimentally demonstrated that 2 equiv of boron reagent are required as implicated in the proposed mechanism. Thus, treatment of a solution of di-*n*-butyl sulfoxide in CH_2Cl_2 containing propene with 1.1 equiv of Me_2BBr at −23 °C for $^1/_2$ h followed by room temperature for 1 h gave the corresponding sulfide in 47% yield, along with 45% of recovered starting material.

Previously[10] we have shown that hydroxyl groups, acetals, benzoates, ethyl esters (in contrast to the trimethylsilyl iodide and (trichloromethyl)silane), and isolated olefins are essentially inert to dimethylboron bromide. In the present study we have shown that sulfoxides could be reduced selectively in the presence of a glycosidic linkage, secondary methyl ethers, and primary *tert*-bu-

(12) Martin, J. C.; Balthazor, T. M. *J. Am. Chem. Soc.* **1977**, *99*, 152.
(13) Johnson, C. R.; Rigau, J. J. *J. Am. Chem. Soc.* **1969**, *91*, 5398.
(14) Arhart, R. J.; Martin, J. C. *J. Am. Chem. Soc.* **1972**, *94*, 4997.
(15) Wilson, G. E., Jr. *Tetrahedron* **1982**, *38*, 2597.
(16) Treatment of di-*n*-butyl sulfoxide with 2.5 equiv of dimethylboron bromide in the absence of a bromine scavenger (−23 °C, 30 min, then 0 °C, 10 min) gave only a 21% yield of the corresponding sulfide along with recovered starting material (52%).

tyldiphenylsilyl (*t*-BDPSi) ethers as exemplified in Table I (entry 8). Free hydroxyl groups likewise did not interfere with the overall transformation (entry 7).[17] Thus the chemoselectivity and predictable reactivity of dimethylboron bromide should make it a reagent of considerable value.

Finally, phosphine oxides and sulfones failed to react under the present reaction conditions.

In summary, dimethylboron bromide and 9-borabicyclo[3.3.1]nonyl bromide rapidly and smoothly deoxygenate dialkyl, aryl alkyl, and diaryl sulfoxides at low temperature under nonreducing and quasi-neutral conditions. As such and because of their well-established reactivity and chemoselectivity,[10] dimethylboron bromide, in particular, and 9-borabicyclo[3.3.1]nonyl bromide should be considered as reagents of choice for the reduction of sulfoxides. Boron tribromide, on the other hand, has certain limitations compared to the dialkylboron bromides in that it is significantly slower in the reduction of diaryl sulfoxides and it reacts with free alcohol groups. In many cases, however, it will serve as an excellent, inexpensive alternative for the reduction of sulfoxides to sulfides.

Experimental Section

General Methods. Crude products were purified by either bulb-to-bulb distillation using a Büchi GKR-50 distillation apparatus or by flash chromatography using 230–400-mesh silica gel (E. Merck). The purity of known compounds was ascertained by TLC using commercial silica gel plates (Analtech, Uniplate-Silica Gel GF) and by spectral means (IR, ^{1}H NMR).

Glassware and syringes were dried in an oven (120 °C) prior to use. Methylene chloride was distilled from CaH_2 and stored over 4-Å molecular sieves.

Dimethylboron bromide was purchased from the Alfa Division of the Ventron Corporation, or it was prepared as described previously.[10c] Care should be taken when manipulating neat dimethylboron bromide as it is *pyrophoric* when exposed to moist air. Solutions (1.0–1.5 M) of this reagent were prepared in dry CH_2Cl_2 and could be stored at −15 °C for several months without noticeable decomposition or handling problems. Solutions of 9-BBN-Br and BBr_3 in CH_2Cl_2 were purchased from the Aldrich Chemical Co.

a. Reduction of Sulfoxides by Me_2BBr. A typical example follows. A cold (−23 °C), stirred solution of diphenyl sulfoxide (2.0 mmol), in 7.1 mL of dry CH_2Cl_2, under argon, was saturated with propene for 5 min. A solution of dimethylboron bromide (1.72 M, 2.91 mL) in CH_2Cl_2 was then added dropwise. After $^1/_2$ h at −23 °C and 10 min at 0 °C the reaction mixture was quenched with 2 mL of saturated aqueous $NaHCO_3$ followed by 2 mL of 10% aqueous sodium thiosulfate. After 2 min, ether (50 mL) was added, the organic layer separated and washed with water (5 mL) and brine (5 mL), and dried over $MgSO_4$. Concentration and reconcentration from MeOH (5 mL) gave, after bulb-to-bulb distillation, pure diphenyl sulfide (94%).

b. Reduction of Sulfoxides by 9-BBN-Br. A typical example follows. A cold (−23 °C), stirred solution of di-*n*-butyl sulfoxide (2.0 mmol), in 5 mL of dry CH_2Cl_2, under argon, was saturated with propene for 5 min. A solution of 9-BBN-Br in CH_2Cl_2 (1.00 M, 5.0 mL) was then added dropwise and the reaction mixture was stirred at −23 °C for $^1/_2$ h and at 0 °C for 10 min. Quenching and workup as detailed above gave a pale yellow oil. Filtration through a short column of silica gel (10 g, elution solvent: hexane–ether, 98:2) gave after bulb-to-bulb distillation of the resultant oil, pure di-*n*-butyl sulfide (95%).

c. Reduction of Sulfoxides by BBr_3. A typical example follows. A cold (−23 °C), stirred solution of dibenzyl sulfoxide (2.0 mmol), in 8 mL of dry CH_2Cl_2, under argon, was saturated with propene for 5 min. A solution of boron tribromide in CH_2Cl_2 (1.00 M, 2.0 mL) was then added and the mixture was stirred at −23 °C for $^1/_2$ h and at 0 °C for 10 min. Quenching and workup as detailed above gave a pale yellow oil. Concentration and reconcentration from MeOH (5 mL) gave, after bulb-to-bulb distillation, pure dibenzyl sulfide (90%).

(17) For the preparation of this compound and the corresponding sulfide. See: Hamel, P. A.; Rokach, J. U.S. Patent 4 237 160.

Acknowledgment. A Natural Sciences and Engineering Research Council of Canada Industrial Research Fellowship (to H. E. Morton) is gratefully acknowledged. We thank Dr. J. Rokach for his support and collaboration and C. Yoakim for many helpful discussions.

Registry No. $Bu_2S{=}O$, 2168-93-6; *sec*-$Bu_2S{=}O$, 13153-06-5; $PhCH_2S(O)Me$, 824-86-2; $(PhCH_2)_2S{=}O$, 621-08-9; $PhS(O)Me$, 1193-82-4; $Ph_2S{=}O$, 945-51-7; Bu_2S, 544-40-1; *sec*-Bu_2S, 626-26-6; $PhCH_2SMe$, 766-92-7; $(PhCH_2)_2S$, 538-74-9; PhSMe, 100-68-5; Ph_2S, 139-66-2; Me_2BBr, 5158-50-9; BBr, 10294-33-4; $HO(CH_2)_2SPh$, 699-12-7; 9-BBN-Br, 22086-45-9; 3-(bromomethyl)dibenzo[*b*,*f*]thiepin, 92055-55-5; 3-(hydroxymethyl)dibenzo[*b*,*f*]thiepin, 77167-91-0; 3-(hydroxymethyl)benzo[*b*,*f*]thiepin 5-oxide, 77167-92-1; 2-(phenylsulfinyl)ethyl 6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (isomer 1), 92078-27-8; 2-(phenylsulfinyl)ethyl 6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-*O*-methyl-α-D-glucopyranoside (isomer 2), 92078-28-9; 2-(phenylthio)ethyl 6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-*O*-methyl-α-D-glucopyranoside, 92078-29-0; methyl 6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-*O*-methyl-β-D-glucopyranside, 91928-35-7; 1-bromo-1-deoxy-6-*O*-(*tert*-butyldiphenylsilyl)-2,3,4-tri-*O*-methyl-D-glucopyranose, 91928-34-6.

Supplementary Material Available: Preparative details and full characterization data (IR, ^{1}H NMR, MS, chemical analyses, and melting points when applicable) for all new compounds (3 pages). Ordering information is given on any current masthead page.

Chiral Synthons from Arabinose. Preparation of 1,3-Diols and β-Benzyloxy Ketones

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Received May 1, 1984

Arabinose is readily available in both enantiomeric forms.[1] Accordingly, the development of arabinose derivatives for use as starting materials in enantiospecific synthesis is of special interest. Chiral 1,3-diol and β-hydroxy ketone units are present in many natural products of biological importance.[2] We now report the preparation of several enantiomerically pure compounds of this type, which have potential as chiral building blocks.

Benzyl 2,3-anhydro-β-D-ribopyranoside[3] (**1**) and the L-enantiomer (**2**) are easily prepared from D- and L-arabinose, respectively (Scheme I). Regiospecific, reductive opening of the oxirane ring was performed with sodium bis(2-methoxyethoxy)aluminum hydride (Red Al, Aldrich) to give benzyl 3-deoxy-β-D- and -L-*xylo*-pyranoside[4] (**3** and **4**). Viti[5] recently found that the use of tetrahydrofuran as solvent in Red Al reduction of epoxy alcohols gave a high 1,3:1,2 diol ratio (normally) > 100:1). However, only acyclic compounds were studied, where complexation of the aluminum hydride reagent with the

(1) Of the pentoses, D- and L-arabinose, D-ribose, and D-xylose are moderately priced.
(2) Masamune, S.; Choy, W. *Aldrichimica Acta* **1982**, *15*, 47.
(3) Garegg, P. *Acta Chem. Scand.* **1960**, *14*, 957.
(4) Methyl 3-deoxy-β-L-xylopyranoside has been prepared: Mukherjee, S.; Todd, A. R. *J. Chem. Soc.* **1947**, 969. *Note added in proof.* Methyl 3,6-dideoxy-α-D-*xylo*- and -α-L-*lyxo*-hexopyranoside were recently reported: Baer, H. H.; Astles, D. J. *Carbohydr. Res.* **1984**, *126*, 343.
(5) Viti, S. M. *Tetrahedron Lett.* **1982**, *23*, 4541.

0022-3263/84/1949-4540$01.50/0