$H_5(CH_2)_2COOCH_3$, 103-25-3; p-$CH_3COC_6H_4(CH_2)_2COOCH_3$, 91671-15-7; $ICH_2COOC_2H_5$, 623-48-3; $CH_3CHICOOC_2H_5$, 31253-08-4; $BrCH_2COOC_2H_5$, 105-36-2; $BrCH_2CH{=}CHCOOCH_3$, 1117-71-1; $C_6H_5CHBrCOOC_2H_5$, 2882-19-1; n-C_3H_7CHO, 123-72-8; $C_2H_5CH(CH_3)COCH_3$, 565-61-7; p-$NCC_6H_4COCH_3$, 1443-80-7; p-$O_2NC_6H_4COCH_3$, 100-19-6; $C_6H_5COCH(CH_3)_2$, 611-70-1; $C_6H_5CH_2COC_6H_5$, 451-40-1; 2,4,6-$(CH_3)_3C_6H_2COCH_3$, 1667-01-2; $C_6H_5CH_2CH_2CHO$, 104-53-0; $(C_6H_5CH_2)_2CO$, 102-04-5; p-$(CH_3)_2NC_6H_4CHO$, 100-10-7; o-$CH_3OC_6H_4CHO$, 135-02-4; $C_6H_5CH{=}CHCHO$, 104-55-2; $C_6H_5CH{=}CHCOC_6H_5$, 94-41-7; p-$BrC_6H_4C(OH)(CH_3)CH_2CH{=}CH_2$, 81336-05-2; $C_6H_5C(OH)(CH_3)CH_2C_6H_5$, 5342-87-0; p-$ClC_6H_4CHOHCH_2C_6H_5$, 31233-66-6; p-$ClC_6H_4COOCH_2C_6H_4Cl$-p, 19048-85-2; p-$IC_6H_4C(OH)(CH_3)CH_2C(CH_3){=}CH_2$, 91671-28-2; p-$NCC_6H_4CHOHCH_2C(CH_3){=}CH_2$, 91671-31-7; $C_6H_5CHOHCH_2C(CH_3){=}CH_2$, 23092-23-1; $C_6H_5C(OH)[CH_2C(CH_3){=}CH_2]_2$, 81925-76-0; p-$ClC_6H_4CHOHCH_2C(CH_3){=}CH_2$, 41801-83-6; p-$ClC_6H_4C(OH)[CH_2C(CH_3){=}CH_2]_2$, 91671-32-8; β-$C_{10}H_7C(OH)(CH_3)CH_2CH{=}CH_2$, 81336-07-4; p-$CH_3OC_6H_4C(OH)(CH_3)CH_2CH{=}CH_2$, 60573-61-7; $C_6H_5CH{=}CHC(OH)(CH_3)CH_2CH{=}CH_2$, 21573-75-1; p-$ClC_6H_4CHOHCH_2CH{=}CH_2$, 14506-33-3; p-$ClC_6H_4CH_2OH$, 873-76-7; p-$BrC_6H_4C(OH)(CH_3)CH_2CH{=}CHC_6H_5$, 91671-33-9; ($R^*,R^*$)-$p$-$BrC_6H_4C(OH)(CH_3)CH(C_6H_5)CH{=}CH_2$, 91671-34-0; ($R^*,S^*$)-$p$-$BrC_6H_4C(OH)(CH_3)CH(C_6H_5)CH{=}CH_2$, 91671-47-5; p-$BrC_6H_4C(OH)(CH_3)CH_2C{\equiv}CH$, 85014-12-6; p-$BrC_6H_4C(OH)(CH_3)CH{=}C{=}CH_2$, 58705-82-1; $C_6H_5CH{=}CHC(OH)(CH_3)CH_2C{\equiv}CH$, 38516-80-2; $C_6H_5CH{=}CHC(OH)(CH_3)CH{=}C{=}CH_2$, 91671-35-1; p-$ClC_6H_4CHOHCH_2C{\equiv}CH$, 42249-99-0; p-$ClC_6H_4CHOHCH{=}C{=}CH_2$, 91671-36-2; $C_6H_5CH{=}CHC(OH)[CH_2C(CH_3){=}CH_2]_2$, 91671-16-8; $C_6H_5(CH_2)_2C(OH)[CH_2C(CH_3){=}CH_2]_2$, 91671-17-9; $CH_2{=}C(CH_3)CH_2C(OH)(CH_3)C_6H_4$-$p$-$(CH_2)_2COOCH_3$, 91671-18-0; n-$C_3H_7CHOHCH_2COOC_2H_5$, 2305-25-1; $C_6H_5CHOHCH_2COOC_2H_5$, 5764-85-2; (R^*,R^*)-$C_2H_5CH(CH_3)C(OH)(CH_3)CH_2COOC_2H_5$, 91671-19-1; ($R^*,S^*$)-$C_2H_5CH(CH_3)C(OH)(CH_3)CH_2COOC_2H_5$, 91671-20-4; p-$IC_6H_4C(OH)(CH_3)CH_2COOC_2H_5$, 91671-21-5; p-$NCC_6H_4C(OH)(CH_3)CH_2COOC_2H_5$, 91671-22-6; p-$O_2NC_6H_4C(OH)(CH_3)CH_2COOC_2H_5$, 91671-23-7; ($R^*,R^*$)-$C_6H_5CHOHCH(CH_3)COOC_2H_5$, 17226-82-3; ($R^*,S^*$)-$C_6H_5CHOHCH(CH_3)COOC_2H_5$, 17226-81-2; ($R^*,R^*$)-$C_6H_5C(OH)(CH_3)CH(CH_3)COOC_2H_5$, 17226-97-0; ($R^*,S^*$)-$C_6H_5C(OH)(CH_3)CH(CH_3)COOC_2H_5$, 17226-96-9; ($R^*,R^*$)-$C_6H_5C(OH)(CH(CH_3)_2)CH(CH_3)COOC_2H_5$, 91671-25-9; ($R^*,S^*$)-$C_6H_5C(OH)(CH(CH_3)_2)CH(CH_3)COOC_2H_5$, 91671-26-0; $C_6H_5C(OH)(CH_3)CH_2COOC_2H_5$, 2293-60-9; $C_6H_5CHOHC(COOCH_3){=}CHCH_3$, 91671-27-1; ($R^*,R^*$)-$C_6H_5CHOHCH(C_6H_5)COOC_2H_5$, 14367-01-2; ($R^*,S^*$)-$C_6H_5CHOHCH(C_6H_5)COOC_2H_5$, 14367-00-1; $C_6H_5C(OH)(CH_3)C_4H_9$-n, 4396-98-9; $C_6H_5CH_2C(OH)(C_6H_5)C_4H_9$-$n$, 84735-50-2; $(C_6H_5CH_2)_2C(OH)C_4H_9$-$n$, 84735-51-3; p-$IC_6H_4C(OH)(CH_3)C_4H_9$-n, 84735-52-4; 2,4,6-$(CH_3)_3C_6H_2C(OH)(CH_3)C_4H_9$-$n$, 84735-53-5; $C_6H_5CH_2CH_2CHOHC_4H_9$-n, 19969-03-0; $C_6H_5C(OH)(CH_3)C_4H_9$-sec, 33484-93-4; $C_6H_5C(OH)(CH_3)C_2H_5$, 1565-75-9; $C_6H_5C(OH)(CH_3)_2$, 617-94-7; $CH_3C(OH)(C_6H_5)_2$, 599-67-7; $C_6H_5C(OH)(CH_3)C(OH)(CH_3)C_6H_5$, 1636-34-6; $C_6H_5CHOHCH_3$, 98-85-1; p-$(CH_3)_2NC_6H_4CHOHC_4H_9$-$n$, 91671-38-4; o-$CH_3OC_6H_4CHOHC_4H_9$-n, 91671-39-5; p-$BrC_6H_4C(OH)(CH_3)C_4H_9$-$n$, 91671-40-8; p-$NCC_6H_4C(OH)(CH_3)C_4H_9$-$n$, 91671-41-9; p-$CH_3OC_6H_4C(OH)(CH_3)C_4H_9$-$n$, 19523-03-6; $C_6H_5CH{=}CHCHOHC_4H_9$-n, 20157-19-1; $C_6H_5CH{=}CHC(OH)(CH_3)C_4H_9$-$n$, 91671-45-3; $C_6H_5CH{=}CHC(OH)(C_6H_5)C_4H_9$-$n$, 53188-81-1; $C_6H_5CH(C_4H_9$-$n)CH_2COC_6H_5$, 1454-57-5; $(C_6H_5CH_2)_2C(OH)C_4H_9$-$t$, 75245-71-5; Ce, 7440-45-1; CeI_3, 7790-87-6; $CeCl_3$, 7790-86-5; $LaCl_3$, 10099-58-8; $NdCl_3$, 10024-93-8; $PrCl_3$, 10361-79-2; $SmCl_3$, 10361-82-7; $YbCl_3$, 10361-91-8; n-C_4H_9Li, 109-72-8; sec-C_4H_9Li, 598-30-1; C_2H_5Li, 811-49-4; CH_3Li, 917-54-4; C_6H_5Li, 591-51-5; t-C_4H_9Li, 594-19-4; n-C_4H_9Br, 109-65-9; t-C_4H_9Cl, 507-20-0; cyclooctanone, 502-49-8; cyclohexanone, 108-94-1; 2-acetylthiophene, 88-15-3; 4-acetoxy-3-methoxyacetophenone, 54771-60-7; piperonal, 120-57-0; 1-allylcyclooctanol, 57670-91-4; 1-benzylcyclohexanol, 1944-01-0; 4-methyl-2-(2-thienyl)-4-penten-2-ol, 91671-29-3; 2-(4-acetoxy-3-methoxyphenyl)-4-methyl-4-penten-2-ol, 91671-30-6; 1-[3,4-(methylenedioxy)phenyl]-3-butyn-2-ol, 91344-61-5; 1-[3,4-(methylenedioxy)phenyl]-2,3-butadien-1-ol, 91671-37-3; 2-furaldehyde, 98-01-1; cyclododecanone, 830-13-7; ethyl 2-(2-furyl)-2-hydroxypropionate, 25408-95-1; ethyl 2-(1-hydroxycyclododecyl)propionate, 72013-81-1; ethyl 4-acetoxy-α-hydroxy-3-methoxy-α-methylbenzeneacetate, 91671-24-8; 1-butylcyclohexanol, 5445-30-7; α-butylfurfuryl alcohol, 30478-77-4; 4-$tert$-butylcyclohexanone, 98-53-3; 1-n-butyl-4-$tert$-butylcyclohexanol, 53188-79-7; $trans$-1-benzoyl-2-phenylcyclopropane, 1145-92-2; $trans$-2-benzoyl-1-cyclohexyl-3-phenylaziridine, 2211-61-2; $trans$-2-benzoyl-3-phenyloxirane, 7570-86-7; 1-[3,4-(methylenedioxy)phenyl]-1-pentanol, 5422-01-5; 1-(2-phenylcyclopropyl)-1-phenyl-1-pentanol (isomer 1), 91671-42-0; 1-(2-phenylcyclopropyl)-1-phenyl-1-pentanol (isomer 2), 91740-20-4; 1-cyclohexyl-2-(1-hydroxy-1-phenylpentyl)-3-phenylaziridine (isomer 1), 91671-43-1; 1-cyclohexyl-2-(1-hydroxy-1-phenylpentyl)-3-phenylaziridine (isomer 2), 91740-21-5; 1,2-epoxy-1,3-diphenyl-3-heptanol (isomer 1), 91671-44-2; 1,2-epoxy-1,3-diphenyl-3-heptanol (isomer 2), 91740-22-6; cyclopentanone, 120-92-3; β-tetralone, 530-93-8; 2-cyclohexenone, 930-68-7; 1-butylcyclopentanol, 1462-97-1; 2-butyl-1,2,3,4-tetrahydro-2-naphthol, 91671-46-4; 1-butyl-2-cyclohexenol, 88116-46-5; 1-$tert$-butylcyclopentanol, 69745-48-8; 1-$tert$-butylcyclohexanol, 20344-52-9.

Dimethylboron Bromide and Diphenylboron Bromide: Cleavage of Acetals and Ketals

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Received February 21, 1984

The cleavage of various acetal and ketal derivatives by the use of dialkyl- and diarylboron halides is described. Acetals and ketals readily react with dimethylboron bromide or diphenylboron bromide at −78 °C to give the corresponding carbonyl compounds in excellent yield. Under similar reaction conditions MEM, MOM, and MTM ethers are smoothly converted to alcohols. Acetonides are also cleaved with dimethylboron bromide while THP and THF ethers and methyl glycosides react at room temperature. Mechanistic considerations of the cleavage reactions are presented. The chemoselective virtues of dimethylboron bromide are summarized.

Acetals and ketals are two of the most useful and versatile functionalities in organic chemistry. They find application, for instance, in the protection of carbonyl, hydroxyl, and diol functions.[1] As such they represent a major component of the available protecting groups which can be used in the elaboration of complex or polyfunctional organic structures.

The only unified approach for the cleavage of an acetal or ketal derivative involves treatment with acids or Lewis acids.[1] Unfortunately the use of strong acids is often required but these may sometimes be precluded by the

(1) Greene, T. W. "*Protective Groups in Organic Synthesis*"; Wiley-Interscience: New York, 1981.

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sensitivity or stability of a given substrate.

Recently in our laboratory, we have been studying[2,3] monofunctional organoborane reagents of the general formula R_2BBr in regards to their capacity to cleave carbon–oxygen bonds. The premises that justified our interest in this class of reagents were (a) the very potent oxygenophilic character of boron, (b) that monofunctional organoboranes should be more selective in reactivity than trihaloboranes and thus allow better control of reaction conditions, and (c) that the electronic and steric nature of R should influence the S_N1 vs. S_N2 reactivity of a given reagent and consequently the overall reaction profile.

Dimethylboron bromide, a representative of this class, was found to be a very efficient and powerful reagent for the cleavage of a variety of ethers[2] (alkyl and aryl alkyl ethers), permitting the regeneration of a parent alcohol from its methyl ether. This reagent also allows for a predictable regiocontrolled opening of substituted cyclic ethers,[2] based on a preponderant S_N2 mechanism. As well, dimethylboron bromide and diphenylboron bromide were found to cleave acetals and ketals[3] in excellent yield.

We report herein on the reactivity of dimethylboron bromide and diphenylboron bromide pertaining to the cleavage of cyclic and acyclic acetals and ketals, tetrahydropyranyl and tetrahydrofuranyl ethers, methyl glycosides, acetonides, MOM (methoxymethyl), MEM ((2-methoxyethoxy)methyl), and MTM ((methylthio)methyl) ethers, and related derivatives.

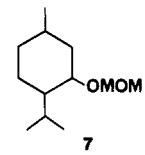
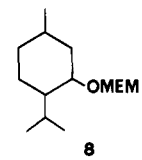
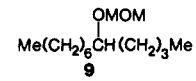
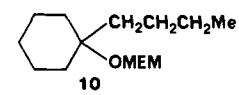
Chemoselectivity and reactivity as well as mechanistic considerations are presented.

Results and Discussion

I. Cleavage of an Acetal. Regeneration of an Alcohol. Acetal derivatives such as MOM,[4] MEM,[5] and MTM[6] ethers have been used widely as protecting groups for alcohols.[1] The cleavage of MOM ethers usually requires[7] strong acidic conditions (HCl, MeOH;[9] PhSH, BF_3-Et_2O[8]), which has somewhat restricted their utilization in organic syntheses. The MEM ethers can be cleaved by Lewis acid ($ZnBr_2$,[5,10] $TiCl_4$[5]), but in some instances, stronger conditions had to be used (*n*-BuLi;[11] TFA;[12] HF[13]). Finally, MTM ethers are usually removed by using Ag^+ or Hg^{2+} salts.[6] Recently trityl tetrafluoroborate[14] and Me_3SiCl–Ac_2O[15] have been reported to carry out the latter transformation.

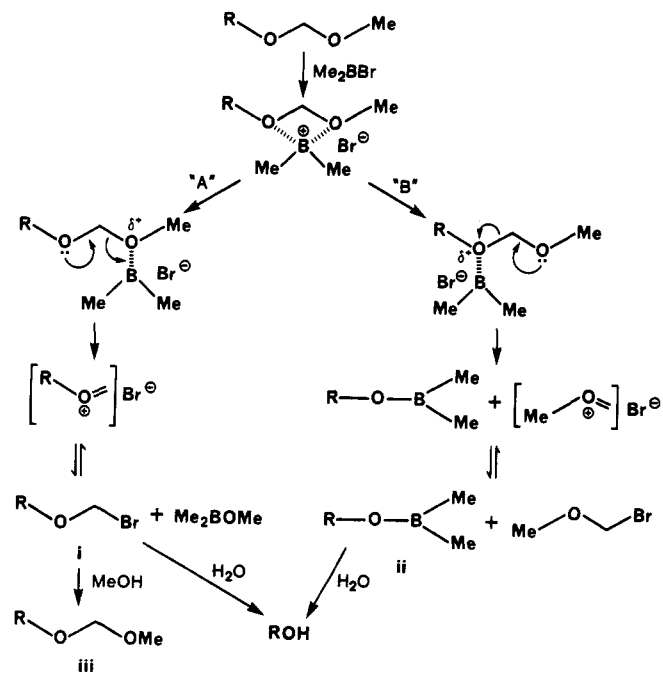
We have found that MOM, MEM,[16] and MTM ethers and similar derivatives are cleaved at −78 °C by Me_2BBr[3] (and Ph_2BBr) to give after workup the parent alcohols in excellent yield. The results are summarized in Table I. Primary MOM (entries 1 and 6), MEM (entry 2), MTM (entry 7), ethoxymethyl (entry 4), and (1-methylethoxy)-methyl ethers (entry 5) react at −78 °C within 1 h to give, after aqueous workup, the corresponding alcohol. Sec-

Table I. Regeneration of Alcohols from Their Acetal Derivatives

entry	substrate	reagent[a]	yield,[b] %
1	$Ph(CH_2)_2CH_2OMOM$ (1)	Me_2BBr_2	88
2	$Ph(CH_2)_2CH_2OMEM$ (2)	Me_2BBr	87
3	2	Ph_2BBr	87
4	$Ph(CH_2)_2CH_2OCH_2OEt$ (3)	Me_2BBr	92
5	$Ph(CH_2)_2CH_2OCH_2OCH(Me)_2$ (4)	Me_2BBr	84
6	$Me(CH_2)_{10}CH_2OMOM$ (5)	Me_2BBr	94
7	$Me(CH_2)_{10}CH_2OMTM$ (6)	Me_2BBr[c]	95
8	 7	Me_2BBr	94
9	 8	Me_2BBr	95
10	 9	Me_2BBr	93
11	 10	Me_2BBr[d]	94

[a] All reactions were carried out at a concentration of 0.1 M using 3 equiv of reagent at −78 C for 1 h. [b] Isolated yields of alcohols. All products were identified by comparison with authentic samples. [c] 4 equiv of reagent were used. After 1 h at −78 °C the reaction mixture was warmed to 0 °C for 1 h. [d] 0.1 equiv of Et_3N was added as an acid scavenger.

Scheme I



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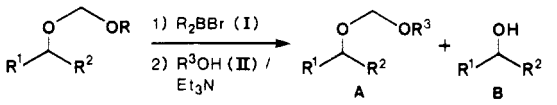
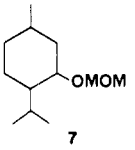
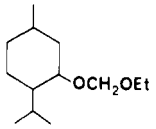
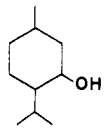
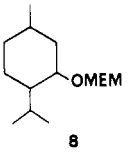
(16) Concurrent with our work, it was shown that 2-chloro-1,3,-dithioborolane could be used to cleave MEM ethers. Williams, D. R.; Sakdarat, S. *Tetrahedron Lett.* **1983**, *24*, 3965.

Table II



entry	substrate	reagents I[a]	reagents II[b]	products (% yield)[c] A	products (% yield)[c] B
1	$Ph(CH_2)_2CH_2OMOM$ (1)	Me_2BBr	MeOH	1[d] (81)	$Ph(CH_2)_2CH_2OH$ (3)
2	1	Me_2BBr	EtOH	3 (73)	$Ph(CH_2)_2CH_2OH$ (5)
3	$Ph(CH_2)_2CH_2OMEM$ (2)	Me_2BBr	MeOH	1 (65)	$Ph(CH_2)_2CH_2OH$ (23)
4	$Ph(CH_2)_2CH_2OCH_2OEt$ (3)	Me_2BBr	MeOH	1 (68)	$Ph(CH_2)_2CH_2OH$ (24)
5	3	Ph_2BBr	MeOH	1 (53)	$Ph(CH_2)_2CH_2OH$ (21)
6	3	9-BBNBr	MeOH	1 (30)	$Ph(CH_2)_2CH_2OH$ (4)
7	$Ph(CH_2)_2CH_2OCH_2OCH(Me)_2$ (4)	Me_2BBr	MeOH	1 (8)	$Ph(CH_2)_2CH_2OH$ (78)
8	$Me(CH_2)_{10}CH_2OMOM$ (5)	Me_2BBr	MeOH	5[d] (93)	$Me(CH_2)_{10}CH_2OH$ (5)
9	 7	Me_2BBr	EtOH	 11 (95)	 (3)
10	 8	Me_2BBr	MeOH	7 (94)	
11	$Me(CH_2)_{10}CH_2OMTM$ (6)	Me_2BBr	MeOH	5 (13)	$Me(CH_2)_{10}CH_2OH$ (81)

[a] All reactions were carried out at a concentration of 0.1 M using 3 equiv of reagent at −78 °C for 1 h. [b] After 1 h at −78 °C the reaction mixtures were quenched with Et_3N (4.0 equiv) followed by an excess of the alcohol and allowed to warm to room temperature. [c] Isolated yields. [d] A miniworkup on an aliquot indicated that the reaction was completed before quenching.

ondary and tertiary MEM and MOM ethers (entries 8–11) react similarly under identical reaction conditions with dimethylboron bromide in excellent yield. Entry 3 of Table I illustrates that diphenylboron bromide is equally effective. The clean generation of a tertiary alcohol (entry 11) without formation of the bromide or elimination to the olefin provides a striking demonstration of the mildness of these reagents.

It was of interest to us to investigate the overall mechanism of this reaction, as illustrated in Scheme I, since two competing reaction pathways (A and B) can be envisioned. Route A, if preponderant, would give rise to the bromomethyl ether derivative i. If route B were favored the boronate ether, derivative ii, would be formed. Both i and ii upon hydrolysis (workup) would then afford the same parent alcohol. However, treatment of the intermediate bromomethyl ether i with a potential nucleophile other than H_2O, for example, MeOH, would give rise to the substituted methyl ether derivative iii, whereas ii would once more yield the parent alcohol. Thus a series of quenching reactions were conducted to determine which reaction pathway, A or B, is favored. The results are summarized in Table II and provide good evidence that both pathways are operative, with predictable preferences, depending upon the structural details of the substrate.

Based on the data in Table II, it appears that the preferred coordination site of the dimethylboron bromide in the MEM and MOM ether series and derivatives thereof is the oxygen of the acetal which suffers from the least steric hindrance. For instance, primary MOM ethers (entries 1, 2, and 8, Table II) react predominantly through path A in a ratio of 25:1 to give after quenching with alcohol in the presence of triethylamine the corresponding acetal derivatives. Therefore it appears that one level of substitution higher on the carbon bearing one of the oxygens of the acetal is enough to direct the complexation of the boron to the least hindered oxygen of the acetal. The secondary MEM and MOM ethers (entries 9 and 10) follow the same trend, favoring even more so the A pathway (ratio 30:1). In the primary ethoxymethyl ether case (entry 4), route A was still favored but to a much smaller degree (ratio 3:1). This lack of direction in the activation by the boron of one of the oxygens of the acetal can be explained by the identity of the substitution level at the carbons α to the oxygens of the acetal. The observed ratio is a reflection of the small difference in the substitution of the carbons β to the acetal (methyl vs. methylene). This ratio was not modified significantly by the use of diphenylboron bromide or 9-BBN-Br (entries 5 and 6). The presence of a methoxy function β to the acetal in the primary MEM case did not change the observed products ratio (entry 3 vs. entry 4).

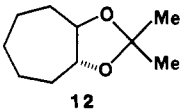
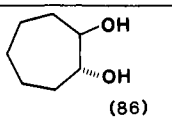
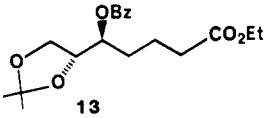
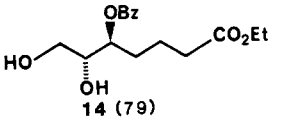
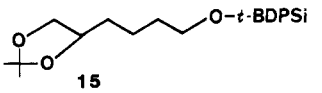
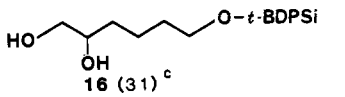
Based on our functional understanding of the mechanism of this reaction, one would expect that pathway B be favored in the primary ether case by going from the methoxymethyl (entry 1) or the ethoxy methyl ether derivatives (entry 4) to a 1-methylethoxy ether derivative (entry 7). Our experimental results agree with this prediction, giving A:B ratios of 27:1, 3:1, and 1:10, respectively.

In the MTM ether case (entry 11) a marked preference to the coordination of the boron to the oxygen rather than to the sulfur is the controlling factor.

In summary, one can predict the site of reactivity of dimethylboron bromide based on an analysis of the substitution levels on the carbons and to the oxygens of the acetal moiety. This should provide an efficient methodology for a predictable interconversion between functional groups (e.g., MEM to MOM, MOM to MTM, etc...).

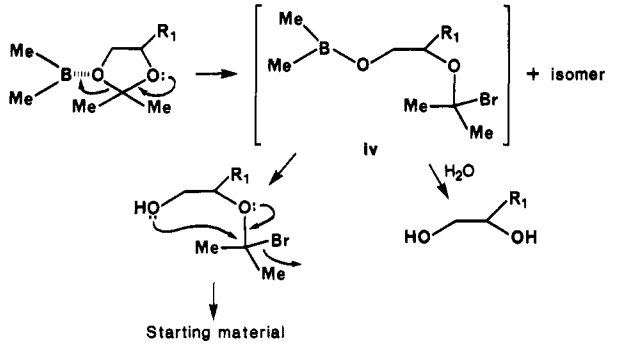
II. Cleavage of Acetonides. Regeneration of Diols. Ketals such as acetonides are used extensively as protecting

Table III. Cleavage of Acetonides Using Me_2BBr[a]

entry	substrate	equiv	temp, °C (time, h)	product (% yield)[b]
1	 **12**	4	-78 (4)	 (86)
2	 **13**	6	-78 (1)	 **14** (79)
3	 **15**	3	-78 (1)	 **16** (31)[c]
4	15	3	-78 (1)	**16** (86)[d]

[a] All reactions were carried out at concentrations of 0.20–0.25 M. [b] Isolated yields. Products were identified by comparison with authentic samples. [c] 64% yield of starting material was isolated. [d] Using Et_3N and n-Bu_4NOH in the workup.

Scheme II



groups for diols. We have found that treatment of acetonides with dimethylboron bromide[2] led to the formation of the corresponding diols in high yield. The results are summarized in Table III.

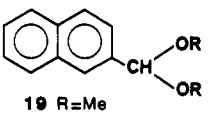
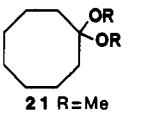
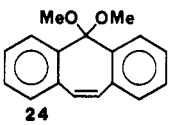
Our understanding of the mechanism of this reaction is illustrated in Scheme II.

Coordination of dimethylboron bromide to the least hindered oxygen of the acetonide moiety followed by subsequent ring opening would give rise to the reaction intermediate iv[17] (Scheme II). During workup, this intermediate (or the corresponding oxonium ion) could yield either the diol or the parent acetonide through an intermolecular or intramolecular reaction. Steric compression of the parent acetonide would favor the intermolecular displacement. In certain cases the lack of steric compression could significantly decrease the yield of the resulting diol as illustrated in entry 3, Table III, in which a substantial amount of starting material was recovered.

One way to improve the efficiency of the cleavage reaction, if one considers that this low yield was due to the recyclization of the opened acetonide in the workup, would be to increase the concentration of the hydroxide ion during workup. This was achieved successfully by treating the cold (-78 °C) reaction mixture with Et_3N followed by n-Bu_4NOH and warming to room temperature. Under these reaction conditions the diol **16** is obtained in 86% yield (entry 4, Table III). It should be noted that *tert*-butyldiphenylsilyl ethers (entry 3), benzoates, and ethyl esters (entry 2) are unaffected under the reported reaction conditions.

III. Cleavage of Acetals and Ketals. Regeneration of the Carbonyl Functionality. Acetals and ketals are traditionally cleaved by using acid-catalyzed exchange ketalization (e.g., H_2SO_4–acetone;[18] *p*-TsOH–acetone;[19] pyr–*p*-TsOH–acetone[20]), acid-catalyzed hydrolysis (e.g., 2 N HCl–THF;[21] $LiBF_4$, H_2O–CH_3CN;[22] SiO_2–H_2O[23]) or

Table IV. Cleavage of Ketals and Acetals Using Me_2BBr[a]

entry	substrate	yield,[b] %
1	$CH_3(CH_2)_7CH(OR)_2$ (**17**, R = Me)	91
2	**18**, R = $-(CH_2)_2-$	35[c]
3	 **19** R=Me	95
4	**20**, R = $-(CH_2)_2-$	95
5	 **21** R=Me	93
6	**22**, R = $-(CH_2)_2-$	92
7	**23**, R = $-CH_2C(CH_3)_2CH_2-$	91[d]
8	 **24**	93
9	 **25** R=Me	98
10	**26**, R = $-(CH_2)_2-$	87[e]

[a] All reactions were carried out at a concentration of 0.1 M using 2 equiv of reagent at -78 °C for 1 h. [b] Isolated yields of aldehydes or ketones. All products were identified by comparison with authentic samples. [c] 65% yield of starting ketal was isolated. [d] 3 equiv of reagent were used at -78 °C for 1 h. [e] 3 equiv of reagent were used. After 1 h at 0 °C and 3 h at room temperature, the reaction mixture was quenched at 0 °C with a solution of n-Bu_4NOH (4 equiv) in CH_2Cl_2.

(17) Bonner, T. G.; Saville, N. M. *J. Chem. Soc.* **1960**, 2851.

(18) Huet, F.; Lechevallier, A.; Conia, J. M. *Tetrahedron Lett.* **1977**, 2521.

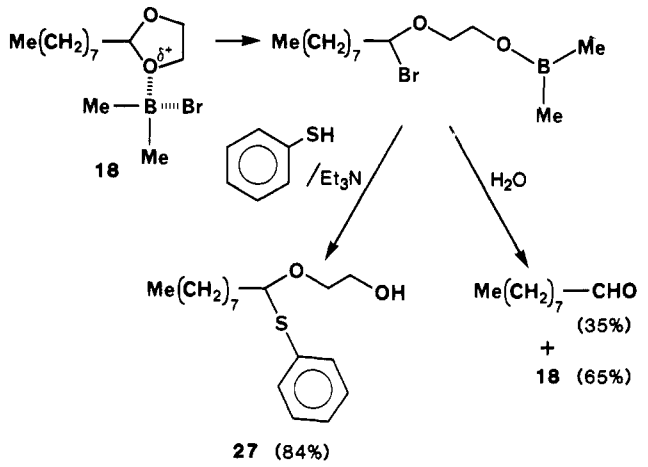
(19) Colvin, E. W.; Raphael, R. A.; Roberts, J. S. *J. Chem. Soc., Chem. Commun.* **1971**, 858.

(20) Sterzcki, R. *Synthesis* **1979**, 724.

(21) Tochtermann, W.; Schnabel, G.; Mannschreck, A. *Liebigs. Ann. Chem.* **1967**, *705*, 169.

(22) Lipshutz, B.; Harvey, D. F. *Synth. Commun.* **1982**, *12*, 267.

Scheme III



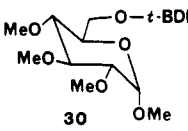
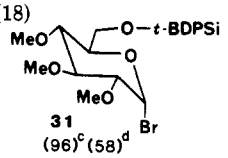
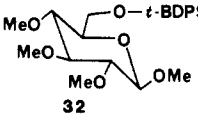
oxidative cleavage ($Ph_3C^+BF_4^-$, CH_2Cl_2).[24] Trimethylsilyl iodide (Me_3SiI)[25] and, more recently, trichloromethylsilane[26] have been shown to transform acyclic ketals to ketones in good yield. In the first case, however, it was noted that the treatment of cyclic ketals with TMSI (e.g., ethylene ketal) led to a complex mixture; no results involving cyclic acetals and ketals have been reported for the latter reagent. Recently titanium tetrachloride (with LiI)[27] in diethyl ether has been reported to cleave acetals and ketals in good yield at room temperature.

We have studied the reactivity of acetals and ketals with dimethylboron bromide with the results summarized in Table IV. We have found that acyclic (entries 1 and 3) or cyclic (entry 4) acetals and acyclic (entries 5 and 8) or cyclic (entries 6 and 7) ketals react with dimethylboron bromide at −78 °C to give after workup the corresponding aldehydes and ketones in excellent yield.

Although the results in Table IV are straightforward, it should be noted that in contrast to its dimethyl ketal analogue **25** and the bicyclic ketal **22**, the ethylene ketal **26** required more vigorous conditions for an efficient regeneration of the parent ketone[29] (entry 10 vs. 6 and 9). This is a reflection of the thermodynamic stability of the [4,5] spiro system which favors the intramolecular displacement of the corresponding bromo ketal in the workup. Once again, addition of n-Bu_4NOH in the workup, as shown previously, favored the formation of the corresponding ketone (entry 10).

The dimethylboron bromide mediated cleavage reaction was much less efficient in the case of ethylene acetal derivatives of straight-chain aldehydes. Under the usual reaction conditions a low yield of the aldehyde resulted, along with recovered starting material (entry 2, Table IV). In this case the addition of n-Bu_4NOH did not increase the overall efficiency of the reaction. The low yield of aldehyde may be explained by a competitive intramolecular displacement of the corresponding bromo acetal intermediate during workup and not by an incapacity of dimethylboron bromide to cleave the carbon–oxygen bond. This was demonstrated by quenching the reaction mixture with thiophenol in the presence of Et_3N. Doing so the mixed acetal **25** was obtained in 84% yield from **18** (Scheme III). The efficient formation of **27** not only supports the intermediacy of a bromo acetal moiety but it underscores the viability of this approach for the preparation of mixed acetals.

Table V. Cleavage of THP, THF, and Methyl Glycosides Using Me_2BBr

entry	substrate	Me_2BBr,[a] equiv	temp[e] (h)	products (% yield)[b]
1	$THPOCH_2$-$(CH_2)_{10}Me$ (**28**)	4.5	RT (8)	$Me(CH_2)_{10}$-CH_2OH (63)
2	$THFOCH_2$-$(CH_2)_{10}Me$ (**29**)	4.5	RT (8)	$Me(CH_2)_{10}$-CH_2OH (86)
3	 **30**	1.8	RT (18)	 **31** (96)[c] (58)[d]
4	 **32**	1.8	RT (18)	**31** (93)[c] (71)[d]

[a] All reactions were carried out at concentrations of 0.20–0.25 M. [b] Isolated yields. All products were identified by comparison with authentic samples. [c] NMR (90 MHz) analysis showed the crude product to be essentially pure material (>95%). [d] Isolated yields after flash chromatography. [e] RT = room temperature.

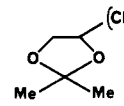
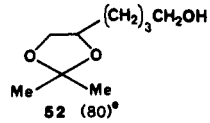
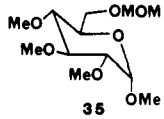
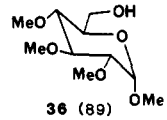
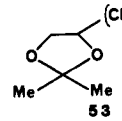
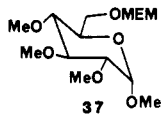
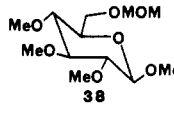
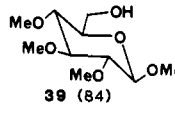
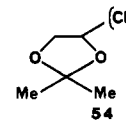
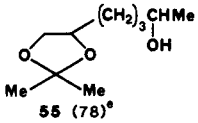
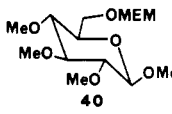
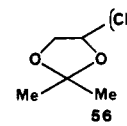
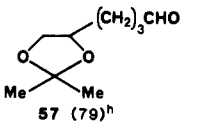
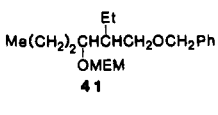
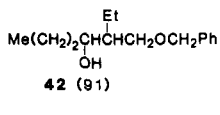
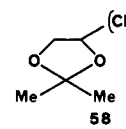
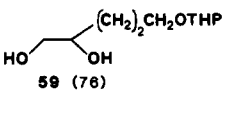
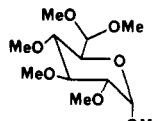
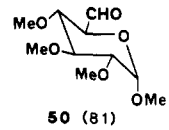
IV. Cleavage of Tetrahydropyranyl Ethers, Tetrahydrofuranyl Ethers, and Methyl Glycosides. Tetrahydropyranyl and tetrahydrofuranyl ethers are cleaved by dimethylboron bromide to give the corresponding alcohols in good yield (see Table V). In these cases, it was found that more demanding reaction conditions were required (entries 1 and 2) since a reasonable cleavage was only achieved at room temperature. Although the reasons for this difference in reactivity are not yet fully understood, one can presume that the steric encumbrance generated by the cyclic moiety prevents an efficient complexation with the reagents, increasing the required activation energy of the reaction. Electronic considerations could also be an important factor.[30]

The conversion of a methyl glycoside into a glycosyl bromide could be achieved by this reagent in good yield (entries 3 and 4). Since halogeno sugars are of prime importance in carbohydrate chemistry leading to different O, C, or S glycosides, the present methodology may be an attractive alternative for their preparation. Two points that could have some importance in the course of a synthetic effort should be mentioned. First of all, no difference of reactivity was noted between the α and β anomers (e.g., **30** and **32**, Table V). Secondly, the cleavage of a methyl glycoside could compete with the cleavage of a primary methyl ether. This was exemplified by the treatment of permethylated α-methyl glucoside with dimethylboron bromide which led to the formation of a number of products.

V. Selectivity. Tables III–V exhibit several examples of excellent chemoselectivity in that dimethylboron bromide did not react with acetates, benzoates, ethyl esters,

(23) Huet, F.; Lechevallier, A.; Pellet, M.; Conia, J. M. *Synthesis* **1978**, 63.
(24) Barton, D. H.R.; Magnus, P. D.; Smith, G.; Zurr, D. *J. Chem. Soc., Chem. Commun.* **1971**, 861.
(25) Jung, M. E.; Andrus, W. A.; Ornstein, P. L. *Tetrahedron Lett.* **1977**, 4175.
(26) Olah, G. A.; Husaien, A.; Singh, B. P.; Mahrotra, A. K. *J. Org. Chem.* **1983**, *48*, 3667.
(27) Balme, G.; Gore, J. *J. Org. Chem.* **1983**, *48*, 3336.
(28) We thank Professor A. I. Meyers for generously supplying a sample of the ketone precursor for the ketals **26** and **27**.
(29) The 2,3-butanediol analogue of ketal **26** was not cleaved satisfactorily by Me_2BBr. Presumably the intramolecular displacement of the halogeno ketal was the preponderant reaction pathway during workup.
(30) An evaluation of this electronic consideration using rigid models is underway in our laboratory.

Table VI. Study of Chemoselectivity Using Me_2BBr[a]

entry	substrate	time, h	product (% yield)[c]	entry	substrate	time, h	product (% yield)[b]
1	$MeOCH_2(CH_2)_6CH_2OMEM$ (33)	1	$MeOCH_2(CH_2)_6CH_2OH$ 34 (91)	12	 51	1	 52 (80)[e]
2	 35	3	 36 (89)	13	 53	1	52 (79)[e]
3	 37	3	36 (88)				
				14	51		52 (41)[f]
4	 38	3	 39 (84)	15	53	1	52 (54)[g]
				16	 54	1	 55 (78)[e]
5	 40	3	39 (86)	17	 56	0.5	 57 (79)[h]
6	 41	1	 42 (91)	18	 58	1	 59 (76)
7	$THPOCH_2(CH_2)_6CH_2OMOM$ (43)	1	$THPOCH_2(CH_2)_6CH_2OH$ 44 (93)				
8	$THPOCH_2(CH_2)_6CH_2OMEM$ (45)	1	44 (94)				
9	*i*-$BDMSiOCH_2(CH_2)_6CH_2OMEM$ (46)	1	*t*-$BDMSiOCH_2(CH_2)_6CH_2OH$ 47 (80)[c]	19	$MOMOCH_2(CH_2)_6CH(OMe)_2$ (60)	1	$MOMOCH_2(CH_2)_6CHO$ 61 (82)[h]
10	*t*-$BDMSiOCH_2(CH_2)_6CH_2OMOM$ (48)	1	47 (81)[d]	20	60	1	61 (36) + $HOCH_2(CH_2)_6CHO$ 62 (41)
11	 49	3	 50 (81)				

[a] All reactions were carried out at concentrations of 0.10–0.25 M using 3 equiv of reagent at −78 °C. [b] Isolated yields. All known products were identified by comparison with authentic samples. New products exhibited spectral properties consistent with the assigned structures and gave satisfactory combustion analysis (±0.4%). [c] 10% of diol was isolated. [d] 8% of diol was isolated. [e] The reaction was carried out in the presence of 3.3 equiv of ether. [f] 44% of triol was isolated. [g] 45% of triol was isolated. [h] The reaction was carried out in ether.

tert-butyldiphenylsilyl ethers,[31] or alkenes.[32]

After having demonstrated the reactivity of this class of reagents toward acetals and ketals, we sought to investigate more fully the relative chemoselectivity of one of these, dimethylboron bromide. The results obtained on a number of polyfunctional substrates are summarized in Table VI.

MOM and MEM ethers could be cleaved selectively at −78 °C, in good yield, in the presence of primary or secondary methyl ethers (entries 1–5). Contrary to the results obtained by Williams et al.,[16] we were able to cleave a MEM ether (entry 6) in the presence of a β-benzyl ether. In this latter case, no diol or 1,3-benzyl migration products were detected.

Selective cleavage of MEM and MOM ethers could also be achieved in the presence of an α- or β-methyl glycoside (entries 2–5) as well as tetrahydroyranyl ethers (entries 7

(31) Unlike their *tert*-butyldiphenylsilyl analogues, *tert*-butyldimethylsilyl ethers readily reacted with Me_2BBr at room temperature to afford the parent alcohols in good yield.

(32) No products were noted at room temperature between dimethylboron bromide and cyclooctene nor 1-dodecene. One should note that α,β-unsaturated ketones react under these conditions to give β-bromo ketones.

and 8). Also, primary *tert*-butyldimethylsilyl ethers (entries 9 and 10) are stable to the above reactions conditions.

The same level of chemoselectivity can be achieved with acetals in order to regenerate a carbonyl functionality. For instance, a dimethyl acetal (entry 11) can be converted in good yield to the parent aldehyde in the presence of methyl ethers and a glycosidic linkage.

The selective cleavage of MEM, MOM, and dimethyl acetal in the presence of an acetonide was also achieved in good yield (entries 12, 13, 16, and 17). In these cases, however, the usual reaction conditions led to lower yields of the resulting acetonides (entries 14 and 15) due to a competing cleavage between acetonides and MEM and MOM ethers. This problem was easily circumvented by the addition of diethyl ether to the reaction mixture (Et_2O/Me_2BBr = 1.1/1). For example, treatment of the MOM acetonide **51** with dimethylboron bromide at −78 °C afforded the alcohol **52** and the corresponding triol in 40% and 41% yields, respectively. In contrast, addition of 1.1 equiv of diethyl ether gave an 80% yield of the alcohol **52**. Presumably, ether behaves as a new coordinating species which effectively competes with the other functionalities involved, slowing the overall reaction and amplifying the difference of reactivity at −78 °C between acetonides and the more reactive acetals.

The same improvement in selectivity, due to the addition of ether, was noted in the cleavage of primary MEM (entry 13), secondary MOM (entry 16), and acyclic acetals (entry 17) in the presence of an acetonide.

Of interest is the selectivity achieved during the cleavage of a dimethyl acetal in the presence of a MOM ether (entry 19). In this case no selectivity was observed under the usual reaction conditions (entry 20) and both groups were cleaved. However, the use of diethyl ether as the reaction solvent (entry 19) resulted in a dramatic improvement in the selectivity, yielding aldehyde **61** as the sole reaction product.

An acetonide can also be cleaved in the presence of a THP ether as illustrated in entry 18.

In summary, oxygen functionalities can be ranked in order of decreasing reactivity with dimethylboron bromide as follows: dimethyl acetal > MOM ≃ MEM ≃ dimethyl ketal ≃ 1,3-dioxolane ≃ 1,3 dioxanes ≃ acetonides ≫ tetrahydropyranyl and tetrahydrofuranyl ethers, *tert*-butyldimethylsilyl ether, ROMe, ROBn > ArOMe ≫ alkenes, acetates, benzoates, ethyl esters, *tert*-butyldiphenylsilyl ethers, and hydroxyls.

Conclusion

Dimethylboron bromide and diphenylboron bromide, because of the very mild reactions conditions involved, their efficiency, and predictable behavior, should be considered as reagents of choice to cleave acetals or ketals.

Dimethylboron bromide represents to date the first reagent in the boron halides class that has the following established characteristics: it reacts through an S_N2 process[2] (contrary to BBr_3); it is, in our opinion, the best reagent to regenerate a parent alcohol from a methyl ether;[2] it also permits the regioselective ring opening of cyclic ethers;[2] it can be used to efficiently regenerate, as illustrated herein, a parent alcohol from MEM, MOM, MTM, THP, and THF ethers, aldehydes or ketones from cyclic or acyclic acetals and ketals and diols from an isopropylidene. Rarely has a single reagent shown this scope and application.

Experimental Section

General Methods. Melting points and distillation temperatures are uncorrected. Infrared (IR) spectra were taken on a Perkin-Elmer Model 681 spectrophotometer. Proton nuclear magnetic resonance (^1H NMR) spectra were obtained by using a Varian EM 390, 90-MHz spectrometer. In all instances, tetramethylsilane was used as a reference. Mass spectrometric measurements were performed by Morgan Schaffer, Montreal, Quebec, using a Hitachi-Perkin Elmer RMU-6D mass spectrometer. Elemental analysis was performed by Guelph Chemical Laboratories Ltd., Guelph, Ontario, or Galbraith Laboratories Inc., Knoxville, TN. Flash chromatography was accomplished by using 230–400 mesh silica gel (E. Merck) according to the procedure developed by Still et al.[33] The purity of known compounds was ascertained by TLC using commercial silica gel plates (Analtech, Uniplate-Silica Gel GF) and by spectral means (IR, ^1H NMR).

All reactions were carried out under an inert atmosphere of argon. Glassware and syringes were dried in an oven (120 °C) prior to use. Chlorinated solvents (CH_2Cl_2, $ClCH_2CH_2Cl$) as well as triethylamine were distilled from CaH_2 and stored over 4-Å molecular sieves. Dry ether was distilled from sodium/benzophenone. MeOH, EtOH, and *i*-PrOH were distilled from Mg and stored over 4-Å molecular sieves. THF was used as purchased (Aldrich Chemical Co. Gold Label).

Dimethylboron bromide and diphenylboron bromide were purchased from the Alfa Division of the Ventron Corporation. Alternatively, dimethylboron bromide was conveniently prepared from tetramethyltin and boron tribromide (vide infra).[34] Care should be taken in manipulating neat dimethylboron bromide as it is *pyrophoric* when exposed to moist air. Solutions of these reagents were prepared in either dry CH_2Cl_2 or $ClCH_2CH_2Cl$ (1.5–2.0 M) and could be stored at −15 °C for several months without noticeable decomposition. A solution of 9-BBN-Br in CH_2Cl_2 was purchased from Aldrich Chemical Co.

MEM, MOM, and MTM ethers were prepared by the methods of Corey et al.[5,6] Acetals and ketals were formed under standard conditions.[1] THP and THF ethers were prepared as described elsewhere.[35] Treatment of diols with *p*-TsOH·H_2O in acetone gave the corresponding acetonides.

Preparation of Dimethylboron Bromide. A dry 50 mL two-necked, round-bottomed flask was equipped with a septum, magnetic stirring bar, and a short-path distillation apparatus utilizing a preweighed 50-mL two-necked, round-bottomed flask with septum as the receiver. After being flushed with argon, the reaction vessel was cooled to −50 °C and charged with BBr_3 (50 mmol). Tetramethyltin (50 mmol) was then added dropwise via cannula over a 30-min period. After the addition was complete the reaction vessel's septum was replaced by a ground glass stopper and the mixture was stirred at −50 °C for an additional period of 30 min and at room temperature for 30 min.

The dimethylboron bromide (bp 31–32 °C) was separated from the coproduct Me_2SnBr_2 by simple distillation (75 °C maximum bath temperature, receiver cooled to 0 °C). Methylene chloride (20 mL) was then added to the receiver to afford a solution of dimethylboron bromide. The receiver was then removed, stoppered, and weighed.

The weight of the solution less the weight of the added solvent gave the yield (42 mmol, 84%) of dimethylboron bromide and thus the concentration of the solution (1.76 M).

Alternatively, with care, the dimethylboron bromide could be isolated neat. This material exhibited spectral properties (^1H NMR) identical with that of commercially available material.

Representative Procedure for the Cleavage of MEM (2, 8, 10, 33, 37, 40, 41, 45, and 46), MOM (1, 5, 7, 9, 35, 38, 43, and 48), MTM (6), and Related Ether Derivatives. Cleavage of Menthol MOM Ether 7. To a cold (−78 °C), stirred solution of the MOM ether **7** (0.97 mmol) in 8.1 mL of dry methylene chloride was added dropwise a solution of dimethylboron bromide (1.78 M, 1.63 mL) in 1,2-dichloroethane. After 1 h at −78 °C the reaction mixture was cannulated into a vigorously stirred mixture of tetrahydrofuran (10 mL) and saturated aqueous sodium bicarbonate (5 mL). After 5 min the mixture was diluted with ether

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(35) Miyashita, M.; Yoshikoshi, A.; Grieco, P. A. *J. Org. Chem.* **1977**, *42*, 3772.

(50 mL), and the organic layer was separated and washed successively with water, 10% aqueous sodium bisulfate, and brine. The aqueous layers were extracted with ether (10 mL) and the organic layers combined. After drying (Na_2SO_4) and concentration, the residue was flash chromatographed on silica gel (eluant, hexane–ethyl acetate, 9:1) to give, after bulb-to-bulb distillation (air-bath temperature 115–120 °C, 15 torr), pure menthol (94%). This material exhibited spectral properties (IR, ^{1}H NMR) identical with that of commercially available menthol.

Representative Procedure for the Preparation of Ethoxymethyl Ethers and Related Derivatives (3, 4, and 11). Preparation of 3-Phenyl-1-propanol Ethoxymethyl Ether (3). To a cold (–78 °C), stirred solution of the MOM ether 1 (1.39 mmol) in 11.9 mL of dry CH_2Cl_2 was added a solution of dimethylboron bromide (2.05 M, 2.03 mL) in 1,2-dichloroethane. After 1 h at –78 °C, the mixture was treated with triethylamine (0.78 mL) followed by dry ethanol (5 mL) and allowed to warm to room temperature. After 1 h the yellow solution was diluted with ether (50 mL) and washed with water, 10% sodium bisulfate, and brine. After drying ($MgSO_4$), the resultant solution was concentrated and subjected to flash chromatography on silica gel (eluant, hexane–ethyl acetate, 4:1) to afford, after bulb-to-bulb distillation (air-bath temperature 100–115 °C, 0.10 torr), pure 3-phenyl-1-propanol ethoxymethyl ether (3) (73%): IR (neat) 3027, 2925, 1113, 1035, 742, 698 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.21 (t, 3 H, J = 7.0 Hz), 1.73–2.10 (m, 2 H), 2.70 (m, 2 H), 3.47–3.73 (overlapping t, 4 H), 4.66 (s, 2 H), 7.13–7.40 (m, 5 H). Anal. Calcd for $C_{12}H_{18}O_2$: C, 74.19; H, 9.33. Found: C, 74.31; H, 9.34.

Further elution of the column gave pure 3-phenyl-1-propanol (5%) which was identical (IR, ^{1}H NMR) with that of commercial material.

Representative Procedures for the Cleavage of Acetonides (12, 13, 15, and 58). (a) Cleavage of *trans*-1,2-Cycloheptanediol Acetonide (12). To a cold (–78 °C), stirred solution of the acetonide 12 (1.0 mmol) in 10.0 mL of dry methylene chloride was added a solution of dimethylboron bromide (1.70 M, 2.35 mL) in the same solvent. After 4 h at –78 °C the reaction mixture was cannulated into a room-temperature, vigorously stirred mixture of tetrahydrofuran (10 mL) and saturated aqueous sodium bicarbonate (5 mL). After 5 min, ethyl acetate (5 mL) was added. The organic layer was separated and the aqeuous layer extracted with additional ethyl acetate (10 mL). The combined organic layers were then washed with brine and dried over $MgSO_4$. Concentration gave a pale yellow oil. Methanol (2 mL) was added (to facilitate removal of the borate ether) and the material reconcentrated. Flash chromatography on silica gel (eluant, ethyl acetate–methylene chloride, 1:1) gave pure *trans*-1,2-cycloheptanediol (86%). This material exhibited spectral properties (IR, ^{1}H NMR) identical with that of commercially available material.

(b) Cleavage of 6-(*tert*-Butyldiphenylsiloxy)-1,2-hexanediol Acetonide (15). To a cold (–78 °C), stirred solution of the acetonide 15 (0.5 mmol) in 1.63 mL of dry methylene chloride was added a solution of dimethylboron bromide (1.73 M, 0.87 mL) in the same solvent. After 1 h at –78 °C triethylamine (2 mmol) and a solution of dry tetrabutylammonium hydroxide (3 mmol) in methylene chloride (1 ml) were sequentially added. The mixture was allowed to warm to room temperature and then quenched with 10% aqueous sodium bisulfate. Normal workup (as above) gave, after flash chromatography on silica gel (eluant, ethyl acetate), pure diol 16 (86%): IR (film) 3380, 3079, 2948, 1459, 1109, 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.30 (s, 9 H), 1.33 (m, 6 H), 2.29 (bs, 1 H), 3.29–3.79 (m, 5 H), 7.26–7.49 (m, 3 H), 7.56–7.76 (m, 2 H); MS, m/e (relative intensity) 297 (4), 237 (15), 200 (84), 199 (100), 180 (27), 139 (36), 81 (78). Anal. Calcd for $C_{22}H_{32}O_3Si$: C, 71.30; H, 8.16. Found: C, 71.20; H, 8.57.

Representative Procedure for the Cleavage of Acetals and Ketals. (a) Cleavage of Acetals and Ketals 17–24. This procedure was identical with that used for the cleavage of MOM and MEM ethers except that 2 equiv of dimethylboron bromide was used.

(b) Cleavage of 2-Benzylcyclohexanone Ethylene Ketal (26). To a cold (0 °C) stirred solution of the ketal 26 (0.27 mmol) in 0.90 mL of dry methylene chloride was added a solution of dimethylboron bromide (1.78 M, 0.46 mL) in the same solvent. After 1 h at 0 °C and 3 h at room temperature the reaction mixture was cooled to 0 °C and treated with a solution of dry tetra-*n*-butylammonium hydroxide (1.0 M, 1.08 mL) in methylene chloride. After 30 min the mixture was quenched with saturated aqueous sodium bicarbonate (1 mL) and diluted with ether (30 mL). The organic layer was separated, washed with water (3 × 5 mL) and brine (5 mL), and dried over $MgSO_4$. Filtration and concentration gave a pale yellow oil which was flash chromatographed (eluant, ethyl acetate–hexane, 1:9) to give pure 2-benzylcyclohexanone (87%). This material exhibited spectral properties (IR, ^{1}H NMR) identical with that of a sample provided.[28]

Preparation of 2-[[1-(Phenylthio)nonyl]oxy]ethanol (27). To a cold (–78 °C) stirred solution of the acetal 18 (1.0 mmol) in 3.9 mL of dry methylene chloride was added a solution of dimethylboron bromide (1.75 M, 1.14 mL) in the same solvent. After 1 h at –78 °C triethylamine (2.3 mmol) and thiophenol (2.0 mmol) were added. After 1 h at –78 °C and 1 h at room temperature, the reaction mixture was treated with saturated aqueous sodium bicarbonate (1 mL) and diluted with ether (30 mL). The organic layer was separated, washed with water (5 mL) and brine (5 mL), and dried over $MgSO_4$. Filtration and concentration gave a yellow oil which was flash chromatographed (eluant, ethyl acetate–hexane, 1:4) to afford the mixed acetal 27 (84%): IR (film) 3415, 3062, 2930, 1588, 1440, 1105 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ (m, 4 H), 4.73 (t, J = 6.3 Hz, 1 H), 7.15–7.37 (m, 3 H), 7.37–7.62 (m, 2 H). Anal. Calcd for $C_{17}H_{28}O_2S$: C, 68.87; H, 9.52. Found: C, 68,.44; H, 9.25.

Representative Procedure for the Cleavage of THP (28) and THF (29) Ethers and Methyl Glycosides (30 and 32). Cleavage of Dodecanol Tetrahydrofuranyl Ether (28). To a cold (0 °C), stirred solution of the tetrahydrofuranyl ether 28 (0.50 mmol) in 0.5 mL of dry, methylene chloride was added a solution of dimethylboron bromide (1.73 M, 1.73 mL) in the same solvent. The cooling bath was removed and the reaction stirred at room temperature for 18 h. Saturated aqueous sodium bicarbonate was then added and the resulting mixture diluted with ether (50 mL). The organic layer was separated, washed with water and brine, and dried over $MgSO_4$. Concentration followed by flash chromatography on silica gel (eluant, hexane–ethyl acetate, 3:1) gave after distillation (air-bath temperature 128–135 °C, 15 torr) pure dodecanol (86%). This material exhibited spectral properties (IR, ^{1}H NMR) identical with that of commercially available material.

Representative Procedure for the Cleavage of MOM (51 and 54) and MEM (53) Ethers in the Presence of an Acetonide. This procedure was identical with that used for the cleavage of MOM and MEM ethers except that 3.3 equiv of ether were included in the reaction mixtures.

Representative Procedure for the Cleavage of Acetals (56 and 60) in Ether. Cleavage of the Acetonide Acetal 56 in Ether. To a cold (–78 °C), stirred solution of the acetonide acetal 56 (0.50 mmol) in 4.4 mL of dry ether was added a solution of dimethylboron bromide (1.60 M, 0.63 mL) in methylene chloride. After 30 min, the mixture was cannulated into a mixture of tetrahydrofuran and saturated aqueous sodium bicarbonate at room temperature. Ether (50 mL) was added and the organic layer washed with water and brine. Drying ($MgSO_4$) followed by concentration and flash chromatography on silica gel (eluant, hexane–ethyl acetate, 9:1) gave the aldehyde 57 (79%). This material exhibited spectral properties identical with that previously reported.[36]

Acknowledgment. A Natural Sciences and Engineering Research Council of Canada industrial research followship (to H. E. Morton) is gratefully acknowledged. We thank Dr. J. Rokach for his support and collaboration.

Registry No. 1, 91898-11-2; 2, 87770-91-0; 3, 91898-12-3; 4, 91898-13-4; 5, 34458-41-8; 6, 8770-95-4; 7, 91898-14-5; 8, 91898-15-6; 9, 87770-92-1; 10, 87770-94-3; 11, 91898-16-7; 12, 41564-28-7; 13, 92007-80-2; 14, 92007-81-3; 15, 91898-17-8; 16, 91898-18-9; 17, 18824-63-0; 18, 5432-30-4; 19, 77196-31-7; 20, 4469-45-8; 21, 25632-03-5; 22, 183-03-9; 23, 27889-58-3; 24, 1087-68-9; 25, 91898-19-0; 26, 91898-20-3; 27, 91898-21-4; 28, 63588-79-4; 29,

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91898-22-5; **30**, 91898-23-6; **31**, 91928-34-6; **32**, 91928-35-7; **33**, 87770-97-6; **34**, 51308-90-8; **35**, 91898-24-7; **36**, 4153-24-6; **37**, 91898-25-8; **38**, 91898-26-9; **39**, 4267-13-4; **40**, 91898-27-0; **41**, 91898-28-1; **42**, 71662-03-8; **43**, 91898-29-2; **44**, 51326-52-4; **45**, 91898-30-5; **46**, 91898-31-6; **47**, 91898-32-7; **48**, 91898-33-8; **49**, 91898-34-9; **50**, 53958-71-7; **51**, 91898-35-0; **52**, 14739-10-7; **53**, 91898-36-1; **54**, 91898-37-2; **55**, 91928-36-8; **56**, 91898-38-3; **57**, 69891-85-6; **58**, 91898-39-4; **59**, 91898-40-7; **60**, 91898-41-8; **61**, 91898-42-9; **62**, 22054-14-4; $Ph(CH_2)_2CH_2OH$, 122-97-4; $Me(CH_2)_{10}CH_2OH$, 112-53-8; $Me(CH_2)_6CH(OH)(CH_2)_3Me$, 10203-33-5; $Me(CH_2)_7CHO$, 124-19-6; Me_2BBr, 5158-50-9; Ph_2BBr, 5123-17-1; Menthol, 1490-04-6; 1-butylcyclohexanol, 5445-30-7; 2-naphthalenecarboxaldehyde, 66-99-9; cyclooctanone, 27457-18-7; dibenzo[*a*,*d*]cycloheptenone, 2222-33-5; 2-benzylcyclohexanone, 946-33-8; *trans*-1,2-cycloheptanediol, 13553-19-0.

Supplementary Material Available: Full spectral data (IR, ^1H NMR, and mass spectrum) for compounds studied in the paper (8 pages). Ordering information is given in any current masthead page.

Synthesis, Thermal Stability, and Chemiluminescence Properties of the Dioxetanes Derived from 1,4-Dioxins

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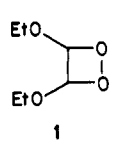
Received March 15, 1984

Photosensitized singlet oxygenation of benzo- and naphtho-1,4-dioxins **3** afforded the corresponding 1,2-dioxetanes **4** in moderate to good yields. Ene products **7** were obtained in those cases in which the 1,4-dioxins **3** bear alkyl substituents. Thermal decomposition of the 1,2-dioxetanes **4** afford the corresponding diesters **5** essentially quantitatively. The X-ray crystal structures of the dioxetanes **4g**, **4h**, and **4j** indicate that the four-membered rings are all essentially planar. These dioxetanes exhibit surprisingly similar thermal stabilities; the free energies of activation ($\Delta G^{\ddagger}$) at 298 K fall within 26 ± 1 kcal/mol, the enthalpies of activation ($\Delta H^{\ddagger}$) within 24 ± 1.5 kcal/mol, and the entropies of activation ($\Delta S^{\ddagger}$) within −6 ± 2 eu. In their chemiluminescence properties they are inefficient sources of chemienergized, electronically excited diester products. The singlet excitation yields (ϕ^S) range between 0.0001% and 0.003% and the triplet excitation yields (ϕ^T) between 0.01% and 3.5%. They represent typical dioxetanes in that preferentially triplet excited carbonyl products are chemienergized.

Introduction

The dyestuff-sensitized photooxygenation of electron-rich alkenes such as dialkoxy-substituted ethylenes has proved itself as one of the effective means of preparing 1,2-dioxetanes.[1] In fact, 3,4-diethoxy-1,2-dioxetane (**1**),



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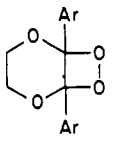
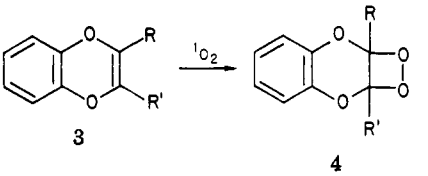


2

which was conveniently prepared from 1,2-diethoxyethylene in this way,[2] constituted one of the first fully characterized 1,2-dioxetanes. Similarly, the singlet oxygenation of cyclic analogues, e.g., 2,3-diaryl-1,4-dioxenes, provided an efficient entry into the 1,2-dioxetanes **2**.[3] The latter have been useful substrates for the mechanistic elucidation of the chemiluminescence properties associated with 1,2-dioxetanes.[4]

In this context we have been interested in the related 1,2-dioxetanes **4**, derived from the singlet oxygenation of the corresponding benzo-1,4-dioxins **3** (eq 1).[5] In view of



3 **4** (1)

the fact that the synthetic problem of preparing derivatives of **3** which are mono- and disubstituted in the 2,3-positions was recently solved,[6] a number of interesting 1,2-dioxetanes **4** were in principle accessible via eq 1. Presently we report on the synthesis and characterization of an extensive series of such dioxetanes, together with the elucidation of their thermal stability and chemiluminescence properties.

Results

Synthetic Work. 1,4-Dioxins 3. In this study the benzo-1,4-dioxins **3a–k** and the 2,3-naphtho-1,4-dioxin **3l**

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