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Oxidation of Diols and Ethers by $NaBrO_3/NaHSO_3$ Reagent

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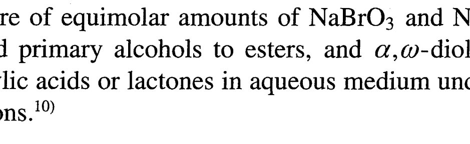
$NaBrO_3$ combined with $NaHSO_3$ was found to be an excellent oxidizing reagent of alcohols, diols, and ethers under mild conditions. A variety of aliphatic and cyclic diols were selectively oxidized with satisfactory yields to the corresponding hydroxy ketones and/or diketones, which are difficult to selectively prepare due to a concomitant formation of cleaved products. For example, 2-hydroxycyclohexanone and 1,2-cyclohexanedione were selectively formed by allowing 1,2-cyclohexanediol to react with $NaBrO_3/NaHSO_3$ reagent in a selected solvent. On the other hand, an alkyl ether, such as dioctyl ether, reacted with $NaBrO_3/NaHSO_3$ in water at room temperature to give octyl octanoate in 82% yield. The same oxidation at higher temperature (60 °C) produced the α-brominated ester, octyl 2-bromooctanoate, which is considered to be formed through an alkenyl alkyl ether as the intermediate. The treatment of 1-ethoxy-1-heptene with $NaBrO_3/NaHSO_3$ afforded ethyl 2-bromoheptanoate and 2-bromoheptanoic acid as the major products.

The oxidative dehydrogenation of alcoholic functions to carbonyl ones and the oxidation of ethers to esters are common transformations in organic synthesis. Therefore, a number of methods have been developed for this purpose.[1] Although sodium bromite ($NaBrO_2$) can oxidize alcohols to ketones,[2] and α,ω-diols to lactones,[3] the reagent is difficult to prepare. Sodium bromate, $NaBrO_3$, is used as an oxidant for $RuCl_3$[4]- and cerium ammonium nitrate (CAN)[5]-catalyzed oxidations of alcohols and esters. In addition, it is reported that it serves as the effective oxidant of alcohols, ethers, and silyl ethers in the presence of Lewis acids,[6] HBr,[7] and Br_2.[8]

In a previous paper, we showed that $NaBrO_3$ in combination with an appropriate reducing agent, such as $NaHSO_3$, generates in situ hypobromous acid, BrOH, and acts as a prominent reagent for the bromohydroxylation of alkenes (Eq. 1).[9] In addition, '$NaBrO_3/NaHSO_3$ reagent', which is a mixture of equimolar amounts of $NaBrO_3$ and $NaHSO_3$, oxidized primary alcohols to esters, and α,ω-diols to dicarboxylic acids or lactones in aqueous medium under mild conditions.[10]



(1)

In this paper, we wish to report on the application of $NaBrO_3/NaHSO_3$ reagent for the selective oxidation of various diols to α-hydroxy ketones and/or diketones, and ethers to esters under mild conditions.

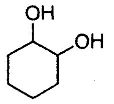
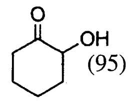
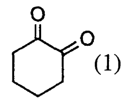
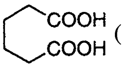
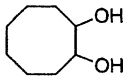
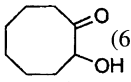
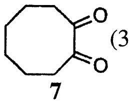
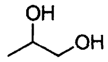
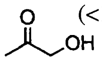
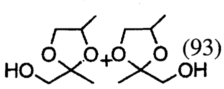
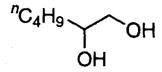
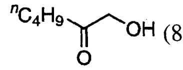
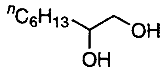
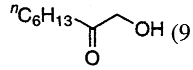
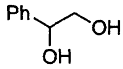
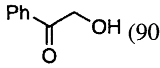
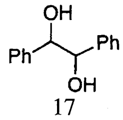
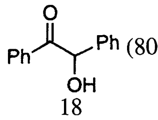
Results

Oxidation of Diols. Since α-hydroxy ketones are of value as intermediates in organic synthesis, these compounds have been prepared from a variety of substrates such as esters,[11] enolates,[12] epoxides,[13] ketones,[14] and alkenes.[15] The direct oxidation of *vic*-diols, which are easily available from alkenes, is one of the most useful candidates for the synthesis of α-hydroxy ketones and 1,2-diketones.[16] However, the oxidation of *vic*-diols to α-hydroxy ketones or 1,2-diketones using conventional methods is difficult to carry out due to the formation of undesired cleavage products, such as carboxylic acids and aldehydes.[17] Therefore, the conversion of *vic*-diols to the corresponding carbonyl compounds is of interest from a synthetic point of view. Kajigaeshi et al. reported that $NaBrO_3$ combined with HBr is an excellent reagent for the oxidation of alcohols to carbonyl compounds, but no oxidation has been examined for *vic*-diols.[7]

We first examined the oxidation of 1,2-cyclohexanediol (**1**) with $NaBrO_3/NaHSO_3$ under various reaction conditions (Table 1, Runs 1—3). The oxidation was achieved by adding dropwise an aqueous $NaHSO_3$ solution over a period of 0.5 h to a mixture of **1** and $NaBrO_3$ (1.2 molar amount with respect to **1**) in aqueous acetonitrile at room temperature to give 2-hydroxy-1-cyclohexanone (**2**) in 95% yield (Run 1), although the oxidation of *vic*-diols with IO_4^- resulted in a cleavage of the carbon–carbon bond.[1] When a $NaHSO_3$ solution was added all at once to the $NaBrO_3$ solution, the yield of **2** lowered to 51% (Run 2). To obtain 1,2-cyclohexanedione (**3**), **1** was oxidized under several conditions. The best result was obtained by the oxidation of **1** with 1.2 molar amount of $NaBrO_3$ and $NaHSO_3$ ($NaBrO_3/NaHSO_3$) reagent in a mixed solvent of CH_3CN/CH_2Cl_2 to give **3** in 74% yield (Run 3). To our best knowledge this is the practical example for the oxidation of **1** to **3** with high selectivity.

The treatment of 1,2-cyclooctanediol (**5**) with $NaBrO_3/NaHSO_3$ under these conditions afforded 2-hy-

Table 1. Oxidation of Various *vic*-Diols by $NaBrO_3/NaHSO_3$[a)]

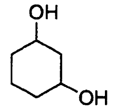
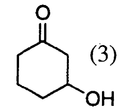
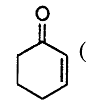
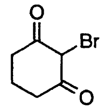
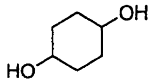
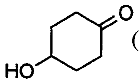
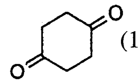
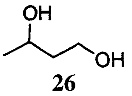
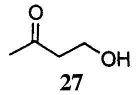
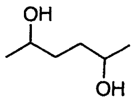
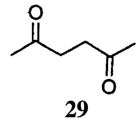
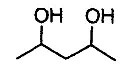
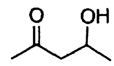
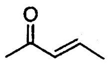
Run	Substrate	Product (yield / %)		
1	 **1**	 (95) **2**		 (1) **3**
2[b)]	**1**	**2**(51) **3**(19)		 (18) **4**
3[c)]	**1**	**2**(8) **3**(74)		**4**(13)
4[d)]	 **5**	 (69) **6**		 (3) **7**
5[e)]	**5**	**6**(<1)		**7**(94)
6	 **8**	 (<1) **9**		 (93) **10**
7	 **11**	 (89) **12**		
8	 **13**	 (91) 14		
9	 15	 (90) 16		
10[e,f)]	 17	 (80) 18		

a) To a solution of diol (5 mmol) and $NaBrO_3$ (6 mmol) in CH_3CN/H_2O (10/3 mL) was added dropwise $NaHSO_3$ (6 mmol) in H_2O (6 mL) during a period of 30 min at room temperature under stirring for 2 h. b) $NaHSO_3$ solution was added all at once. c) Diol (3 mmol) was allowed to react in $CH_3CN/CH_2Cl_2/H_2O$ (6/3/5.4 mL) for 3 h. d) 6 h. e) Each 2.4 molar amounts of $NaBrO_3$ and $NaHSO_3$ with respect to substrate was used. f) Diol (2.5 mmol) was used.

droxy-1-cyclooctanone (**6**) in 69% yield (Run 4). In contrast to the oxidation of **1**, where diketone **3** was difficult to obtain, **5** could be converted into 1,2-cyclooctanedione (**7**) upon a treatment with 2.4 molar amounts of $NaBrO_3/NaHSO_3$ (Run 5). The oxidation of 1,2-propanediol (**8**) gave the acetal **10** in 93% yield. This is because 1-hydroxy-2-propanone (**9**), which is a primary product of **8**, is considered to be easily subject to acetalization with **8** (Run 6). In contrast, 1, 2-hexanediol (**11**) and 1,2-octanediol (**13**) were selectively oxidized to the corresponding hydroxy ketones, **12** and **14**, in high yields without formation of the corresponding acetals (Runs 7 and 8). It is interesting to note that the primary hydroxy groups of these substrates were not entirely oxidized, even when 2 molar amounts of $NaBrO_3/NaHSO_3$ reagent were employed. Similarly, the oxidation of 1,2-diphenyl-1,2-ethanediol (**17**) with 1.2 molar amount of $NaBrO_3/NaHSO_3$ gave hydroxy ketone **18**. Upon treatment of **17** with 2.4 molar amounts of $NaBrO_3/NaHSO_3$, **18** was obtained as the major product (80%) (Run 10).

Table 2 shows the oxidation of various diols using the $NaBrO_3/NaHSO_3$ reagent. When 1,3-cyclohexanediol (**19**) was treated with 1.2 molar amount of $NaBrO_3/NaHSO_3$, 2-cyclohexenone (**21**) was obtained rather than 3-hydroxy-1-cyclohexanone (**20**) as the major product (80%) (Run 1). Although **19** was allowed to react with excess $NaBrO_3/NaHSO_3$ (3.6 molar amounts) to prepare 1,3-cyclohexanedione, undesired 2-bromo-1,3-cyclohexanedione (**22**) was formed in 71% yield (Run 2). The reaction path for the formation of **22** will be discussed later. 1,4-Cyclohexanediol (**23**) was converted into 4-hydroxycyclohexanone (**24**) and 1,4-cyclohexanedione (**25**) with 1.2 molar amount and 2.4 molar amounts of $NaBrO_3/NaHSO_3$, respectively, in good yields (Runs 3 and 4). The oxidation of 2,5-hexanediol (**28**) with $NaBrO_3/NaHSO_3$ (2.4 molar amounts) produced 2,5-hexanedione (**29**) in almost quantitative yield (Run 6). When oxidation of 2,4-pentanediol (**30**) with 1.2 molar amount of $NaBrO_3/NaHSO_3$, hydroxy ketone **31** was formed in 91% yield (Run 7).

Table 2. Oxidation of Various Diols by $NaBrO_3/NaHSO_3$[a)]

Run	Substrate	Product (yield/%)	
1	 **19**	 (3) **20**	 (80) **21**
2[b)]	**19**	**20**(<1)	 (71) **22**
3[c)]	 **23**	 (78) **24**	 (10) **25**
4[d,e)]	**23**	**24**(<1)	**25**(93)
5	 **26**	 (90) **27**	
6[d)]	 **28**	 (98) **29**	
7	 **30**	 (91) **31**	 (<1) **32**

a) To a solution of diol (5 mmol) and $NaBrO_3$ (6 mmol) in CH_3CN/H_2O (10/3 mL) was added dropwise $NaHSO_3$ (6 mmol) in H_2O (6 mL) during a period of 15 min at room temperature under stirring for 4 h. b) $NaBrO_3/NaHSO_3$ (3.6/3.6 mol. amounts). c) 2 h. d) $NaBrO_3/NaHSO_3$ (2.4/2.4 mol. amounts). e) 6 h.

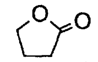
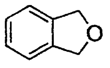
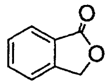
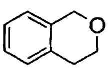
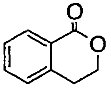
Oxidation of Ethers. Several methods have been developed for the direct transformation of ethers to esters.[18] In general, although chromium and manganese reagents, such as CrO_3,[19] $(PhCH_2NEt_3)MnO_4$,[20] and $Zn(MnO_4)_2$/silica gel,[21] are known to be good oxidants, these oxidants produce environmentally unfavorable compounds. $NaIO_4$ is also used in the RuO_4-catalyzed oxidation of ethers.[22] Kajigaeshi et al. showed that dibutyl- and dihexyl ethers are oxidized to the corresponding esters by $NaBrO_3$ combined with HBr in 54 and 75% yields, respectively.[7]

$NaBrO_3/NaHSO_3$ reagent was found to be efficient for the oxidation of ethers to esters under mild conditions. In order to confirm the optimum reaction conditions, dioctyl ether (**33**) was chosen as a model substrate and allowed to react with $NaBrO_3/NaHSO_3$ under various reaction conditions (Eq. 2 and Table 3). The oxidation of **33** with 2 molar amounts of $NaBrO_3/NaHSO_3$ reagent in CH_3CN/H_2O produced octyl octanoate (**34**) and octanoic acid (**35**) in 67% and 27% yields, respectively (Run 1). Previously, we reported that the oxidative esterification of alcohols by the $NaBrO_3/NaHSO_3$ system was advantageously achieved in an aqueous medium.[10] Hence, **33** was reacted in water to give **34** in 82% yield (Run 2). It is important that the oxidation proceeds satisfactorily in water, although the conventional oxidation by $NaBrO_3$ in the presence of HBr is carried out in CH_2Cl_2. The equimolar oxidation of **33** with $NaBrO_3/NaHSO_3$ gave **34** in moderate yield, even if the reaction was prolonged to 40 h (Runs 3 and 4). Needless to say, no reaction took place when **33** was treated with $NaBrO_3$ alone in the absence of $NaHSO_3$ (Run 5). The same oxidation at higher temperature (60 °C) produced the α-bromo ester **36** in 32% yield together with **34** (40%) and **35** (14%) (Run 6).

We also examined the oxidation of several ethers other than **33** to verify the generality of the present procedure (Table 4). Dihexyl ether and diundecyl ether were successfully converted into the corresponding esters in good yields (Runs 1 and 2).

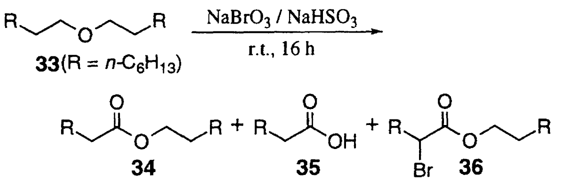
It is interesting to note that the oxidation of an unsymmetrical alkyl ether with $NaBrO_3/NaHSO_3$ gave several possible esters obtained by the exchange of the alkyl group. The oxidation of ethyl octyl ether (**37**) produced octyl octanoate (**34**) (44%) rather than the expected esters, methyl nonanoate (**38**) (13%) and ethyl octanoate (**39**) (7%) (Run 3). The formation of **34** in this reaction will be discussed later. Cyclic ethers led to the corresponding lactones in good yields (Runs 4—6). For example, tetrahydrofuran led to γ-butyrolac-

Table 4. Oxidation of Ethers by $NaBrO_3/NaHSO_3$[a)]

Run	Substrate	Product (yield / %)
1	$(^{n}C_6H_{13})_2O$	$^{n}C_5H_{11}CO_2{}^{n}C_6H_{13}$ (82) $^{n}C_5H_{11}COOH$ (18)
2	$(^{n}C_{11}H_{23})_2O$	$^{n}C_{10}H_{21}CO_2{}^{n}C_{11}H_{23}$ (78) $^{n}C_{10}H_{21}COOH$ (18)
3	$^{n}C_8H_{17}OC_2H_5$ (**37**)	**34** (44) **35** (31) $^{n}C_8H_{17}CO_2CH_3$ (**38**) (13) $^{n}C_7H_{15}CO_2C_2H_5$ (**39**) (7)
4		 (68)
5[b)]		 (96)
6		 (80)

a) Substrate (2.5 mmol) was allowed to react with $NaBrO_3$ /$NaHSO_3$ (5/5 mmol) in H_2O (10 mL) at room temperature for 16 h. b) $NaBrO_3/NaHSO_3$ (3/3 mmol) was used.

Table 3. Oxidation of Dioctyl Ether (**33**) by $NaBrO_3/NaHSO_3$ Under Various Reaction Conditions[a)]



(2)

Run	$NaBrO_3$	$NaHSO_3$	Solvent	Conv.	Yield (%)		
	(mol. amounts)	(mol. amounts)	mL	%	**34**	**35**	**36**
1	2	2	CH_3CN/H_2O (5/5)	100	67	27	<1
2	2	2	H_2O (10)	100	82	18	<1
3	1	1	H_2O (10)	62	34	4	<1
4[b)]	1	1	H_2O (10)	65	38	5	<1
5	1	0	H_2O (10)	0	0	0	0
6[c)]	2	2	H_2O (10)	100	40	14	32

a) **33** (2.5 mmol) was allowed to react with $NaBrO_3/NaHSO_3$ at room temperature for 16 h. b) 40 h. c) 60 °C.

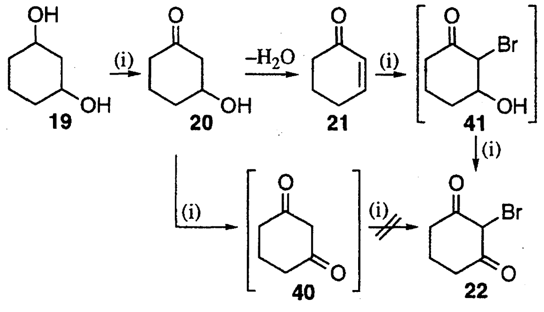
tone as the sole product (Run 4). 1,3-Dihydroisobenzofuran underwent the smooth oxidation with 1.2 molar amount of $NaBrO_3/NaHSO_3$ affording phthalide in excellent yield (Run 5), and isochroman gave 3,4-dihydroisocoumarin in 80% yield (Run 6).

Discussions

During the oxidation of 1,3-cyclohexanediol **19** with 3.6 molar amounts of $NaBrO_3/NaHSO_3$, 2-bromo-1,3-cyclohexanedione **22** was obtained in preference to the expected 1,3-cyclohexanedione (**40**) (Table 2, Run 2). A plausible reaction path for the production of **22** from **19** is shown in Scheme 1. In a previous paper, we showed that enones upon treatment with $NaBrO_3/NaHSO_3$ are smoothly converted into the corresponding bromohydrins. Indeed, an independent reaction of **21** with $NaBrO_3/NaHSO_3$ (3.6 molar amounts) under the same conditions as the oxidation of **19** gave **22** in 87% yield. It is reasonable to propose that the resulting hydroxy ketone **20** was easily subjected to dehydration to enone **21** in preference to dehydrogenation to **40**, and the resulting **21** was bromohydroxylated to **41** and finally dehydrogenated to the **22**. An alternative path for the formation of **22** via the bromination of dione **40** may be possible. Indeed, the treatment of **40** with 2.4 molar amounts of $NaBrO_3/NaHSO_3$ afforded **22** in 92% yield, but the fact that **40** was not detected during any stage in the oxidation of **19** with $NaBrO_3/NaHSO_3$ may exclude the direct bromination of **40**.

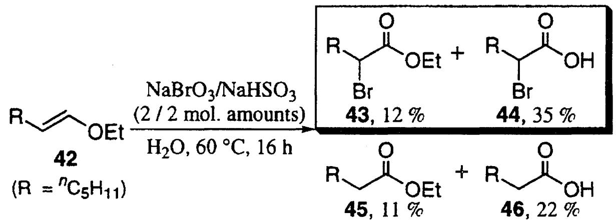
As shown in Table 3, the oxidation of dioctyl ether (**33**) with $NaBrO_3/NaHSO_3$ reagent at room temperature produced the octyl octanoate **34** in good yield, while the reaction at 60 °C resulted in the α-bromo ester **36** together with **34** and octanoic acid **35**. Although **36** was considered to be formed from **34**, an independent reaction of **34** with 2 molar amounts of $NaBrO_3/NaHSO_3$ reagent at 60 °C produced a small amount of **35**, but not bromo ester **36**.

In a previous paper, we showed that the reaction of cyclohexene with $NaBrO_3/NaHSO_3$ proceeds via the bromonium ion mechanism to produce *trans*-2-bromocyclohexan-1-ol in high selectivity, but no product, such as 1-bromo-2-cyclohexene, which is considered to be formed via radical process, is produced.[9] In view of these facts and results obtained here, the oxidation of ethers with $NaBrO_3/NaHSO_3$ reagent seems to involve an ionic process rather than a radical process. Thus, a plausible reaction path for the oxidation of **33** with $NaBrO_3/NaHSO_3$ reagent is shown in Scheme 2. The reaction is thought to be initiated by the abstraction of hydride ion from **33** by $NaBrO_3/NaHSO_3$ to form an oxonium ion **A** which appears to be immediately converted into a hemiacetal **B**, followed by ester **34** via the oxidative dehydrogenation of **B**. At higher temperature, the dehydration of acetal **B** to alkenyl ether **C** may be possible. Under these conditions, **C** is believed to be subject to bromohydroxylation with $NaBrO_3/NaHSO_3$ to form bromohydrin **E**, which is subsequently oxidized to the α-bromo ester **36**. Indeed, the treatment of ethyl 1-heptenyl ether (**42**) by $NaBrO_3/NaHSO_3$ (2 molar amounts) at 60 °C for 16 h afforded ethyl 2-bromoheptanoate (**43**) (12%), 2-bromoheptanoic acid (**44**) (35%) and hydrated products, **45** (11%) and **46** (22%) (Eq. 3).



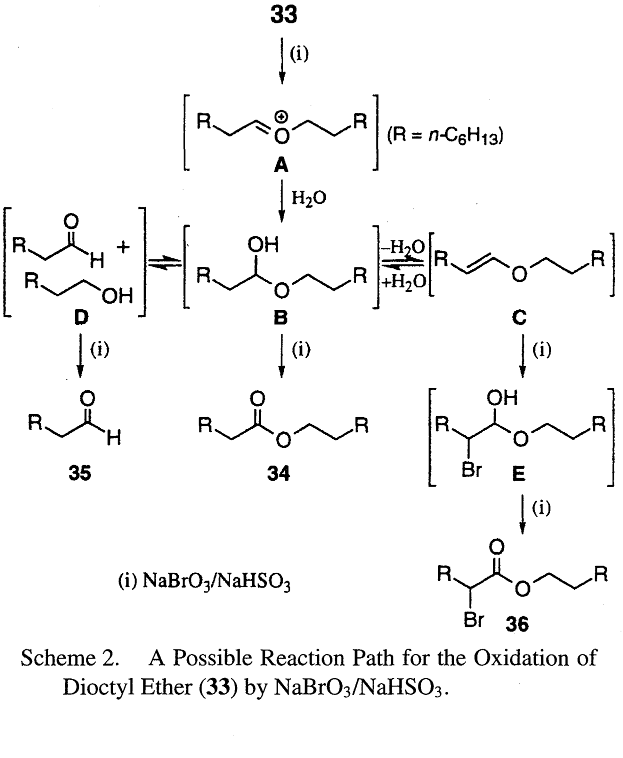
(i) $NaBrO_3/NaHSO_3$

Scheme 1. A Possible Reaction Path for the Oxidation of 1,3-Cyclohexanediol (**19**) by $NaBrO_3/NaHSO_3$.

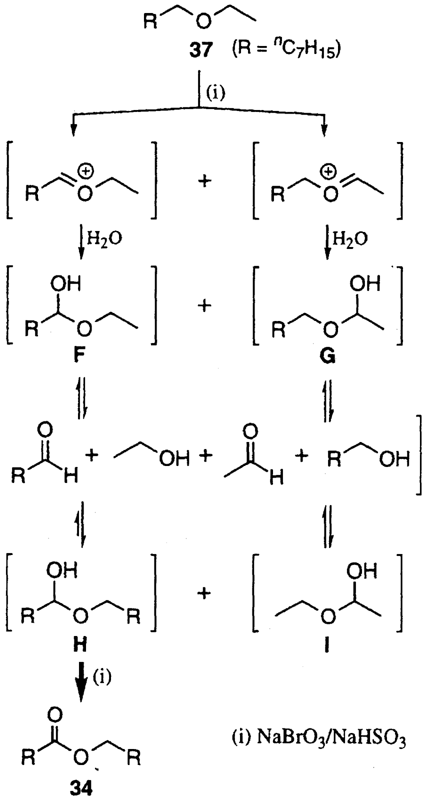


(3)

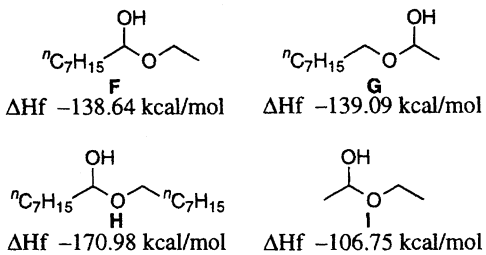
In the oxidation of unsymmetrical ethyl octyl ether **37**, we showed that the unexpected product, octyl octanoate **34**, was formed in 44% yield along with the expected esters, **38** (13%) and **39** (7%) (Table 4, Run 3). In order to obtain information on the formation of **34** by the exchange reaction between **38** and **39**, an equimolar mixture of **38** and **39** was allowed to react with $NaBrO_3/NaHSO_3$ under the same conditions as the oxidation of **37**. However, ester **34** was not obtained.



Scheme 2. A Possible Reaction Path for the Oxidation of Dioctyl Ether (**33**) by $NaBrO_3/NaHSO_3$.



Scheme 3. A Possible Reaction Path for the Oxidation of Ethyl Octyl Ether (**37**) by $NaBrO_3/NaHSO_3$.



Scheme 4.

Hence, it is reasonable to predict that **34** is not formed by transesterification between **38** and **39**. We would like to suggest the following reaction path for the oxidation of **37** with $NaBrO_3/NaHSO_3$ (Scheme 3). At the early stage of the reaction, hemiacetals **F** and **G** are probably formed, and are in equilibrium with the corresponding aldehydes and alcohols. The exchange reactions among the hemiacetals would result in four possible hemiacetals, (**F**, **G**, **H**, and **I**) (Scheme 4). The heat of formation of these hemiacetals calculated using the PM3 method showed that **H** is the most stable product.[23] Consequently, the formation of **34** is preferred over the other esters. This observation is in accord with the experimental result for the oxidation of **37**.

In conclusion, the oxidation of diols and ethers was successfully achieved by using $NaBrO_3/NaHSO_3$ reagent under mild conditions. This provides a convenient methodology for the selective oxidation of diols and ethers in high yields.

Experimental

General Procedures. Diols and ethers except for **17** and **37** were commercially available. Compounds **17** and **37** were synthesized by conventional methods. GC analysis was performed with a flame ionization detector using a 0.2 mm × 25 m capillary column (OV-1, OV-17). ${}^1H$- and ${}^{13}C$ NMR were measured at 270 and 67.5 MHz, respectively, in $CDCl_3$ with Me_4Si as the internal standard. Infrared (IR) spectra were measured using NaCl plates or KBr disks. GC-MS spectra were obtained at an ionization energy of 70 eV. The yields of the products were estimated from the peak areas based on the internal-standard technique.

General Procedures for the Oxidation of Diols with $NaBrO_3/NaHSO_3$ Reagent. To a solution of $NaBrO_3$ (12 mmol) in water (6 mL) was added the diols (5 mmol) in acetonitrile (10 mL) followed by the dropwise addition of a solution of $NaHSO_3$ (12 mmol) in water (12 mL) over a period of about 15—30 min. The mixture was then stirred at room temperature for 2—6 h. The reaction mixture was poured into 50 mL of ether. After separation of the organic phase, the aqueous layer was extracted twice with ether. The combined organic layer was washed with anhydrous $Na_2S_2O_3$ solution and dried over $MgSO_4$. After filtration, the ether was removed in vacuum, and the residue was purified by column chromatography (silica gel, hexane : ethyl acetate = 10 : 1) to give the α-hydroxy ketone and/or diketone. The products were identified through a comparison of the isolated products with authentic samples.

General Procedures for the Oxidation of Ethers with $NaBrO_3/NaHSO_3$ Reagent. To a solution of $NaBrO_3$ (5 mmol) in water (5 mL) was added ether (2.5 mmol) followed by the dropwise addition of a solution of $NaHSO_3$ (5 mmol) in water (5 mL) over a period of about 15 min; the mixture was stirred at room temperature for 16 h. The products were purified by the same method as previously described.

The products were identified by a comparison of their spectral data with those obtained by esterification between the corresponding acids and alcohols in the presence of sulfuric acid in refluxing dichloromethane. 3,4-Dihydroisocoumarin was identified by a comparison to its previously reported spectral data.[24]

Octyl 2-Bromooctanoate (36): ${}^1H$ NMR ($CDCl_3/Me_4Si$) δ = 4.23—4.14 (m, 3 H), 2.06—1.99 (m, 2 H), 1.69—1.61 (m, 2 H), 1.41—1.26 (m, 20 H), 0.89 (t, J = 6.74 Hz, 6H); ${}^{13}C$ NMR ($CDCl_3/Me_4Si$) δ = 169.9, 65.9, 46.1, 34.9, 31.7, 31.4, 29.1, 28.4, 28.3, 27.1, 25.7, 22.5, 22.4, 14.0, 13.9.

Reaction of 1-Ethoxy-1-heptene (42) with $NaBrO_3/NaHSO_3$ Reagent. The starting material **42** was synthesized using literature procedures.[25] To a solution of $NaBrO_3$ (5 mmol) in water (5 mL) was added **42** (2.5 mmol) followed by the dropwise addition of a solution of $NaHSO_3$ (5 mmol) in water (5 mL) over a period of about 15 min. The mixture was then stirred at 60 °C for 16 h. The products, **43** and **45**, were purified by the same method as previously described. Compounds **44** and **46** were isolated as the ethyl esters, **43** and **45**, respectively, after a treatment of the reaction mixture with ethanol in the presence of a catalytic amount of sulfunic acid.

Ethyl 2-Bromoheptanoate (43): ${}^1H$ NMR ($CDCl_3/Me_4Si$) δ = 4.27—4.11 (m, 3 H), 2.06—1.96 (m, 2 H), 1.38—1.22 (m, 6 H), 1.03 (t, J = 7.26 Hz, 3 H), 0.89 (t, J = 6.60 Hz, 3 H); ${}^{13}C$ NMR ($CDCl_3/Me_4Si$) δ = 169.9, 61.8, 46.1, 34.8, 30.9, 26.9, 22.3, 13.9, 13.8.

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