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Efficient Oxidation of Organic Compounds with Sodium and Silver Bromates $NaBrO_3$, $AgBrO_3$, in Non-Aqueous Solvents in the Presence of Lewis Acids[1)]

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The synthetic utility of sodium and silver bromates in the presence of Lewis acids as catalysts in organic solvents is described. They are efficient for the oxidation of alcohols, acyloins, and hydroquinones to their corresponding carbonyl compounds. The oxidation coupling of thiols performs well in the absence of the catalysts. Silver bromate is able to transform primary benzylic and saturated alcohols, aldehydes, and primary benzylic carbon–hydrogen bonds to their carboxylic acids efficiently. Secondary benzylic carbon–hydrogen bonds are oxidized to their carbonyl compounds with sodium and silver bromates.

The total syntheses of complex molecules demand new methods in different areas of organic chemistry. Therefore, the development of reagents is always rewarding to synthetic organic chemists.

Oxidation is one of the most important classes of organic reactions from different points of views and proceeding them in aprotic organic solvents has found valuable applications in modern organic synthesis. Along this line of interest, reagents are developed and then introduced in the literature.[2—12)]

The bromate anion BrO_3^- is a potentially is an interesting candidate for the oxidation of organic compounds.[13,14)] A literature search has shown that only a few reports are available which deal with the direct oxidation of organic compounds with sodium bromate in strong aqueous acidic media.[3,15—17)] Protic and aqueous media restrict the application of this method for the oxidation of sensitive compounds.

An aqueous solution of sodium bromate has been used as a reoxidant in the reaction of cerium(IV) ammonium nitrate (CAN), cerium(IV) sulfate, and ruthenium trichloride[3)] as oxidants in the oxidation of alcohols to aldehydes and ketones.[18—21)]

Potassium bromate has been used for the bromination of deactivated aromatic compounds in the presence of sulfuric acid.[22)] This oxidant in the presence of bromine in water converts primary alcohols to their corresponding esters and secondary alcohols to their ketones.[23,24)]

The bromate anion BrO_3^- in neutral and alkaline aqueous solutions has an oxidation reduction potential of $E_0=0.61$ V, and in aqueous acidic media a potential equal to 1.52 V.[13,14)] The structure of the bromate ion is that of a triangular pyramid whose O–Br–O angle is about 110 °. The Br–O distance varies with the nature of the cation with which the bromate is associated in the crystals.[13)] Releasing this oxidation potential for the transformation of functional groups in aprotic and non-aqueous solvents is a useful practical achievement.

Lewis acid catalysis in different areas of organic chemistry is well established. Along this line we have reported a promoted selective silylation of alcohols with HMDS in the presence of zinc chloride[1a)] and a selective Ritter reaction[1b)] in the presence of boron trifluoride etherate. Very recently, we have introduced a new method for the conversion of trimethylsilyl ethers to their carbonyl compounds or their carboxylic acids by using $NaBrO_3$ and $AgBrO_3$ in the presence of $AlCl_3$ as a catalyst.[1c)] In this paper we now report, for the first time that silver bromate in the presence of different Lewis acids is able to oxidize different substrates in organic solvents, such as ether, tetrahydrofuran, and acetonitrile, at room temperature or under reflux condition. Sodium bromate can also react as an oxidizing reagent in the presence of Lewis acids in an organic solvent, such as acetonitrile, under reflux condition.

Results and Discussion

Sodium bromate is a cheap and a commercially available compound. Silver bromate was easily prepared from boiling aqueous solutions of potassium bromate and silver nitrate in quantitative yield.[1c)] This stable compound is a white powder which could be stored for months without losing its oxidation ability.

The catalytic effects of several Lewis acids upon the activity of silver bromate were thoroughly studied. For this aim, the oxidation of benzyl alcohol to benzaldehyde in ether and at room temperature in the presence of $AlCl_3$, $SnCl_2{\cdot}2H_2O$, $NbCl_5$, $PdCl_2$, $HgCl_2$, $CoCl_2{\cdot}6H_2O$, $NiCl_2$, $FeCl_3$, $MnCl_2{\cdot}4H_2O$, $ZnCl_2$ and

$BF_3\cdot Et_2O$ was investigated. Surprisingly, only $AlCl_3$, $SnCl_2\cdot 2H_2O$, and $NbCl_5$ were recognized to be effevtive catalysts. The experimental results are given in Table 1. Therefore, the more familiar and the most effective one $AlCl_3$ was chosen to be the catalyst through this investigation. The experimental results for choosing a proper solvent for the oxidation are also tabulated in Table 2. CH_3CN, THF, and Et_2O were suitable solvents for oxidations with $AgBrO_3$ at room temperature or under reflux conditions. Sodium bromate did not work properly at room temperature in the above mentioned solvents but did work in refluxing acetonitrile. The effects of different Lewis acids upon the reactivity of sodium bromate were also investigated. $AlCl_3$ and $SnCl_2\cdot H_2O$ were recognized to be efficient promoters for oxidations with this oxidant, and $AlCl_3$ was chosen to be the catalyst. The optimum molar ratios of $AlCl_3$ towards the substrate and the oxidant varies between 0.1—0.5 mole according to the nature of the substrates (indicated in Tables 3, 4, and 5).

Barium manganate,$^{7)}$ barium permanganate,$^{4)}$ and barium ferrate$^{6)}$ have shown drastic abilities for the oxidation of different functional groups. We therefore examined the oxidation ability of barium bromate. This compound was quite ineffective oxidant under similar conditions. This observation shows the effect of the cation upon the reactivity of the oxo anion.

Table 1. Percent Conversion of Benzyl Alcohol to Benzaldehyde with Silver Bromate in the Presence of Different Lewis Acids in Ether at Room Temperature

Time (min)	5	15	30	60	90	120	150	180
Lewis acid								
$AlCl_3$	27	78	100	—	—	—	—	—
$SnCl_2\cdot 2H_2O$	0	8	19	79	100	—	—	—
$NbCl_5$	0	5	13	27	45	65	80	100
$PdCl_2$	0	0	0	0	0	0	1	3
$HgCl_2$	0	0	0	0	0	0	0	0
$CoCl_2\cdot 6H_2O$	0	0	0	0	0	0	0	0
$NiCl_2$	0	0	0	0	0	0	0	0
$FeCl_3$	0	0	0	0	0	3	4	6
$MnCl_2\cdot 4H_2O$	0	0	0	0	0	1	1	2
$ZnCl_2$	0	0	0	0	0	0	0	0
$BF_3\cdot Et_2O$	0	0	1	3	5	8	8	10

$PhCH_2OH : AgBrO_3 :$ Lewis acid$=1:1:0.2$.

Table 2. Percent Conversion of Benzyl Alcohol to Benzaldehyde with Silver Bromate in the Presence of Aluminium Chloride in Different Solvents at Room Temperature

Time (min)	5	15	30	45	90	120
Solvent						
Ether	27	78	100	—	—	—
Acetonitrile	25	68	78	100	—	—
Tetrahydrofuran	24	63	83	100	—	—
Methylene Chloride	6	21	29	30	32	34
Chloroform	10	27	38	45	49	53
n-Hexane	0	2	8	16	26	31

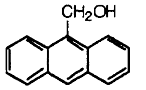
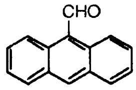
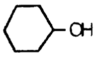
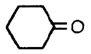
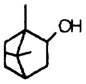
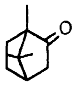
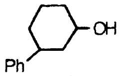
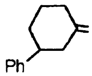
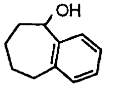
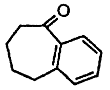
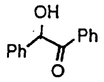
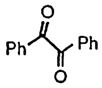
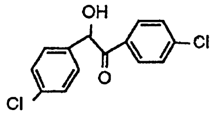
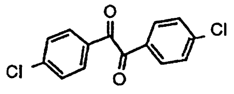
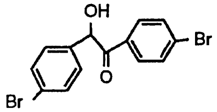
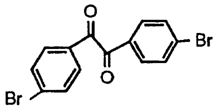
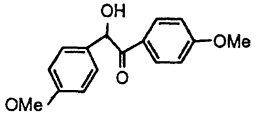
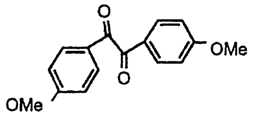
$PhCH_2OH : AgBrO_3 : AlCl_3=1:1:0.2$.

In general, silver bromate was more reactive than its sodium analogue, and also reacted under milder conditions. The effect may be due to a structural change of the anion,$^{13)}$ increasing the partial solubility of the reagent or Lewis acid property of cation. The work-up with silver bromate was usually easier because the generated bromine was converted to bromide ion, which was precipitated as silver bromide. The generated bromine from sodium bromate oxidation remained in the reaction mixture, and should have been eliminated by washing it with sodium sulfite solution.

Primary and secondary alcohols were converted with silver bromate to their corresponding carbonyl compounds very efficiently in the presence of 0.2—0.5 molar ratios of $AlCl_3$ in Et_2O at room temperature. The overoxidation of primary alcohols to their carboxylic acids was not observed under controlled reaction conditions. Sodium bromate under a similar condition was an ineffective oxidant, and only 12—14% conversion was observed. However, this reagent in refluxing acetonitrile, in the presence of $AlCl_3$ was able to convert alcohols to their carbonyl compounds in 40—100% yields (Table 3).

Silver bromate was able to oxidize *p*-hydroquinone to *p*-benzoquinone at room temperature in the presence of 0.2 molar ratio of $AlCl_3$ in ether in excellent yield (Table 3). Although sodium bromate under the same reaction condition produced the quinone in poor yield, in acetonitrile under reflux conditions a yield promotion of the product was observed. Both sodium and silver bromates in refluxing acetonitrile were able to convert acyloins to their diketones in high yields in the presence of 0.5 molar ratio of $AlCl_3$ (Table 3). Primary benzylic and saturated alcohols were also oxidized with silver bromate to their corresponding carboxylic acids in 82—98% yields in the presence of 0.1—0.3 molar ratios of the catalyst in refluxing acetonitrile. Sodium bromate was not able to proceed this transformation easily (Table 3). Silver bromate was an effective oxidant for converting of benzylic and saturated aldehydes to their carboxylic acids in refluxing acetonitrile in the presence of 0.1—0.3 molar ratios of $AlCl_3$. Phthaldehydic acid and phthaldehyde were converted to phthalic anhydride in excellent yields. Sodium bromate under the same reaction condition was not an effective oxidant for the above-mentioned purpose, and the carboxylic acid and the anhydride were produced in low yields (Table 4). Allylic aldehydes were not oxidized to their carboxylic acids properly with these oxidants, and many unidentified fragmentation products were obtained. Silver and sodium bromates in refluxing acetonitrile as well as in the presence of the catalyst were able to oxidize secondary benzylic carbon–hydrogen bonds to their corresponding ketones (Table 5). Although primary benzylic

Table 3. Conversion of Hydroxy Compounds with AgBrO$_3$(I) and NaBrO$_3$(II) to Aldehydes, Ketones, and Carboxylic Acids

No.	Substrate	Product	Yield % (h)		AlCl$_3$ molar ratio		Mp (°C) or Bp (°C)/Torr	
			(I)	(II)	(I)	(II)	Found	Reported
1	PhCH$_2$OH	PhCHO	100 (0.5)[a]	100 (0.5)[a]	0.3	0.3	175—177/760	175—178/760
2	4-ClC$_6$H$_4$CH$_2$OH	4-ClC$_6$H$_4$CHO	95 (0.8)	85 (1)	0.3	0.3	48—50	47—50
3	4-BrC$_6$H$_4$CH$_2$OH	4-BC$_6$H$_4$CHO	93 (1.1)	87 (1)	0.3	0.3	56—58	56—58
4	4-NO$_2$C$_6$H$_4$CH$_2$OH	4-NO$_2$C$_6$H$_4$CHO	85 (2.5)	85 (1)	0.3	0.3	103—105	103—106
5			70 (0.75)	40 (1.5)	0.3	0.3	101—103	100—103
6	PhCHOHPh	PhCOPh	98 (0.25)	87 (1)m	0.3	0.3	48—50	49—51
7	PhCHOHCH$_3$	PhCOCH$_3$	90 (1)	85 (0.75)	0.3	0.3	200—202/760	202—204/760
8	C$_6$H$_{13}$CHOHCH$_3$	C$_6$H$_{13}$COCH$_3$	93 (0.5)	38 (2)[a]	0.2	0.3	172/760	173/760
9			89 (0.5)	39 (2)[a]	0.2	0.3	153—155/760	155/760
10			93 (0.5)	43 (2)[a]	0.2	0.3	178—180	179—181
11			63 (0.25)	12 (2)	0.2	0.3	78—80	78—80
12			90 (0.5)	87 (0.75)			268—270/760	270/760
13	p-Hydroquinone	p-Benzoqinone	90 (0.3)	75 (0.5)			113—115	113—115
14			97 (0.5)	97 (0.75)			94—95	94—95
15			90 (1.5)	94 (2)			197—199	199
16			97 (1)	95 (1)			222—224	223—225
17			52 (1.5)	96 (1.5)			131—133	132—134
18	PhCH$_2$OH	PhCO$_2$H	87 (0.7)	21 (3)			121—123	121—123
19	4-ClC$_6$H$_4$CH$_2$OH	4-ClC$_6$H$_4$CO$_2$H	97 (0.5)	17 (3)	0.1	0.1	237—240	239—241
20	4-BrC$_6$H$_4$CH$_2$OH	4-BrC$_6$H$_4$CO$_2$H	96 (0.5)	16 (3)	0.1	0.1	251—253	252—254
21	4-NO$_2$C$_6$H$_4$CH$_2$OH	4-NO$_2$C$_6$H$_4$CO$_2$H	98 (0.4)	15 (3)	0.1	0.1	237—239	239—241
22	3-NO$_2$C$_6$H$_4$CH$_2$OH	3-NO$_2$C$_6$H$_4$CO$_2$H	93 (1)	0 (2)	0.1	0.1	138—140	139—141
23	2-ClC$_6$H$_4$CH$_2$OH	2-ClC$_6$H$_4$CO$_2$H	88 (0.5)	0 (2)	0.3	0.3	137—139	137—139
24	n-C$_{11}$H$_{23}$CH$_2$OH	n-C$_{11}$H$_{23}$CO$_2$H	82 (0.65)	26 (2)[a]	0.3	0.3	43—45	44—46
25	n-C$_7$H$_{15}$CH$_2$OH	n-C$_7$H$_{15}$CO$_2$H	83 (0.65)	34 (4)[a]	0.3	0.3	236/760	238/760
26	n-C$_6$H$_{13}$CH$_2$OH	n-C$_6$H$_{13}$CO$_2$H	80 (0.65)	24 (2)[a]	0.3	0.3	221—223/760	223/760
27	(CH$_3$)$_2$CHCH$_2$OH	(CH$_3$)$_2$CHCO$_2$H	83 (0.65)	0 (2)[a]	0.3	0.3	175—177/760	175—177/760

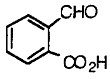
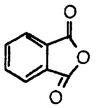
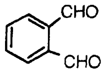
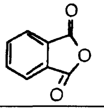
a) GLC yields. b) Conversion of alcohols to carbonyl compounds was performed in Et$_2$O at room temperature (Entries 1—17) and to carboxylic acid in refluxing CH$_3$CN (Entries 18—27) with AgBrO$_3$. c) Conversion of alcohols to carbonyl compounds (Entries 1—17) or carboxylic acids (Entries 18—27) was performed in refluxing CH$_3$CN. Carboxylic acids production required longer reaction time. d) 1 Torr=133.322 Pa.

carbon–hydrogen bonds remained intact with sodium bromate, silver bromate was able to convert them to their carboxylic acids (Table 5).

Silver bromate in the absence of a catalyst in ether or a mixture of ether/ethanol at room temperature was able to oxidize thiols to their disulfides in 65—88% yields (Table 6).

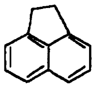
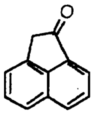
Sodium bromate was quite ineffective for transforming the thiols to their disulfides at room temperature, but in refluxing CH$_3$CN proceeded efficiently in high yields (Table 6). Sulfides and oximes were not cleanly oxidized with these oxidants.

Table 4. Conversion of Aldehydes to Carboxylic Acids with $AgBrO_3$(I) and $NaBrO_3$(II)

No.	Substrate	Product	Yield % (h)		$AlCl_3$ molar ratio		Mp (°C) or Bp (°C)/Torr	
			(I)	(II)	(I)	(II)	Found	Reported[25]
1	PhCHO	$PhCO_2H$	90 (0.25)	23 (3)	0.1	0.2	121—123	121—123
2	4-ClC_6H_4CHO	4-$ClC_6H_4CO_2H$	97 (0.25)	20 (4)	0.1	0.2	237—240	239—241
3	BrC_6H_4CHO	4-$BrC_6H_4CO_2H$	96 (0.3)	15 (0.3)	0.1	0.2	251—253	252—254
4	4-$NO_2C_6H_4CHO$	4-$NO_2C_6H_4CO_2H$	98 (0.25)	10 (3)	0.1	0.2	237—239	239—241
5	4-MeC_6H_4CHO	4-$MC_6H_4CO_2H$	88 (0.5)	0 (3)	0.1	0.2	179—181	179—181
6	4-$MeOC_6H_4CHO$	4-$MeOC_6H_4CO_2H$	82 (0.5)	40 (6)	0.3	—	179—181	180—182
7	4-$ACNHC_6H_4CHO$	4-$ACNHC_6H_4CO_2H$	65 (1)	0 (1)	0.3	—	257—259	257—260
8	n-$C_6H_{13}CHO$	n-$C_6H_{13}CO_2H$	88 (0.5)	0 (1)	0.2	—	221—223/760	223/760
9	$(CH_3)_2CHCHO$	$(CH_3)_2CHCO_2H$	90 (0.5)	0 (1)	0.2	—	152—154/760	153—154/760
10	n-C_4H_9CHO	n-$C_4H_9CO_2H$	93 (0.5)	0 (1)	0.2	—	184—185/760	185/760
11			93 (0.25)	45 (6)	0.2	0.2	131—133	131—133
12			93 (0.25)	45 (6)	0.2	0.2	131—133	131—133

a) In the absence of $AlCl_3$, 4-chlorobenzaldehyde was converted to 4-chlorobenzoic acid in only 5% yield after 2 h with $AgBrO_3$ (Entry 2).

Table 5. Oxidation of Benzylic C–H Bonds with $AgBrO_3$(I) and $NaBrO_3$(II) to Carbonyl and Carboxylic Acid Functions

No.	Substrate	Product	Yield % (h)		$AlCl_3$ molar ratio		Mp (°C) or Bp (°C)/Torr	
			(I)	(II)	(I)	(II)	Found	Reported[25]
1	$PhCH_2Ph$	PhCOPh	95 (0.75)	82 (2)	0.3	0.3	48—50	49—51
2	$PhCH_2CH_3$	$PhCOCH_3$	72 (1.6)	45 (2)	0.3	0.3	202—204/760	202—204/760
3			40 (3.5)	0 (3)	0.3	0.5	118—204/760	121
4	$PhCH_3$	$PhCO_2H$ PhCHO	65 (3) 15	0 (3)	0.5	0.5	121—123 175—177/760	121—123 175—178/760
5	4-$ClC_6H_4CH_3$	4-$ClC_6H_4CO_2H$	91 (3)	0 (3)	0.5	0.5	237—240	239—241
6	4-$BrC_6H_4CH_3$	4-$BrC_6H_4CO_2H$	93 (3)[a]	0 (3)	0.5	0.5	251—253	252—254
7	2-$BrC_6H_4CH_3$	2-$BrC_6H_4CO_2H$	74 (3)	0 (3)	0.5	0.5	137—139	137—139
8	2-$BrC_6H_4CH_3$	2-$BrC_6H_4CO_2H$	74 (3)	0 (3)	0.5	0.5	148—150	147—150

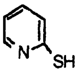
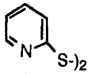
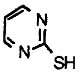
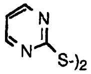
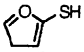
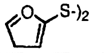
a) In the absence of $AlCl_3$, 4-bromotoluene remained intact after 6 h in the presence of $AgBrO_3$ (Entry 6).

In order to show the oxidation abilities of the two bromates we compared some of our results with some of those reported for halosilanes/chromium trioxide (HSC),[9] bipyridychromium peroxide complexes (BCPC),[5] and barium permanganate (BPM)[4] with respect to their yields and the time required for the reactions (Table 7).

Conclusion

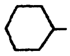
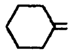
In this study we introduced a new methodology for the oxidation of organic compounds in organic solvents and under aprotic conditions. We have also shown the drastic effect of the cation upon the type, selectivity, and efficiencies of the bromate anion as an oxidant. The oxidation abilities of the oxidants under our studies were quite solvent dependent; by changing the solvents the pathway of the reactions have been changed. Since the reactions were proceeded in a heterogeneous media, the work-up of the reaction mixture was easy and usually, by the simple filtration, followed by a chromatography, a pure product was obtained. The work-up of the reaction mixture of silver bromate was much easier than its sodium analogue, and the yields of the products of silver bromate oxidations were usually higher. Sodium bromate was ineffective for the oxidation of some classes of organic compounds, and was also an ineffective oxidant at room temperature. The stability, easy preparation, and availability of the reagents, easy work-up, rather mild reaction conditions, and high yields of the products, make this method a useful addition to the present methodologies, and make these reagents practical bench-top oxidants.

Table 6. Dimerization of Thiols with $AgBrO_3$ and $NaBrO_3$

No.	Substrate	Product	Yield % (h)		Mp (°C) or Bp (°C)/Torr	
			$AgBrO_3$	$NaBrO_3$	Found	Reported[25]
1	PhSH	PhSSPh	80 (0.2)[a]	90 (1)	57—59	58—60
2	$3\text{-}CH_3C_6H_4SH$	$(3\text{-}CH_3C_6H_4S\text{–})_2$	82 (0.2)[a]	84 (2)	47—49	49
3	$PhCH_2SH$	$(PhCH_2S\text{–})_2$	65 (0.5)[a]	88 (1)	68—70	69—72
4			86 (0.2)[b]	85 (1)	55—57	56—58
5			88 (0.2)[b]	80 (1.3)	141—143	141—145
6			82 (0.2)[a]	90 (1)	—	112—115/0.5

a) Reaction was performed in Et_2O at r.t. b) Reaction was performed in Et_2O/EtOH at r.t. or under reflux condition.

Table 7. Some Comparison of the Results of $AgBrO_3$ and $NaBrO_3$ with Those Obtained from Halosilanes Chromium Trioxide (HSC),[9] 2, 2′-Bipyridylchromium Peroxide (BDCP),[5] and Barium Permanganate (BPM)[4]

No.	Substrate	Product	Yield % (h)		Yield% (h) reported by other methods		
			$AgBrO_3$	$NaBrO_3$	(HSC)[9]	(BPCP)[5]	(BPM)[4]
1	$PhCH_2OH$	PhCHO	100 (0.5)	100 (0.5)	81 (0.75)	95 (1)	92 (0.25)
2	$4\text{-}NO_2C_6H_4CH_2OH$	$4\text{-}NO_2C_6H_4CO_2H$	85 (2.5)	85 (1)	87 (3)	0 (4)	90 (0.5)
3	PhCHOHPh	PhCOPh	98 (0.25)	87 (1)	61 (4)	95 (1)	99 (1)
4	$C_6H_{13}CHOHCH_3$	$C_6H_{13}COCH_3$	93 (0.5)	38 (2)	—	95 (0.2)	90 (0.5)
5			89 (0.5)	39 (2)	50 (20)	85 (3)	60 (2.25)
6	*p*-Hydroquinone	*p*-Benzoquinone	90 (0.3)	75 (0.5)	—	95 (0.2)	90 (0.5)
7	Benzoin	Benzil	97 (0.5)	97 (0.75)	—	90 (3)	96 (0.25)
8	$PhCH_2OH$	$PhCO_2H$	87 (0.7)	21 (3)	—	—	100 (4)
9	$4\text{-}NO_2C_6H_4CH_2OH$	$4\text{-}NO_2C_6H_4CO_2H$	98 (0.4)	15 (3)	—	—	45 (24)
10	$n\text{-}C_7H_{15}CH_2OH$	$n\text{-}C_7H_{15}CO_2H$	83 (0.65)	34 (4)	—	—	10 (10)
11	PhCHO	$PhCO_2H$	90 (0.25)	23 (3)	—	—	90 (3.5)
12	$PhCH_2Ph$	PhCOPh	95 (0.75)	82 (2)	—	—	73 (3.5)
13	$PhCH_2CH_3$	$PhCOCH_3$	72 (1.6)	45 (2)	—	—	75 (4)
14	$PhCH_3$	$PhCO_2H$	65 (3)	0 (3)	57 (45)	—	0 (12)
15	PhSH	PhSSPh	80 (0.2)	90 (1)	93 (0.25)	—	92 (2)
16	$PhCH_2SH$	$(PhCH_2S\text{–})_2$	65 (0.5)	88 (1)	95 (0.5)	100 (0.25)	88 (2.5)

Experimental

General. All of the yields refer to isolated products, unless otherwise indicated. All of the oxidation products were characterized by a comparison of their spectral and physical data with those of known samples. The melting points were determined in open capillaries with a Galen Kamp Melting Point Apparatus. IR spectra were run on Perkin–Elmer IR-157-G and a Perkin–Elmer 781 spectrophotometers. The NMR spectra were recorded on a Hitachi, R-2413, 60 MHz spectrometer. A purity determination of the substrats was accomplished by TLC on silica-gel polygram SIL G/UV 254 plates or GLC on a Schimadzu Model GC-8A instrument with a flame-ionization detector and using a column of 15% carbowax 20M/chromosorb-W acid washed 60—80 mesh. The chemicals were either prepared in our laboratories or purchased from Fluka, BDH and Merck Chemical Companies. The products were separated and purified by different chromatography techniques.

Oxidation of Borneol to Camphor as a Typical Procedure for the Conversion of Alcohols to Their Corresponding Ketones with Silver Bromate. In a round-bottomed flask (100 ml) equipped with a condenser and a magnetic stirrer, borneol (0.46 g, 3 mmol) in acetonitrile (30 ml) was mixed with silver bromate (0.7 g, 3 mmol) and aluminium chloride (0.08 g, 0.6 mmol) and refluxed for 0.5 h. The progress of the reaction was monitored by GLC. The reaction mixture was filtered and the filter cake was washed with acetonitrile and carbon tetrachloride several times (130 ml). The combined filtrates were evaporated on a rotary evaporator. Purification of the resulting crude material by column chromatography on silica gel (eluent: CCl_4/ether: 5/1) afforded pure camphor; yield 0.141 g, 93%, mp 178—180 °C, lit,[25] 179—181 °C, (Table 3).

Oxidation of 1-Dodecanol to Dodecanoic Acid as a Typical Procedure for the Oxidation of Primary Saturated Alcohols to Their Corresponding Carboxylic Acids with Silver Bromate. To a mixture of silver bromate (0.85 g, 3 mmol) and aluminium chloride (0.12 g, 0.9 mmol) in acetonitrile (30 ml) in a two-necked round-bottomed flask (100 ml), a solution of 1-dodecanol (0.56 g, 3 mmol) in acetonitrile (20 ml) was added dropwise under reflux condition. The reaction mixture was further refluxed for 0.4 h and filtered. The solid residue was washed with acetonitrile and carbon tetrachloride several times (50 ml). The combined filtrates were evaporated on a rotary evaporator. The residue was redissolved in ether (60 ml), and the resulting yellow solution treated with a sodium sulfite solution (20%, 50 ml) in order to decompose any excess bromine. The organic layer was separated and the aqueous layer extracted with ether (3×30 ml). The ethereal solution was extracted with 3M NaOH (3×40 ml) (1 M=1 mol dm^{-3}). The organic layer was separated and evaporated. The residue was chromatographed on a silica-gel column in order to isolate the neutral product (ester); yield 9—12%. The aqueous layer was acidified with concd HCl and extracted with ether (3×40 ml). The ether extract was evaporated and the residue was purified on a silica-gel column. The acid was obtained; yield 0.49 g, 82%, mp 43—45 °C, lit,[25] 44—46 °C, (Table 3).

Oxidation of *p*-Bromobenzaldehyde to *p*-Bromobenzoic Acid as a Typical Procedure for the Conversion of Aldehydes to Their Corresponding Carboxylic Acids with Silver Bromate. A solution of *p*-bromobenzaldehyde (0.55 g, 3 mmol) in acetonitrile (40 ml) was treated with silver bromate (0.7 g, 3 mmol) and aluminium chloride (0.04 g, 0.2 mmol) and refluxed for 0.3 h. The progress of the reaction was followed by TLC (eluent: CCl_4/ether: 2/1). After completion of the reaction, the mixture was refluxed further for 0.5 h in order to precipitate the produced bromide as silver bromide. The reaction mixture was filtered and the solid residue was washed with acetonitrile and carbon tetrachloride several times (120 ml). The combined filtrates were evaporated and the resulting crude material was purified on silica-gel plates (eluent: CCl_4/ether: 2/1). Evaporation of the solvent gave pure *p*-bromobenzoic acid; yield 0.58 g, 96%, mp 251—253 °C, lit,[25] 252—254 °C, (Table 4).

Oxidation of Diphenylmethane to Benzophenone as a Typical Procedure for the Conversion of Secondary Benzylic Carbon–Hydrogen Bonds to Their Corresponding Ketones with Silver Bromate. To a solution of diphenylmethane (0.5 g, 3 mmol) in acetonitrile (20 ml), silver bromate (0.71 g, 3 mmol) and aluminium chloride (0.01 g, 0.9 mmol) were added and refluxed for 0.75 h. The progress of the reaction was monitored by TLC (eluent: CCl_4/ether: 4/1). The reaction mixture was filtered and the solid material was washed with acetonitrile and carbon tetrachloride several times (120 ml). The combined filtrates were evaporated to afford a crude product. Purification of the crude product with silica-gel plates (eluent: CCl_4/ether: 4/1) afforded pure benzophenone yield; 0.52 g, 95%, mp 47—49 °C lit,[25] 49—51 ° C, (Table 5).

Oxidation of *p*-Chlorotoluene to *p*-Chlorobenzoic Acid as a Typical Procedure for Conversion of Primary Benzylic Carbon–Hydrogen Bonds to Their Corresponding Carboxylic Acid with Silver Bromate. In a round-bottomed flask (100 ml) equipped with a condenser and a magnetic stirrer, *p*-chlorotoluene (0.37 g, 3 mmol) in acetonitrile (20 ml) was mixed with silver bromate (1.4 g, 6 mmol), and aluminium chloride (0.2 g, 0.15 mmol) and refluxed for 3 h. The progress of the reaction was followed by TLC (eluent: CCl_4/ether: 4/1). The reaction mixture was filtered and the solid residue was washed with acetonitrile and carbon tetrachloride several times (120 ml). The filtrate was evaporated and the resulting crude material purified on silica-gel plates (eluent: CCl_4/ether: 1/1). Evaporation of the solvent afforded pure *p*-chlorobenzoic acid; yield, 0.426 g, 91%, mp 237—240 °C, lit,[25] 239—241 °C, (Table 5).

Oxidation of Thiophenol to Phenyldisulfide as a Typical Procedure for the Conversion of Thiols to Disulfides with Silver Bromate. In a round-bottomed flask (100 ml), a solution of thiophenol (0.033 g, 3 mmol) in ether (30 ml) was treated with silver bromate (0.71 g, 3 mmol); the reaction mixture was stirred magnetically at room temperature for 0.2 h. The progress of the reaction was followed by TLC (eluent: CCl_4/ether: 6/1). The reaction mixture was filtered and the solid redisue was washed with carbon tetrachloride several times (120 ml). The combined filtrates were evaporated, and the resulting crude material was redissolved in ether (60 ml). The reddish-brown solution was treated with a sodium sulfite solution (20%, 50 ml) in order to decompose excess bromine. The organic layer was separated and the aqueous layer was extracted with ether (3×40 ml). The solvent was removed from the combined organic extracts and resulting crude product was purified on silica-gel plates (eluent: CCl_4/ether: 6/1) to afford pure phenyldisulfide; yeild, 0.264 g, 80%, mp 57—59 °C, lit,[25] 58—60 °C, (Table 6).

General Procedure for the Oxidation of Hydroxy Compounds to Their Corresponding Carbonyl Compounds with Sodium Bromate. In a round-bottomed flask (100 ml) equipped with a magnetic stirrer and a condenser, a solution of hydroxy compound (3 mmol) in acetonitrile (30—60 ml) was prepared. Sodium bromate (3—6 mmol) and aluminium chloride (0.6—1.5 mmol) were added to the solution and refluxed for 0.5—2 h. The progress of the reaction was monitored by TLC (eluent: CCl_4/ether: or GLC). The reaction mixture was filtered and the solid residue was washed with acetonitrile and carbon tetrachloride several times (120 ml). The filtrates were combined together and evaporated on a rotary evaporator; the residue was redissolved in ether (50 ml). The resulting yellow solution was treated with sodium sulfite (20%, 50 ml) in order to decompose excess bromine. The organic layer was separated and the aqueous layer was extracted with ether (3×40 ml). The solvent was evaporated and the resulting crude material was purified on silica-gel plates or a silica-gel column with an appropriate eluent. A pure product was obtained; yields 12—100%, (Table 3).

General Procedure for the Oxidation of Aldehydes to Their Corresponding Carboxylic Acids with Sodium Bromate. In a round-bottomed flask (100 ml) equipped with a magnetic stirrer and a condenser, a solution of aldehyde (3 mmol) in acetonitrile (30—50 ml) was prepared. Sodium bromate (3—6 mmol) and aluminium chloride (0.6—1.5 mmol) were added to the solution and refluxed for 3—6 h. The progress of the reaction was monitored by TLC (eluent: CCl_4/ether: 2/1—1/1). The mixture was filtered and the solid material was washed with acetonitrile and carbon tetrachloride several times (100 ml). The combined filtrates were evaporated and the residue was redissolved in ether (50 ml). The resulting yellow solution was treated with 20% aqueous sodium sulfite solution (50 ml) in order to remove excess bromine. The organic layer was separated and the aqueous layer was extracted with ether (3×50 ml). The combined organic extracts were dried on $MgSO_4$ and after evaporation of the solvent, the crude material was purified on silica-gel plates (eluent: CCl_4/ether: 2/1—1/1). Pure carboxylic acid was obtained; yields; 10—54%, (Table 4).

Oxidation of Diphenylmethane to Benzophenone as a Typical Procedure for the Conversion of Secondary Benzylic Carbon Hydrogen Bonds to Their Corresponding Ketones with Sodium Bromate. A solution of diphenylmethane (0.5 g, 3 mmol) in acetonitrile (30 ml) was treated with sodium bromate (0.45 g, 3 mmol) and aluminium chloride (0.42 g, 0.9 mmol). The reaction mixture was stirred under reflux condition for 2 h, and the progress of the reaction was followed by TLC (eluent: CCl_4/ether: 4/1). The reaction mixture was filtered and the solid material was washed with acetonitrile and carbon tetrachloride several times (100 ml). The combined filtrates were evaporated and the residue was redissolved in ether (40 ml). The resulting yellow solution was treated with 20% aqueous sodium sulfite solution (40 ml) in order to remove excess bromine. The organic layer was separated and the aqueous layer was extracted with ether (3×40 ml). The combined extracts were dried on $MgSO_4$ and the solvent was evaporated on a rotary evaporator, to afford crude material. Purification of the crude material with silica-gel plates (eluent: CCl_4/ether: 4/1) afforded pure benzophenone; yield; 0.45 g, 82% mp 48—50 °C, lit,[25] 49—51 °C, (Table 5).

General Procedure for Oxidation of Thiols to Their Corresponding Disulfides with Sodium Bromate. In a round-bottomed flask (100 ml) equipped with a magnetic stirrer and a condenser a solution of thiol (3 mmol) in acetonitrile (30 ml) was treated with sodium bromate (0.453 g, 3 mmol) and refluxed for 1—2 h. The progress of the reaction was monitored by TCL. The reaction mixture was filtered and the solid residue was washed with acetonitrile and carbon tetrachloride several times (100 ml). The combined filtrates were evaporated on a rotary evaporator, and the residue was redissolved in ether (50 ml). The reddish solution was treated with sodium sulfite solution (20%, 40 ml) in order to decompose the excess of bromine. The organic layer was separated and the aqueous layer was extracted with ether (3×40 ml). The combined organic extracts were dried on $MgSO_4$ and the solvent was evaporated. The resulting crude material was purified on silica gel plates with appropriate eluent. Pure disulfide was obtained; yield; 80—90%, (Table 6).

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