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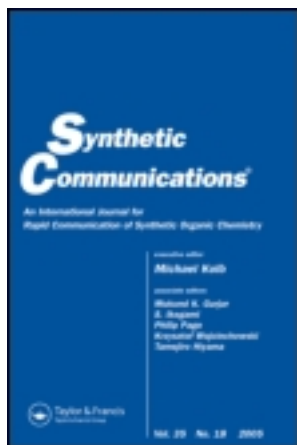
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Silica Sulfuric Acid Catalysis the Oxidation of Organic Compounds with Sodium Bromate

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ABSTRACT

The oxidation of organic compounds by sodium bromate/silica sulfuric acid under solvent-free conditions and in CH_2Cl_2 have been studied at room temperature.

Key Words: Sulfides; Sulfoxides; Alkylarenes; Solvent-free; Thiols; Disulfides; Oxidation; Silica sulfuric acid.

Sodium bromate is commercially available as a stable solid, which potentially is an interesting candidate for the oxidation of organic compounds because of its capability in multi-electron transfer. Thermodynamically sodium bromate is a strong oxidant, but according to the literature, bromate

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itself is not able to oxidize organic compounds. It is usually used in aqueous media in the presence of co-reactants such as: NaHSO_3 ,^[1] HBr ,^[2] Br_2 ,^[3] NH_4Cl ,^[4-6] FeCl_3 ,^[7] cerium(IV) ammonium nitrate (CAN),^[8] H_2SO_4 ,^[9] KHSO_4 ,^[10] $(\text{CH}_3(\text{CH}_2)_3)_4\text{NHSO}_4$,^[11] ion exchange resin (IER),^[12] $\text{NaBrO}_3/\text{Mg}(\text{HSO}_4)_2$,^[13] and HClO_4 .^[14] In most of these oxidation systems, the removal of excess sodium bromate from reaction mixture and separation of bromate or bromide from co-reactant salts is difficult (except of HBr , Br_2 , and IER).

In continuation of our studies on the oxidation of organic compounds with sodium bromate,^[4-7,11-13,15] we have introduced a solid silica sulfuric acid catalytic reaction in the oxidation of the wide range of organic compounds under solvent-free and heterogeneous conditions in CH_2Cl_2 by sodium bromate. This reaction not only overcomes the above-mentioned disadvantages but also has other advantages: easy and quick separation of the products from the oxidant and catalyst, high yields, and faster reactions. Because of a higher concentration of oxidant, lower reaction temperature, less toxic effluent can be used and other waste problems can be minimized. In addition, the catalyst does not have the problem of the limited use of bromate due to its insolubility in almost all organic solvents.

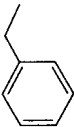
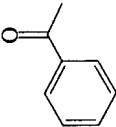
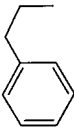
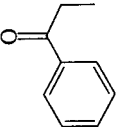
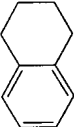
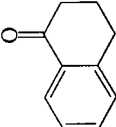
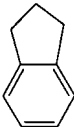
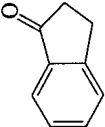
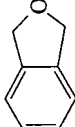
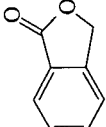
As can be seen in Table 1, alkylarenes are converted into the corresponding α -ketones in good yields under solvent-free conditions at room temperature. As indicated in Sch. 1, the reaction displays an interesting selectivity for compounds containing oxygen as part of a cyclic side chain without C–O bond cleavage. The unique selectivity in the oxidation reaction demonstrated in Sch. 1 is an attractive synthesis, since the resulting ketones are useful intermediates for preparing indenenes and their homologues via reduction and dehydration and dihydroisocoumarines and similar compounds.^[16]

As shown in Table 1, similar results are obtained when reactions are carried out under heterogeneous conditions in which the reductant is dissolved in an inert solvent such as CH_2Cl_2 . However, the reaction times are increased from 2–4.45 hr to 4–6.30 hr at room temperature.

Also, we obtained this reagent capable of oxidizing toluene and *p*-xylene to corresponding carboxylic acid under solvent-free conditions and in CH_2Cl_2 .

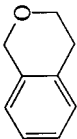
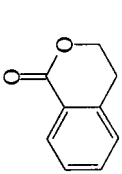
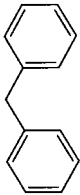
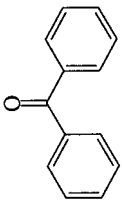
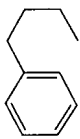
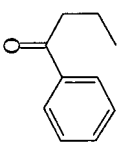
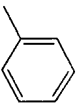
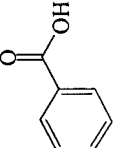
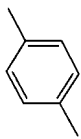
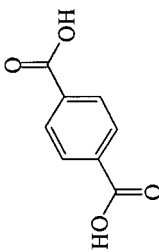
A great number of oxidizing agents can affect the conversion of sulfides into sulfoxides.^[17-21] However, the susceptibility of sulfoxides to further oxidation narrows the choice of reagents for the oxidation of sulfides to sulfoxides. As a consequence, the introduction of new methods and/or further work on technical improvements to overcome the limitations are still important experimental challenges.

Table 1. Oxidation of alkylarenes to the corresponding carbonyl compounds by $\text{NaBrO}_3/\text{SiO}_2\text{-OSO}_3\text{H}$ under solvent-free conditions (I) and in CH_2Cl_2 (II) at room temperature.

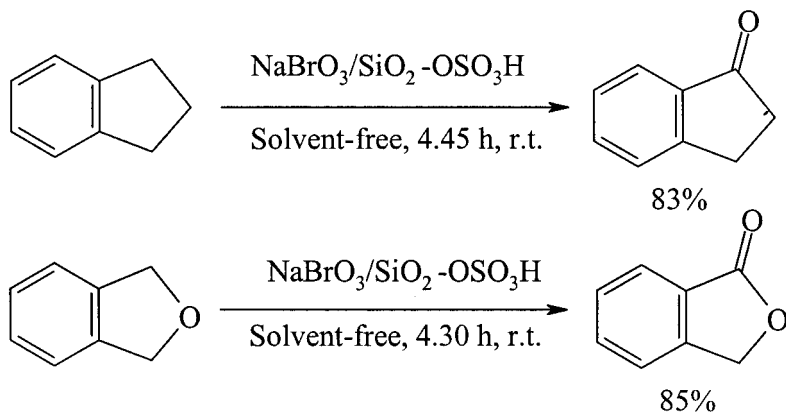
Entry	Reactant	Product	Yield(%)/ time (hr) (I)	Yield(%)/ time (hr) (II)	M.P. of 2,4- DNP (°C)	M.P. or B.P./ product (°C)
1			90/3.30	95/5	247–250 (250) ^a	198–199 (200)/760 ^a
2			92/3	90/5.30	190–191 (191) ^a	215–216 (218)/760 ^a
3			98/3	92/5	—	253–254 (255)/760 ^b
4			83/4.45	85/6	253–256 (258) ^a	41–42 (42) ^b
5			85/4.30	80/6.30	—	72–74 (71–74) ^b

(continued)

Table 1. Continued.

Entry	Reactant	Product	Yield(%)/ time (hr) (I)	Yield(%)/ time (hr) (II)	M.P. of 2,4- DNP (°C)	M.P. or B.P./torr of product (°C)
6			85/3.30	83/5	—	37–39 (38–39) ^b
7			80/4	95/7	237–238 (239) ^a	47–49 (48) ^b
8			88/4.30	85/6	—	228–229 (230)/760 ^a
9			96/2	85/4	—	120–122 (121) ^b
10			95/2.30	90/5	—	Sub. (Sub.) ^b

^aFrom ref. 31.^bFrom ref. 28.



Scheme 1. Oxidation of alkylarenes.

As can be seen from Table 2, aryl and alkyl sulfides are converted into the corresponding sulfoxides with $\text{NaBrO}_3/\text{SiO}_2\text{-OSO}_3\text{H}$ in good yields under solvent-free conditions and in CH_2Cl_2 at room temperature. This is a highly useful reaction for the preparation of sulfoxides (Sch. 2), which are important intermediates in the synthesis of many organic compounds.^[22] The observation that benzyl phenyl sulfide and dibenzyl sulfide (entries 8 and 9) are oxidized to the corresponding sulfoxides indicates the reactions proceed by way of an oxygen transfer mechanism. If the reaction involved electron transfer instead of oxygen transfer, substantial amounts of benzaldehyde would have been formed.^[23,24]

We found that NaBrO_3 in the absence of silica sulfuric acid in CH_2Cl_2 is able to transform dialkyl sulfides to corresponding sulfoxides (entries 11–13), but under the same conditions, this reagent is not capable of oxidizing aryl sulfides (entries 14–16). Both alkyl and aryl sulfides are not oxidized by NaBrO_3 in the absence of silica sulfuric acid under solvent-free conditions at room temperature (entries 11–16).

Thus, we examined the possibility of the oxidation of sulfoxides to sulfones with $\text{NaBrO}_3/\text{SiO}_2\text{-OSO}_3\text{H}$ under solvent-free conditions and CH_2Cl_2 at room temperature. As indicated in Table 2 (entries 17 and 18), both alkyl and aryl sulfoxides are resistant to oxidation after a few days.

As indicated in Table 3, thiols are converted into the corresponding disulfides in good yields under very mild conditions (Sch. 3). The times required compared favorably with those for solvent-free oxidation of thiols using other oxidants.^[25,26] The times required for complete reaction under solvent-free conditions and in CH_2Cl_2 is about equal.

Table 2. Oxidation of alkyl and aryl sulfides to the corresponding sulfoxides by NaBrO₃/SiO₂-OSO₃H under solvent-free conditions (I) and in CH₂Cl₂ (II) at room temperature.

Entry	Reactant	Product	Yield (%) ^a /time (hr) (I)	Yield (%) ^a /time (hr) (II)	M.P. (°C) or B.P. (°C)
1	(CH ₃) ₂ S	(CH ₃) ₂ SO	90/0.50	80/0.50	182–191 (189) ^b
2	(CH ₃ CH ₂) ₂ S	(CH ₃ CH ₂) ₂ SO	85/0.50	83/0.45	103–105 (104) ^b
3	[CH ₃ (CH ₂) ₃] ₂ S	[CH ₃ (CH ₂) ₃] ₂ SO	83/1	85/1	30–32/6 (32/6) ^b
4	[CH ₃ (CH ₂) ₇] ₂ S	[CH ₃ (CH ₂) ₇] ₂ SO	93/0.40	96/1.10	72–74 (71–72) ^c
5	(C ₆ H ₅) ₂ S	(C ₆ H ₅) ₂ SO	75/4	60/24	71–73 (70.5) ^d
6	C ₆ H ₅ SCH ₃	C ₆ H ₅ SOCH ₃	85/1	90/2	32–34 (33–34) ^e
7	C ₆ H ₅ SCH ₂ CH ₃	C ₆ H ₅ SOCH ₂ CH ₃	82/1	85/2.50	147–148/13 (146/13) ^e
8	(C ₆ H ₅ CH ₂) ₂ S	(C ₆ H ₅ CH ₂) ₂ SO	85/2.50	80/3	135–137 (133–135) ^e
9	C ₆ H ₅ CH ₂ SC ₆ H ₅	C ₆ H ₅ CH ₂ SOC ₆ H ₅	75/2	70/3	43–45 (42–44) ^e
10	<i>p</i> -BrC ₆ H ₄ SCH ₃	<i>p</i> -BrC ₆ H ₄ SOCH ₃	90/0.45	83/1	82–83 (83–84) ^e
11 ^e	(CH ₃) ₂ S	(CH ₃) ₂ SO	—/20	85/4	190–191 (189) ^b
12 ^e	[CH ₃ (CH ₂) ₃] ₂ S	[CH ₃ (CH ₂) ₃] ₂ SO	—/20	80/4	28–30/6 (32/6) ^b
13 ^e	[CH ₃ (CH ₂) ₇] ₂ S	[CH ₃ (CH ₂) ₇] ₂ SO	—/20	75/4	73–74 (71–72) ^e
14 ^e	(C ₆ H ₅) ₂ S	No reaction	—/24	—/6	—
15 ^e	C ₆ H ₅ SCH ₃	No reaction	—/24	—/4	—
16 ^e	C ₆ H ₅ SCH ₂ CH ₃	No reaction	—/24	—/4	—
17 ^f	C ₆ H ₅ SOCH ₃	C ₆ H ₅ SOCH ₃	—/72	—/48	—
18 ^f	[CH ₃ (CH ₂) ₇] ₂ SO	[CH ₃ (CH ₂) ₇] ₂ SO	—/24	—/48	—

^aIsolated yield.

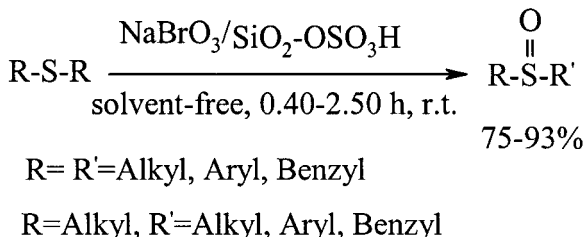
^bFrom ref. 28.

^cFrom ref. 29.

^dFrom ref. 32.

^eIn the absence of SiO₂–OSO₃H.

^fIsolated sulfoxide without any transformation to sulfone.



Scheme 2. Oxidation of sulfides.

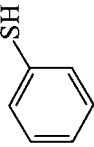
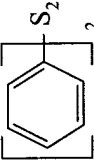

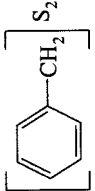
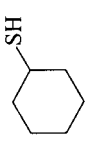
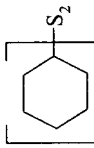
EXPERIMENTAL

All products are known compounds, which were identified by comparison of their physical and spectral data with literature values. Melting points were measured on an Electrothermal 9100 apparatus and are uncorrected. Infrared spectra were recorded as neat films or as KBr pellets on a Shimadzu IR-470 spectrometer. NMR spectra were recorded on a Bruker DRX-500 Avance spectrometer at 500 MHz with CDCl_3 as the solvent and $(\text{CH}_3)_4\text{Si}$ as the internal standard. Yields refer to isolated products or 2,4-dinitrophenylhydrazone derivatives (2,4-DNP) of carbonyl compounds. Silica sulfuric acid was prepared according to published procedure.^[27]

Oxidation of Alkylarenes in Solid State—Typical Procedure

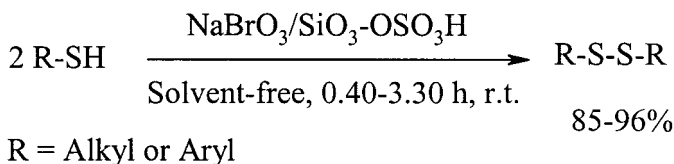
Indan (0.12 g, 1 mmol) was added to a mixture of NaBrO_3 (0.47 g, 3 mmol), $\text{SiO}_2\text{-OSO}_3\text{H}$ (1.10 g, 3 mmol), and wet SiO_2 (0.60 g, 50% w/w) and stirred at room temperature. The progress of reaction was followed by thin layer chromatography (TLC) (eluant: *n*-hexane/EtOAc: 5/1). When the reaction was complete (4.45 hr), methylene chloride (15 mL) was added and the product mixture was filtered through a sinter glass funnel and the residue washed with methylene chloride (10 mL). The filtrate was treated with saturated aqueous sodium thiosulfate (2.5 mL) in order to reduce any residual oxidant. The organic layer was separated and the aqueous layer extracted with methylene chloride (10 mL). The combined organic layers were dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the pure 1-indanone (0.11 g, 0.83 mmol, 83%). This product was identified by comparison with authentic 1-indanone using TLC, melting point (41–42°C; lit.^[28] 42°C) and ^1H NMR (500 MHz, CDCl_3): δ 2.63 (t, J 6.10 Hz, 2H), 3.09 (t, J 6.08 Hz, 2H), 7.08–7.80 (m, 4H).

Table 3. Oxidation of alkyl and aryl thiols to the corresponding disulfides by $\text{NaBrO}_3/\text{SiO}_2\text{-OSO}_3\text{H}$ under solvent-free conditions (I) and in CH_2Cl_2 (II) at room temperature.

Entry	Reactant	Product	Yield (%) / time (hr) (I)	Yield (%) / time (hr) (II)	M.P. (°C) or B.P. (°C)
1			96/2	95/2.30	57–58 (58–60) ^a
2			93/3.30	96/5	70–71 (71–72) ^a
3			85/0.50	88/1.30	126–129 (125–130) ^a
4	$\text{C}_3\text{H}_7\text{SH}$	$(\text{C}_3\text{H}_7)_2\text{S}_2$	85/0.40	90/1.15	193–195 (194) ^a
5	$\text{C}_4\text{H}_9\text{SH}$	$(\text{C}_4\text{H}_9)_2\text{S}_2$	90/0.40	90/1.15	190–191 (192) ^a
6	$\text{C}_8\text{H}_{17}\text{SH}$	$(\text{C}_8\text{H}_{17})_2\text{S}_2$	90/0.40	93/1.30	185–187 (186–188) ^b

^aFrom Ref.^[30].

^bFrom Ref.^[29].



Scheme 3. Oxidation of thiols.

Oxidation of Alkylarenes in CH₂Cl₂—Typical Procedure

Indan (0.12 g, 1 mmol) was added to a mixture of NaBrO₃ (0.47 g, 3 mmol), SiO₂-OSO₃H (1.10 g, 3 mmol), and wet SiO₂ (0.60 g, 50% w/w) in CH₂Cl₂ (20 mL) and stirred at room temperature. The progress of reaction was followed by TLC (eluant: *n*-hexane/EtOAc: 5/1). When the reaction was completed (6 hr), the product mixture was filtered through a sinter glass funnel and the residue washed with methylene chloride (15 mL). The filtrate was treated with saturated aqueous sodium thiosulfate (2.5 mL) in order to reduce any residual oxidant. The organic layer was separated and the aqueous layer extracted with methylene chloride (10 mL). The combined organic layers were dried over anhydrous magnesium sulfate. Evaporation of the solvent gave the pure 1-indanone (0.112 g, 0.85 mmol, 85%). This product was identified by comparison with authentic 1-indanone using TLC, melting point (41°C–42°C; lit.^[28] 42°C).

Oxidation of 4-Bromothioanisol in Solid State— Typical Procedure

4-Bromothioanisol (0.21 g, 1 mmol) was added to a mixture of NaBrO₃ (0.47 g, 3 mmol), SiO₂-OSO₃H (1.10 g, 3 mmol), and wet SiO₂ (0.60 g, 50% w/w) and stirred magnetically for 0.45 hr. The product was separated by washing with methylene chloride (15 mL). This filtrate was washed with saturated aqueous sodium thiosulfate (2.5 mL) in order to reduce any residual oxidant and dried over anhydrous MgSO₄ and filtered. Evaporation of the filtrate afforded the corresponding sulfoxide as a pale yellow solid compound, which was purified by recrystallization from EtOH to afford the pure product; yield, 0.20 g (90%); mp 82°C–83°C (lit.^[29] 83°C–84°C).

Oxidation of Dioctyl Sulfide in CH₂Cl₂—Typical Procedure

Dioctyl sulfide (0.26 g, 1 mmol) was added to a mixture of NaBrO₃ (0.47 g, 3 mmol), SiO₂-OSO₃H (1.10 g, 3 mmol), and wet SiO₂ (0.60 g, 50%

w/w) in CH_2Cl_2 (20 mL) and stirred at room temperature for 1.10 hr. The resulting mixture was filtered and washed with methylene chloride (20 mL). The combined organic layers were washed with saturated aqueous sodium thiosulfate (2.5 mL) in order to reduce any residual oxidant and dried over anhydrous MgSO_4 and filtered. Evaporation of the filtrate afforded dioctyl sulfoxide as a colorless solid, which was purified by recrystallization from EtOH to afford the pure product; yield, 0.26 g (96%); mp 71°C – 73°C (lit.^[29] 71°C – 72°C).

Oxidation of Benzyl Thiol in Solid State—Typical Procedure

Benzyl thiol (0.12 g, 1 mmol) was added to a mixture of NaBrO_3 (0.47 g, 3 mmol), $\text{SiO}_2\text{-OSO}_3\text{H}$ (1.10 g, 3 mmol), and wet SiO_2 (0.40 g, 50% w/w) and stirred magnetically for 3.30 hr. The resulting mixture was filtered and washed with methylene chloride (20 mL). The combined organic layers were washed with saturated aqueous sodium thiosulfate (2.5 mL) in order to reduce any residual oxidant and dried over anhydrous MgSO_4 and filtered. The solvent was evaporated to give benzyldisulfide (0.11 g, 0.46 mmol, 93%), which produced only one TLC spot and melted at 70°C – 71°C (lit.^[30] 71°C – 72°C).

Oxidation of Benzyl Thiol in CH_2Cl_2 —Typical Procedure

Benzyl thiol (0.12 g, 1 mmol) was added to a mixture of NaBrO_3 (0.47 g, 3 mmol), $\text{SiO}_2\text{-OSO}_3\text{H}$ (1.10 g, 3 mmol), and wet SiO_2 (0.40 g, 50% w/w) in CH_2Cl_2 (20 mL) and stirred at room temperature for 5 hr. The resulting mixture was filtered and washed with methylene chloride (20 mL). The combined organic layers were washed with saturated aqueous sodium thiosulfate (2.5 mL) in order to reduce any residual oxidant and dried over anhydrous MgSO_4 and filtered. The solvent was evaporated to give benzyldisulfide (0.12 g, 0.48 mmol, 96%), which produced only one TLC spot and melted at 69°C – 71°C (lit.^[30] 71°C – 72°C).

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