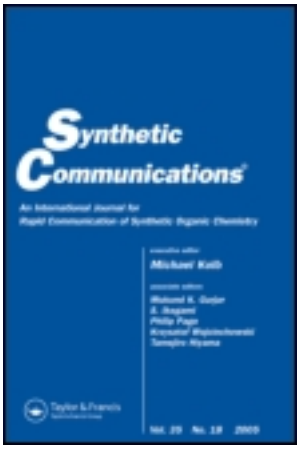

Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsyc20

Fast and Efficient Synthesis of Sulfinamides by the Oxidation of Sulfenamides Using Potassium Fluoride and m-Chloroperoxybenzoic Acid

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Accepted author version posted online: 17 Nov 2011.Published online: 27 Feb 2012.

To cite this article: Mrityunjoy Datta & Alan J. Buglass (2012) Fast and Efficient Synthesis of Sulfinamides by the Oxidation of Sulfenamides Using Potassium Fluoride and m-Chloroperoxybenzoic Acid, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 42:12, 1760-1769, DOI: 10.1080/00397911.2010.543748

To link to this article: http://dx.doi.org/10.1080/00397911.2010.543748

Synthetic Communications®, 42: 1760–1769, 2012

ISSN: 0039-7911 print/1532-2432 online
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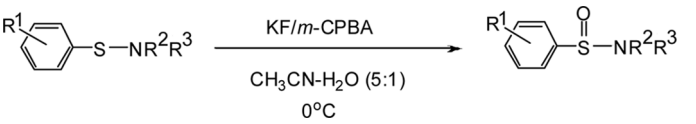
Department of Chemistry, Korea Advanced Institute of Science and Technology, Daejeon, Republic of Korea

GRAPHICAL ABSTRACT



Abstract *A procedure for the synthesis of* N-*alkyl-,* N-*cycloalkyl-,* N,N-*dialkyl-, and* N-*arylarenesulfinamides from the corresponding sulfenamides using KF*/m*–chloroperoxybenzoic acid (CPBA) in CH_3CN-H_2O is described. High efficiency (fast reactions, ease of manipulation, and good yields) and absence of overoxidation are the major advantageous features of this protocol.*

Keywords KF/*m*-CPBA; oxidation; sulfenamides; sulfinamides

INTRODUCTION

The chiral sulfinyl group [R-S(O)-] is an important functional group for the control of numerous asymmetric synthesis because it effectively transfers chirality to a wide range of centers.[1] Sulfinamides[2] are useful sulfinyl chiral auxiliaries for synthesis of amines,[3] aziridines,[4] sulfoximines and related species,[5] benzothiazines,[6] olefins, and ketones.[7] Sulfinamides[2b,c] play pivotal roles in modern asymmetric synthesis as key precursors of chiral molecules and also as organocatalysts in the enantioselective reduction of ketimines.[8] In particular, cyclic sulfinamides[9] are used as synthetic intermediates[10] and have elicited interest in medicinal chemistry.[11] They have also been used in materials science as imaging agents.[12] Moreover, in view of the growing use of sulfonamides[13] as antibacterial agents, hypoglycemic agents, antiviral agents, anti-inflammatory agents, and protease inhibitors[14] we were interested in the synthesis of sulfinamides as these can serve as precursors of corresponding sulfonamides.

Received October 11, 2010.
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There are various procedures reported for the preparation of sulfinamides from sulfinic acids,[15] sulfinates,[16] sulfinyl chlorides,[17] thiosulfinates,[18] *N*-sulfinylamines,[19] oxathiazolidine oxide,[20] sulfoximines,[21] benzothiazines[22] and homolytic substitution at the sulfur atom.[23] These reactions often require two or more synthetic steps. Additionally, sulfinamides can be obtained from sulfonyl chlorides[24] but sulfonamides are also produced as by-products, thus presenting a serious drawback. Also, the harsh conditions frequently required for synthesis of the sulfonyl chlorides and the difficulty in handling and storing these often lachrymatory and water-sensitive agents give cause for concern. Very recently, sulfinamides were synthesized from methyl sulfinates[13] with lithium amide, but the method required strict control of the very low temperature (−78 °C).

There are several reports on the synthesis of sulfinamides via the oxidation of sulfenamides, although each one is rather limited in scope.[25] Sagramora et al.[25a] used (+)-monopercamphoric acid, whereas Davis et al.[25b] and Harpp and Back[25c] used chloroperoxybenzonic acid(*m*-CPBA) in chlorinated hydrocarbon solvents to produce *N*-alkylidenearenesulfinamides and *N*-(alkylsulfinyl)phthalimides, respectively. Moreover, *m*-CPBA has been used to oxidize sulfenamides to sulfonamides, rather than sulfinamides, using a sulfenamide– *m*-CPBA molar ratio of 13.5:30.[25d] Additionally, there is a report on the *N*-chlorosuccinimide oxidation of *N*,*N*-dialkylalkanesulfenamides to the corresponding sulfinamides, in dichloromethane solvent.[25e]

In view of the available methods, our aim was to devise a one-step nonstereoselective synthesis of sulfinamides by oxidation of sulfenamides, using *m*-CPBA or other oxidizing agents. A one-step process would be useful and would increase the exploration of sulfinamide chemistry.

RESULTS AND DISCUSSION

Initially, we used 1 equivalent of *m*-CPBA, which led to the formation of sulfinamide, along with corresponding sulfonamide, within a few minutes, even at −20 °C. However, we could not control the formation of sulfonamide. Moreover, partial solubility of *m*-CPBA in dichloromethane and the separation of by-product *m*-chlorobenzoic acid was also a serious problem. Other oxidizing agents also gave a mixture of sulfinamide and sulfonamide in every case.

The KF/*m*-CPBA reagent, sometimes known as Camps's reagent, was first described by Camps et al.[26] and used in the Baeyer–Villiger oxidation of substituted benzaldehydes to formates and in the epoxidation of alkenes. It was originally used as a solid-phase reagent (i.e., as a slurry in dichloromethane), in a substrate–KF–*m*-CPBA ratio of 0.4:2:1, but the stability of the *m*-CPBA · KF complex was demonstrated to be greater in homogeneous solution.[27]

Recently, KF/*m*-CPBA system has been used in the preparation of 1-phenylsulfonylindolyl methyl sulfoxides[28] and also for the oxidation of thioglycosides to glycosyl sulfoxides[29] without any overoxidation. Previously, the KF/*m*-CPBA system had been successfully employed for the preparation of glycal epoxides,[30] the conversion of epoxy ketones into epoxy esters,[31] and the oxidative conversion of fluorodimethylsilyl groups to hydroxyl groups,[32] the so-called Tamao-Kumada[33] reaction. Also, it has been observed that azides can be converted to nitro compounds and sulfides can be oxidized to sulfones using $HOF \cdot CH_3CN$.[34]

Agnihotri and Misra suggested[29] that KF/*m*-CPBA in CH_3CN-H_2O may produce $KOF \cdot CH_3CN$, whose conjugate acid was demonstrated earlier as a most powerful oxygen-transfer agent[34] and it is noteworthy that the CH_3CN-H_2O (5:1) solvent system was found to be most effective in producing better yields than other commonly used solvents, such as dichloromethane, tetrahydrofuran (THF), or CH_3CN.

On the basis of these observations, we decided to explore the KF/*m*-CPBA system in acetonitrile–water for the general oxidation of sulfenamides (prepared by standard methods[35]) to sulfinamides, in the molar ratio substrate–KF–*m*-CPBA of 0.5:1:1, supposing that the highly electrophilic nature of oxygen atom of $KOF \cdot CH_3CN$ could be used for oxidation of sulfenamides to sulfinamides without overoxidation to sulfonamides.

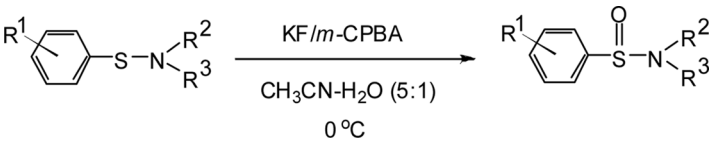
The results of oxidation of *N*-alkyl-, *N*-cycloalkyl-, *N*,*N*-dialkyl-, and *N*-arylarenesulfenamides employing KF/*m*-CPBA in CH_3CN-H_2O at 0 °C (Scheme 1) are presented in Table 1. It can be seen that all 18 substrates were transformed rapidly to the corresponding sulfinamides at 0 °C in good yields. Indeed, under these conditions, the lowest recorded yield was 82% and the slowest oxidation took 20 min.

The rate of oxidation appears to be dependent on both the electronic nature of the aromatic substituents and steric hindrance caused by *ortho* substituents on both *S*-aryl and *N*-aryl rings of *N*-arylarenesulfenamides. By contrast, the nature of the alkyl groups in *N*-alkylarenesulfenamides seems to have little influence on either the reaction rate or yield.

The most rapid oxidation occurs when *para* electron donors (^{t}Bu, Me, MeO) are present in either or both of the aromatic rings of *N*-arylarenesulfenamides (Table 1 entries 8, 9, and 15) and also when present in the *S*-aryl group (entries 6, 7,10, and 11). Conversely, *para* electron-withdrawing groups (Cl, NO_2) in the *S*-aryl group appear to promote slower oxidation (entries 1–3 and 18). Slowest oxidation is claimed for *N*-arylarenesulfenamides with two *ortho* methyl groups in the *N*-aryl ring (entries 2 and 4), probably because of steric hindrance.

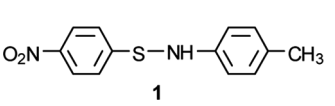
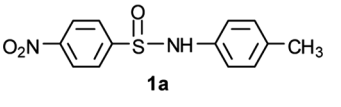
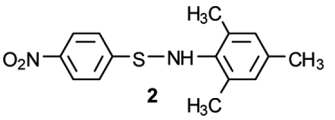
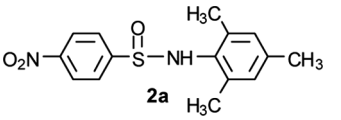
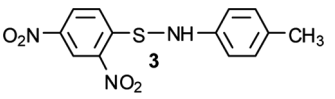
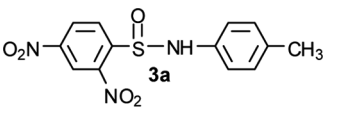
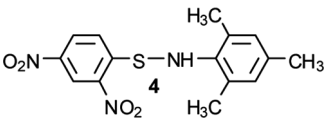
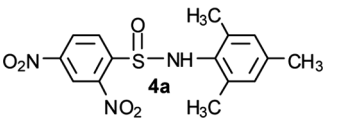
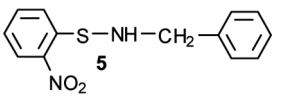
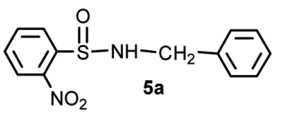
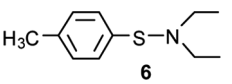
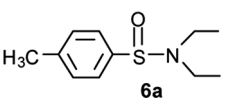
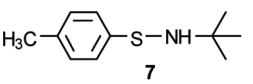
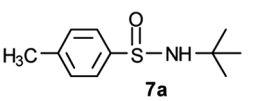
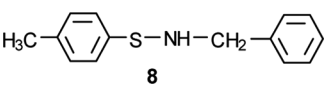
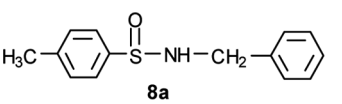
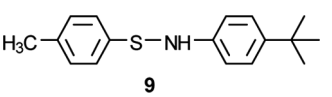
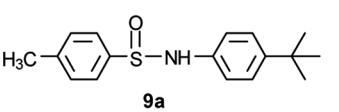
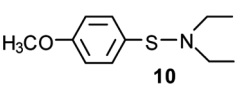
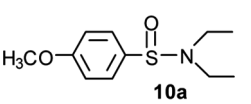
These observations are in accord with the suggestion that KF/*m*-CPBA in acetonitrile water behaves like or generates $KOF \cdot CH_3CN$,[29] whereupon oxygen is transferred to sulfur via nucleophilic attack of a sulfenamide sulfur lone pair of electrons on the highly electrophilic oxygen of HOF, produced by salt hydrolysis of KOF. The presence of *ortho* and/or *para* electron donors in the sulfenamide *S*-aryl ring increases the electron density at sulfur, thereby increasing the reactivity, whereas the presence of electron acceptors in this ring has the opposite effect.

In the solid state, the N-C(aryl) bond in *N*-arylalkanesulfinamides is much shorter (1.408 Å for *N*-pheny-*tert*-butanesulfinamidel) than N-C(alkyl) bonds of *N*-alkylalkanesulfinamides (1.470–1.530 Å), a result of significant interaction of the



Scheme 1. Synthesis of arenesulfinamides.

Table 1. Synthesis of sulfinamides with KF/*m*-CPBA in CH_3CN-H_2O (5:1) at 0 °C

Entry	Substrate	Product	Time (min)[a]	Yield (%)[b]
1	 **1**	 **1a**	12	95
2	 **2**	 **2a**	15	90
3	 **3**	 **3a**	15	84
4	 **4**	 **4a**	20	88
5	 **5**	 **5a**	10	87
6	 **6**	 **6a**	8	90
7	 **7**	 **7a**	8	83
8	 **8**	 **8a**	7	91
9	 **9**	 **9a**	5	94
10	 **10**	 **10a**	8	88

(*Continued*)

Table 1. Continued

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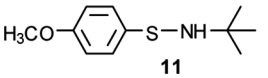
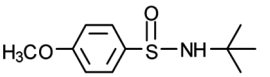
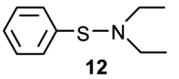
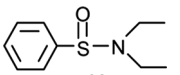
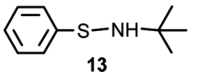
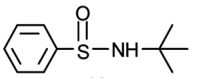
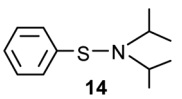
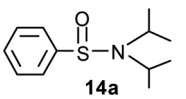
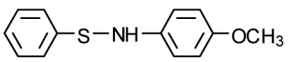
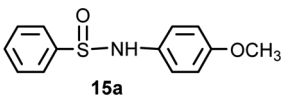
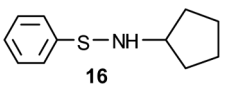
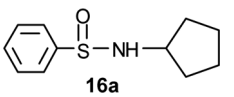
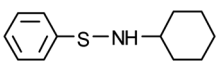
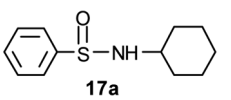
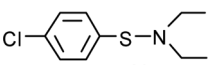
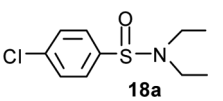
11	 **11**	 **11a**	8	86
12	 **12**	 **12a**	10	85
13	 **13**	 **13a**	10	84
14	 **14**	 **14a**	10	87
15	 **15**	 **15a**	7	88
16	 **16**	 **16a**	10	82
17	 **17**	 **17a**	10	90
18	 **18**	 **18a**	12	82

[a]Time to completion of reaction, as determined by TLC (silica gel, dichloromethane–hexane [1:1]).

[b]Yields refer to chromatographically isolated pure products, which were identified by their spectral characteristics (IR, ^{1}H NMR, ^{13}C NMR, EIMS) and microanalysis (**1a**–**4a**) or by comparison of melting point and spectral data with literature data (**5a**–**18a**).

nitrogen lone pair with the *N*-aryl π–system.[36] Such interaction lowers the electron density at sulfur. However, the aforementioned interaction is weakened if there is a *para* electron donor in the *N*-aryl ring, as indicated by a rather longer N-C(aryl) bond (1.423 Å) in *N*-(4-methoxyphenyl)-*tert*-butanesulfinamide.[37] It is reasonable to suppose that this argument can be applied to the corresponding sulfenamides, thus explaining why those with a powerful *N*-aryl electron donor in the *para* position (Table I; entries 9 and 15) are among the most reactive.

CONCLUSION

In conclusion, we have synthesized several sulfinamides from the corresponding sulfenamides using KF/*m*-CPBA in CH_3CN-H_2O. High reaction rates, manipulative simplicity, generality, lack of serious hazards, and absence of overoxidation are the main advantages of this method. We hope this to be a method of choice for nonstereoselective preparation of sulfinamides, particularly for high-throughput chemistry.

EXPERIMENTAL

Reagents and chemicals were purchased from commercial sources and used as received. Chromatographic separations were carried out using Sigma-Aldrich silica gel (230–400 mesh). Analytical thin-layer chromatographym (TLC) was performed on Sigma-Aldrich silica-gel TLC plates with ultraviolet indicator. The melting points reported were measured with a Reichert hot-stage apparatus and are uncorrected. Infrared (IR) spectra were recorded on a Perkin-Elmer 1600 series Fourier transform (FT)–IR spectrometer. ^{1}H NMR and ^{13}C NMR spectra were recorded at room temperature on a Bruker ARX-400 spectrometer at 400 MHZ and 100 MHZ respectively and are reported in parts per million (ppm, δ) from tetramethylsilane (TMS: δ 0.0 ppm).

General Procedure for the Synthesis of Sulfinamides from Sulfenamides

Typical experimental procedure for **1a**: 70% *m*-CPBA (660 mg, 3.84 mmol) was added to a solution of KF (223 mg, 3.84 mmol) in CH_3CN-H_2O (20 mL, v/v 5:1), and the reaction mixture was stirred at 0 °C for 30 min. To this ice-cooled reaction mixture, *N*-(4-methylphenyl)-4-nitrobenzenesulfenamide (500 mg, 1.92 mmol, entry 1) was added in aliquots and stirred for 12 min. After completion of the reaction (TLC-monitored), it was then poured into saturated aqueous $NaHCO_3$ solution and extracted with ethyl acetate (3×30 mL). The organic extracts were combined, dried over $MgSO_4$, and concentrated under reduced pressure. The residue was purified by column chromatography (CH_2Cl_2– hexane, 1:4) to afford *N*-(4-methylphenyl)-4-nitrobenzenesulfinamide (**1a**) as a yellow powder (503 mg, 95%). Other sulfinamides were prepared in an analogous manner.

Spectroscopic and Other Data for 1a–18a

***N*-(4-Methylphenyl)-4-nitrobenzenesulfinamide (1a).** Mp 150–151 °C; FTIR (KBr) ν_{max} (cm^{-1}) 3030, 1530, 1511, 1476, 1432, 1346, 1097, 1069, 1014, 936, 856. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, $J = 7.0$, 1.6 Hz, 2H), 7.96–7.93 (m, 2H) 7.06 (d, $J = 8.2$ Hz, 2H), 6.95 (d, $J = 8.3$ Hz, 2H), 6.11 (bs, 1H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.23, 149.70, 136.50, 134.75, 130.11, 127.17, 124.10, 120.85, 20.77. EIMS *m*/*z* (%) 276 ($M^{+\cdot}$, 16), 107 (40), 106 ($M^{+\cdot}$– ArSO, 100). Anal. calcd. for $C_{13}H_{12}N_2O_3S$: C, 56.52; H, 4.34; N, 10.15. Found: C, 56.55; H, 4.31; N, 10.13.

***N*-(2,4,6-Trimethylphenyl)-4-nitrobenzenesulfinamide (2a).** Mp 140 °C; FTIR (KBr) ν_{max} (cm^{-1}) 3320, 3037, 2918, 1605, 1531, 1482, 349, 1144, 1095, 1069, 1013, 854. ^1H NMR (400 MHz, $CDCl_3$) δ 8.39 (dd, $J = 7.0$, 1.7 Hz, 2H), 8.09 (dd, $J = 6.9$, 1.7 Hz, 2H), 6.91 (s, 2H), 5.57 (bs, 1H), 2.37 (s, 6H), 2.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.65, 149.73, 136.54, 133.87, 133.51, 129.68, 126.78, 124.08, 20.72, 19.03. EIMS m/z (%) 304 ($M^{+\cdot}$, 55), 170 ($M^{+\cdot}$– ArNH, 12), 134 ($M^{+\cdot}$– ArSO, 100), 119 (11), 91 (50). Anal. calcd. for $C_{15}H_{16}N_2O_3S$: C, 59.21; H, 5.26; N, 9.21. Found: C, 59.23; H, 5.20; N, 9.25.

***N*-(4-Methylphenyl)-2,4-dinitrobenzenesulfinamide (3a).** Mp 134 °C; FTIR (KBr) ν_{max} (cm^{-1}) 3106, 3079, 2359, 1669, 1605, 1541, 1511, 1345, 1083, 106, 1016, 858. ^1H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, $J = 2.1$ Hz, 1H), 8.57 (dd, $J = 8.5$, 2.1 Hz, 1H), 8.42 (d, $J = 8.5$ Hz, 1H), 7.01 (d, $J = 8.2$ Hz, 2H), 6.88 (d, $J = 8.2$ Hz, 2H), 5.95 (bs, 1H), 2.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.65, 147.60, 146.29, 136.03, 135.58, 130.08, 129.48, 128.0, 121.87, 120.57, 20.82. EIMS *m/z* (%) 322 (MH^+, 12), 321 ($M^{+\cdot}$, 72), 240 (12), 216 (9), 106 ($M^{+\cdot}$– ArSO, 100). Anal. calcd. for $C_{13}H_{11}N_3O_5S$: C, 48.56; H, 3.43; N, 13.08. Found: C, 48.58; H, 3.44; N, 13.05.

***N*-(2,4,6-Trimethylphenyl)-2,4-dinitrobenzenesulfinamide (4a).** Mp 133 °C; FTIR (KBr) ν_{max} (cm^{-1}) 3035, 2367, 1597, 1541, 1479, 1347, 1105, 927, 910, 833, 816. ^1H NMR (400 MHz, $CDCl_3$) δ 8.96 (d, $J = 2.2$ Hz, 1H), 8.64 (dd, $J = 8.5$, 2.2 Hz, 1H), 8.49 (d, $J = 8.5$ Hz, 1H), 6.84 (s, 2H), 5.68 (s, 1H), 2.23 (s, 3H), 2.21 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.64, 149.04, 146.20, 136.97, 134.87, 131.76, 129.82, 128.53, 128.04, 120.36, 20.80, 18.88. EIMS *m/z* (%) 349 ($M^{+\cdot}$, 22), 215 ($M^{+\cdot}$– ArNH, 10), 134 ($M^{+\cdot}$– ArSO, 100). Anal. calcd. for $C_{15}H_{15}N_3O_5S$: C, 51.58; H, 4.30; N, 12.03. Found: C, 51.55; H, 4.33; N, 12.01.

Compounds 5a–18a. Compounds **5a**–**18a** have been reported previously, and each was identified by comparison of actual and literature melting points and/or spectral data, as follows. **5a** (mp 90 °C; lit.[24] 88–89 °C), **6a** (colorless oil[38]), **7a** (mp 52–54 °C; lit.[39] 50–52 °C), **8a** (mp 76–77 °C; lit.[39] 77–79 °C), **9a** (mp 126 °C; lit.[24] 128 °C), **10a** (colorless oil[13]), **11a** (orange oil[13]), **12a** (colorless oil[40]), **13a** (mp 76–78 °C; lit.[13] 75–76 °C), **14a** (colorless liquid[24]), **15a** (mp 106–108 °C; lit.[24] 105–106 °C), **16a** (mp 88–90 °C; lit.[24] 88–89 °C), **17a** (mp 114 °C; lit.[24] 116–118 °C), and **18a** (colorless oil[13]).

ACKNOWLEDGMENT

Financial support from Korea Advanced Institute of Science and Technology (KAIST) is gratefully acknowledged.

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