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trans-(±)-2-*tert*-Butyl-3-phenyloxaziridine: A Unique Reagent for the Oxidation of Thiolates into Sulfenates

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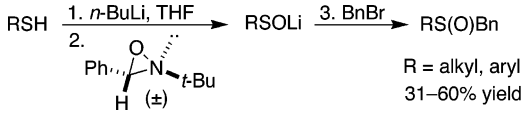
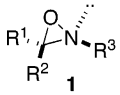


Aliphatic thiolates were efficiently converted into the corresponding sulfenates by smooth oxidation with *trans*-(±)-2-*tert*-butyl-3-phenyloxaziridine at room temperature (five examples). Subsequent electrophilic quench with benzyl bromide led to sulfoxides (*S*-alkylation) in good to moderate yields. Application of the protocol to an aromatic substrate was also successful. This work represents the first valuable example of the use of this poorly active oxidizing agent in synthetic organic chemistry without the need for activating conditions.

Since their discovery 50 years ago, oxaziridines **1**, characterized by a reactive strained C, N, O three-membered ring, have been widely investigated in organic synthesis as both aminating and oxygenating agents.[1] The predominance of one process over another is significantly affected by varying the substitution pattern on the nitrogen atom. It has been established that the amino group transfer is the normal pathway for *N*-H, *N*-alkyl, *N*-acyl, and *N*-alkoxycarbonyl systems.[2] In contrast, a shift of reactivity toward the oxygen center[3] is observed with structures possessing bulky or electron-withdrawing groups, from which *N*-sulfonyl derivatives have particularly emerged. These reagents have been extensively used in various oxygen transfer reactions with nucleophiles, thus including epoxidation of olefins, enolate-mediated hydroxylation of carbonyl compounds and oxidation of sulfides to sulfoxides.[4]



	R^1	R^2	R^3
a	*t*-Bu	Me	SO_2Ph
b	*t*-Bu	Me	$P(O)Ph_2$
c	H	H	*t*-Bu
d	4-$NO_2C_6H_4$	H	*t*-Bu
e	Ph	H	*t*-Bu

A few years ago, an original[5] synthetic utility involving lithium thiolates (R^1S^-) as substrates was reported by our group[6] which allowed an efficient and straightforward[7] access to the corresponding sulfenate salts (R^1SO^-) (Scheme 1). The unusual *N*-sulfonyloxaziridine **1a** derived from pinacolone was thus introduced as the ideal reagent. Treatment in situ with aliphatic halides led to sulfoxides **3** in good to excellent yields. The scope of the reaction sequence is broad with successful applications toward aryl, 1-alkenyl, and 1-alkynyl species. In contrast, extension of the protocol with the more nucleophilic alkanethiolates (R^1 = alkyl) failed. Instead of the desired monooxidation product, the sulfinate salt (R^1SO_2Li) was isolated as a consequence of an unwanted double oxidation reaction. Similar disappointing results were also obtained with a screening of a range of milder *N*-sulfonyl derivatives,[8] thus exemplifying the difficulty to control the sulfenate oxidation stage.[9]

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(7) Alternative routes to sulfenate species consist of manipulation of sulfoxides possessing an appropriate functionality, the most relevant contributions being the oxidative cleavage of 1-alkynyl sulfoxides with a Pd(0)-catalyst followed by transmetalation with Et_2Zn, an addition/elimination methodology with β-sulfinylacrylates, a retro-Michael reaction initiated by a base from β-sulfinyl esters, and finally, the fluoride-mediated deprotection of 2-(trimethylsilyl)ethyl sulfoxides. See ref 5a and: (a) Caupène, C.; Boudou, C.; Perrio, S.; Metzner, P. *J. Org. Chem.* **2005**, *70*, 2812−2815. (b) Maitro, G.; Prestat, G.; Madec, D.; Poli, G. *J. Org. Chem.* **2006**, *71*, 7449−7454. (c) Maitro, G.; Vogel, S.; Prestat, G.; Madec, D.; Poli, G. *Org. Lett.* **2006**, *8*, 5951−5954. (d) Foucoin, F.; Caupène, C.; Lohier, J.-F.; Sopková−de Oliveira Santos, J.; Perrio, S.; Metzner, P. *Synthesis* **2007**, 1315−1324.

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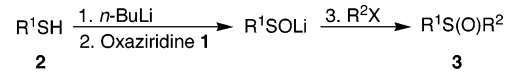
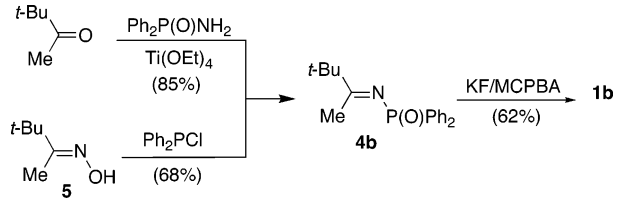
SCHEME 1. Sulfenates by Oxidation of Thiolates



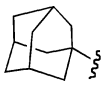
SCHEME 2. Synthesis of *N*-Phosphinoyloxaziridine 1b



We were then convinced that variations on the nitrogen center could afford an appropriately configured reagent. A literature survey clearly indicates that incorporation of a phosphinoyl group[10] could perfectly be adapted, as illustrated by the reduced reactivity by a factor of 7 of 3,3-dimethyl-2-(diphenylphosphinoyl)oxaziridine relative to its sulfonyl congener in the oxidation of methyl phenyl sulfoxide into the corresponding sulfone.[11] Ultimately if still milder oxidants are required, *N*-*tert*-butyl structures might also be potential candidates.[12] These compounds are almost inert as shown with the trivial oxidation of dimethyl sulfide into DMSO induced by the dihydro compound **1c** which is complete within 10 h at 80 °C.[12b] More valuable but sparse applications require activating conditions such as the use of high pressures techniques (800 MPa at 100 °C) or introduction of Brønsted or Lewis acids.[13] We wish to present herein the results of our investigation to provide sulfenate anions in the alkane series, which led us to evaluate various families of oxaziridines.

We decided to focus first on the unreported *N*-phosphinoyloxaziridine **1b** that possesses a backbone similar to **1a**. This would rapidly allow us to gauge the impact of the nitrogen susbtituent in our reaction. The synthesis of **1b** was carried out as described in Scheme 2. Heating pinacolone and diphenylphosphinamide in the presence of $Ti(OEt)_4$ (2 equiv) followed by hydrolysis with aqueous 2 M NaOH solution and filtration of the titanium oxides led to the corresponding *N*-phosphinoylimine **4b** in 85% crude yield, without any further purification required.[14] Alternatively, imine **4b** can be prepared in 68% from pinacolone oxime **5** via reaction with chlorodiphenylphosphine in the presence of triethylamine followed by free radical rearrangement[15] of the initially formed phosphorus(III) oxime ester. *N*-Phosphinoylimines often tend to decompose[16] to the parent carbonyl compound and phosphinic amide either on standing or during attempted purification, but imine precursor **4b** proved to be strikingly stable and purification by flash column chromatography on silica gel can be achieved. Subsequent oxidation mediated by a CH_2Cl_2 suspension of anhydrous 1:2 *m*-CPBA and potassium fluoride (4 equiv) initially devised by Camps[17] afforded oxaziridine **1b** in 62% yield, exclusively as a *trans* stereoisomer (see the Supporting Information for the X-ray structure).

TABLE 1. Oxidation of Thiolates with *N*-Phosphinoyloxaziridine 1b According to Scheme 1

entry	thiol	R^1	*T* (°C)	solvent	sulfoxide[a]	yield[b] (%)
1	**2a**	Bn	−78	THF	**3a**	0
2	**2b**	c-C_6H_{11}	−78	THF	**3b**	0
3	**2c**	*t*-Bu	−78	THF	**3c**	10
4	**2d**		−78	THF	**3d**	6
5	**2c**	*t*-Bu	−100	Trapp mixture[c]	**3c**	3

[a] All reactions were performed on a 1 mmol scale in solvent (5 mL) using thiol **2**, *n*-BuLi (1.05 equiv), oxaziridine **1b** (1.05 equiv), and BnBr (2 equiv). [b] Isolated yield. [c] THF/Et_2O/pentane (4:4:1).

Evaluation of the newly synthesized *N*-phosphinoyloxaziridine **1b** in the title reaction began with benzyl thiol **2a** according to the following protocol. Initial deprotonation was carried out with *n*-BuLi in THF solution and the resulting lithium thiolate was treated at −78 °C with 1.05 equiv of **1b** for 30 min. Benzyl bromide was then added to trap the eventual sulfenate salt produced. After standard workup, analysis of the crude mixture unfortunately revealed the absence of the anticipated sulfoxide **3a** (Table 1, entry 1). A similar failure was also observed starting with cyclohexanethiol (entry 2). Use of *tert*-butyl mercaptan led to a first hit with detection of sulfoxide **3c** albeit in a low 10% yield (entry 3). Another tertiary substrate, i.e., 1-adamantanethiol **2d**, was also subjected to the reaction sequence to afford target **3d** in only 6% yield (entry 4). In all those experiments, oxidizing agent **1b** was totally consumed as a result of a preferred over oxidation into sulfinates.[18] This reaction was not minimized when the reaction was carried out at a lower temperature (−100 °C) using this time the Trapp mixture[19] as

(8) We previously reported that the outcome of the oxidation reaction with aromatic thiolates highly depends on the oxaziridine structure: Sandrinelli, F.; Perrio, S.; Beslin, P. *Org. Lett.* **1999**, *1*, 1177−1180.

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solvent (entry 5). Important to mention is that the inevitable presence of the parent imine **4b** in all crude products did not disturb the final purification on silica gel.[20] Having established that alkanesulfinates were still the major oxidation products using an *N*-phosphinoyl reagent, we then decided to direct our attention toward the milder *N*-*tert*-butyl derivatives.

As the substitution on the ring carbon center is known to have a pronounced influence on the reactivity of oxaziridines, we targeted the three structures **1c**−**e** already described in the literature, namely 2-*tert*-butyloxaziridine, 2-*tert*-butyl-3-(4-nitrophenyl)oxaziridine, and 2-*tert*-butyl-3-phenyloxaziridine. A comparative study for the oxidation rate of triphenyl phosphine in its oxide indicates that this collection displays really distinct oxidizing powers, with the phenyl compound **1e** as the less reactive one.[12b] All compounds were easily and efficiently prepared by condensation[21] of the appropriate carbonyl compound with *tert*-butyl amine to afford the corresponding Schiff base[22] with subsequent oxidation[23] mediated with the Camps complex. In the case of **1d** and **1e**, a single diastereoisomer was produced with a *trans* configuration.[22b]

Oxaziridines **1c**−**e** were then tested with our reaction sequence using *tert*-butanethiol, for which in our hands encouraging results were already observed. As we could expect, this set of reagents exhibits a slower reactivity than all the preceding ones, no reaction taking place at −78 °C. We then decided to examine for each the influence of the temperature, the results being summarized in Figure 1. The best conditions for the simplest oxaziridine **1c** involve oxidation at −40 °C and allowed formation of *tert*-butyl benzyl sulfoxide in a markedly improved 38% yield (compare with the 10% value previously obtained). An even better yield of 46% was observed with a slow addition of the oxidant with a syringe pump over 3 h. Starting with the *p*-nitrobenzaldehyde derivative **1d**, an optimal yield of 43% was obtained at −30 °C. However, over-oxidation into sulfinates was never suppressed with both reagents **1c** and **1d**. Finally,

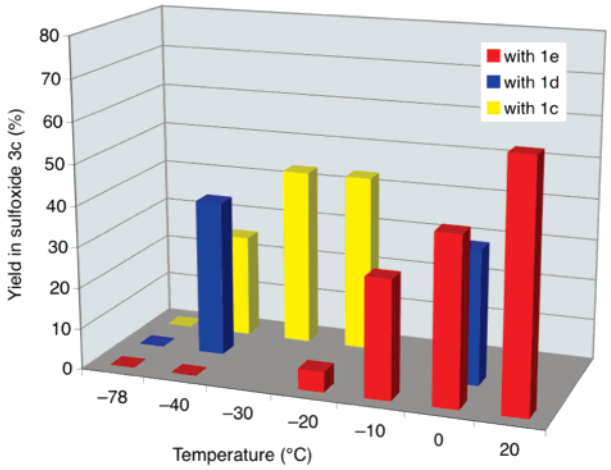
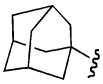


FIGURE 1. Reaction of *tert*-butanethiolate (R^1 = *t*-Bu) in THF with oxaziridines **1c**−**e** and benzyl bromide (R^2 = Bn) according to Scheme 1.

TABLE 2. Oxidation of Thiolates with Oxaziridine 1e According to Scheme 1

entry	thiol	R	sulfoxide[a]	yield[b] (%)
1	**2c**	*t*-Bu	**3c**	59
2	**2d**		**3d**	52[c]
3	**2b**	c-C_6H_{11}	**3b**	42[c]
4	**2a**	Bn	**3a**	58[c]
5	**2e**	*n*-Bu	**3e**	31[c]
6	**2f**	4-MeC_6H_4	**3f**	60[c]

[a] All reactions were performed on a 1 mmol scale at 20 °C in THF (5 mL) using thiol **2**, *n*-BuLi (1.05 equiv), oxaziridine **1e** (1.05 equiv), and BnBr (2 equiv). [b] Isolated yield. [c] Sulfinate salt was detected in the aqueous layer.

phenyloxaziridine **1e** was found to be the most desirable oxidant. While it appeared to be totally inert at temperatures below −20 °C, the anticipated sulfoxide was produced in 29% yield at −10 °C. A better yield of 41% yield was obtained at the higher temperature of 0 °C. Inspection of the ^{1}H NMR spectrum of the crude product revealed that some unreacted oxidant was still present. As a consequence, the temperature was raised to 20 °C, thus giving an increase to a 59% yield along with total disappearance of the oxaziridine. Analysis of the aqueous layer indicated that over oxidation into the sulfinate salt did not take place. In summary, these studies revealed that optimal reaction conditions involve the treatment of lithium thiolates in THF solution with phenyl oxaziridine **1e** (1.05 equiv) at 20 °C for 30 min.

The scope of the reaction sequence in terms of substrate structure was examined by reacting a series of lithium thiolates with oxaziridine **1e**, and the results are recorded in Table 2. An additional successful example involving a tertiary thiolate was obtained with 1-adamantanethiol **2d**, and the final sulfoxide **3d** was isolated in 52% yield (entry 2). Secondary thiolates are also suitable substrates, as highlighted by the formation of the cyclohexyl derivative **3b** in 42% yield (entry 3). Benzylic and *n*-butyl derivatives were also produced in 58 and 31% yields respectively (entries 4−5). The protocol can also be extended to aromatic substrates, thus supplying *p*-tolyl sulfoxide **3f** in 60% yield (entry 6). The oxaziridine reagent was systematically

(18) Lithium sulfinates produced didn't react with alkyl halides to furnish sulfones under the reaction conditions. After workup, they were isolated from the aqueous layer and easily characterized by ^{1}H NMR spectroscopy. As a single equivalent of oxidant was employed, sulfinate formation implied systematically the presence of unreacted thiolate, which upon the electrophilic quench was readily converted in situ into the corresponding thioether.

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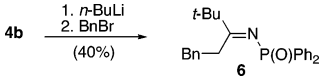
(20) When an excess of *n*-BuLi was introduced, benzylated imine **6** was detected. Its formation was interpreted by hydrogen abstraction on the methyl substituent of the liberated imine **4b**, followed by *C*-alkylation of the resulting azaallyl anion. As a checking experiment, direct reaction with **4b** in the presence of a stoichiometric amount of base furnished **6** in 40% yield. For precedents with other imines, see: (a) Smith, J. K.; Bergbreiter, D. E.; Newcomb, M. *J. Am. Chem. Soc.* **1983**, *105*, 4396−4400. (b) Ito, K.; Nitta, M. *Heterocycles* **1993**, *36*, 2247−2254. (c) Kobayashi, T.; Kariuchi, H.; Kato, H. *Bull. Chem. Soc. Jpn* **1991**, *64*, 392−395.



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consumed in all experiments but over oxidation into sulfinate salts was not avoided with most of the substrates. Furthermore, benzyl sulfenate esters which could result of a competing *O*-alkylation of the ambident sulfenate intermediate were never detected.[24]

In conclusion, we showed that the oxidation of thiolate in sulfenate is amenable to the generation of aliphatic species, using *trans* 2-*tert*-butyl-3-phenyloxaziridine (**1e**). The necessity to employ an *N*-*tert*-butyl structure, which in fact is a very weak oxidant, is the hallmark of this chemistry. The reaction conditions being also compatible with an aromatic substrate, this reagent is obviously the most general one for this reaction. This work also broadens the scope of applications of oxaziridines, with an emphasis of the ability to dramatically tune their oxidizing power through variations of substituents on the carbon and nitrogen centers. Future work will seek to develop further developments of sulfenic acid anions in organic synthesis.

Experimental Section

Typical Procedure for the Synthesis of Sulfoxides via Sulfenate Salts. A solution of *n*-BuLi (760 μL of a 1.47 N solution in hexanes, 1.12 mmol, 1.05 equiv) was added dropwise at 20 °C to a solution of thiol **2** (1 mmol, 1 equiv) in THF (5 mL). After 15 min, a solution of *N*-*tert*-butyloxaziridine **1e** (193 mg, 1.09 mmol, 1.09 equiv) in THF (2 mL) was added slowly at 20 °C. The reaction mixture was stirred at 20 °C for 30 min, treated with benzyl bromide (250 μL, 2 mmol, 2 equiv), and stirred for 4 h. H_2O (10 mL) was added, and the solution was extracted with ethyl acetate (3 × 25 mL). The combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue was purified on silica gel to afford sulfoxide **3.**

Benzylsulfinylmethylbenzene 3a.[25] Following the general procedure described above with thiol **2a** (R^1 = Bn, 120 μL, 1 mmol) as substrate, sulfoxide **3d** was obtained after chromatography purification (diethyl ether) as a white solid (133 mg, 0.58 mmol, 58%). TLC (diethyl ether) R_f = 0.26. Mp: 129−131 °C, CH_2Cl_2 (lit.[25] 133 °C). ^{1}H NMR (400 MHz) δ: 3.88 and 3.93 (AB, J = 13.0, 2H), 7.27−7.41 (m, 10H). ^{13}C NMR (63 MHz) δ: 57.3, 128.3, 128.9, 130.2, 130.3. IR (KBr, cm^{-1}) ν: 1030, 2926, 2956, 3030. MS (EI) *m/z*: 230 (M^+, 3), 91 (100), 65 (21).

[(1-Adamantylsulfinyl)methyl]benzene 3d. Following the general procedure described above but at 0 °C with 1-adamantanethiol **2d** (160 mg, 0.95 mmol) as substrate, sulfoxide **3d** was obtained after chromatography purification (pentane/diethyl ether, 50:50) as a white solid (136 mg, 0.5 mmol, 52%). TLC (diethyl ether) R_f = 0.36. Mp: 148−150 °C. ^{1}H NMR (400 MHz) δ: 1.75−1.84 (m, 6H), 1.90−2.00 (m, 6H), 2.23 (br s, 3H), 3.71 and 3.85 (AB system, J = 12.8, 2H), 7.30−7.37 (m, 5H). ^{13}C NMR (100 MHz) δ: 28.9, 35.4, 36.5, 51.1, 56.2, 128.1, 128.9, 130.2, 132.2. IR (KBr, cm^{-1}) ν: 1020, 2900, 3030. MS (CI, isobutane) *m/z*: 313 [$(M + C_3H_3)^+$, 4], 275 (MH^+, 100), 259 (24), 199 (4), 135 (23), 107 (11), 91 (5), 79 (13). HRMS (CI, isobutane): calcd for $C_{17}H_{23}OS$ 275.1470, found 275.1458

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Supporting Information Available: General methods of the Experimental Section, full spectroscopic data for **1**−**6**, and X-ray structure of **1b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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