Guanidine Bases in Synthesis: Extending the Scope of the Corey–Chaykovsky Epoxidation

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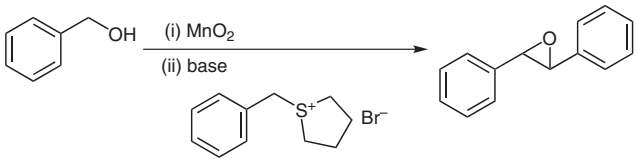
Abstract: Guanidine bases, such as 1,5,7-triazabicyclo[4.4.0]dec-1-ene (TBD) or 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-1-ene (MTBD), are highly effective reagents for the in situ generation of sulfonium ylides from sulfonium salts in Corey–Chaykovsky epoxidation reactions of aldehydes. These reactions proceed rapidly to produce the corresponding epoxides in excellent yields and with high selectivity for the *trans* product. Significantly, this reagent combination is applicable to both nonenolizable and enolizable aldehydes and α,β-unsaturated aldehydes.

Key words: guanidine bases, in situ ylide generation, Corey–Chaykovsky epoxidation, epoxides, enolizable aldehydes

Endeavors to replace multistep chemical syntheses with more efficient synthetic sequences are a goal that has attracted considerable recent interest, and a number of elegant and diverse strategies have been reported as solutions to this problem.[1] In particular, both sequential and tandem reaction sequences, in which multiple reactions are combined into a single synthetic operation, offer significant potential advantages over traditional methodology.[2] Typical approaches involve the coupling of transformations to allow for two, or more, reactions to be carried out in a single reaction vessel without the requirement to purify intermediate products. In addition to the obvious improvement in efficiency and operational simplicity, a further benefit of this strategy is that unstable products need not be isolated, as they are rapidly transformed by a subsequent reaction into more stable products which can be isolated.

We recently demonstrated that unactivated diols undergo an efficient tandem oxidation–olefination sequence in the presence of manganese dioxide (MnO_2) and phosphonium ylides to produce α,β-unsaturated hydroxy esters.[3] In this protocol, the required ylides are generated in situ from a phosphonium salt in the presence of an organic guanidine base, such as 1,5,7-triazabicyclo[4.4.0]dec-1-ene (TBD). We reasoned that sulfonium ylides should be generated under similar conditions by employing sulfonium salts in place of phosphonium salts. This would potentially allow access to a highly flexible strategy for the synthesis of epoxides since these bases are tolerant of both aerobic conditions and moisture, and are used in a monophasic organic solvent system. Furthermore, given our previous experience in the development of tandem reaction sequences involving phosphonium salts, we rationalized that both a sequential and a tandem oxidation–epoxidation strategy, using alcohols in place of aldehydes and incorporating an oxidation step into the reaction sequence, was an achievable goal (Scheme 1).



Scheme 1 Manganese dioxide mediated sequential oxidation–epoxidation reactions

Epoxides are important functional groups in synthesis as they undergo stereospecific nucleophilic ring opening to yield bifunctional compounds or rearrangement reactions to give carbonyl compounds.[4] Amongst the nonoxidative routes developed to date, the synthesis of epoxides from sulfonium ylides and carbonyl compounds continues to be a vibrant area of research, and has been developed into highly flexible methodology for the preparation of these valuable materials.[5] Subsequent research has identified a number of innovative routes for the generation of sulfonium ylides,[5,6] however, the most commonly encountered reaction conditions continue to employ basic reagents to deprotonate a sulfonium salt. The choice of bases studied to date, however, remains limited to a relatively small number of candidates. Indeed, the use of alternative reagents, in particular organic bases, has received surprisingly little attention, and to date, only the very strong phosphazene bases have routinely been employed for ylide generation in epoxidation processes.[7]

The application of nonionic nitrogen bases as reagents for organic synthesis has found considerable application, however, they have yet to achieve the same widespread use as their ionic counterparts. The application of these reagents, and the more recently introduced guanidine bases, has provided a myriad of opportunities to expand into base-mediated chemistry previously carried out under inert atmospheres and anhydrous reaction conditions.[8] Given our previous experience with guanidine bases, their reported use as highly efficient promoters for the generation of nucleophiles[9] and, importantly, their very low nucleophilicity, we identified these reagents as ideal candidates for further study. Therefore, our initial investigations considered the ability of sulfonium salt **1**, readily

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synthesized from tetrahydrothiophene and benzyl bromide, to undergo deprotonation in the presence of a range of organic bases (Figure 1) and subsequent reaction with benzaldehyde to produce stilbene oxide (Table 1).

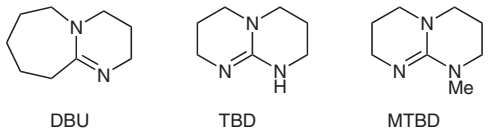
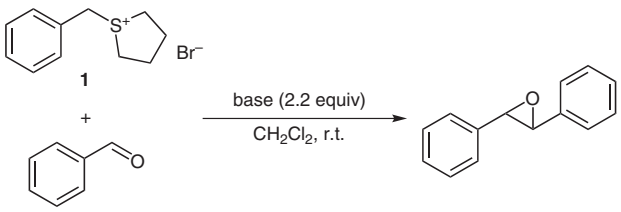


Figure 1 Structures of organic bases

Unsurprisingly, triethylamine gave no conversion of the aldehyde into epoxide as this is the weakest of the four bases employed, however, when 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) was employed, a good conversion of benzaldehyde into stilbene oxide was observed. On changing to the more basic (TBD) or 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-1-ene (MTBD), we were delighted to observe that complete consumption of benzaldehyde occurred in less than 10 minutes to give stilbene oxide as the only observable product with high selectivity for the expected *trans* isomer. As these guanidine bases are similar in both reactivity and base strength, TBD was chosen for all further reactions due to ease of handling and the lower cost of this reagent.

Table 1 Synthesis of Stilbene Oxide



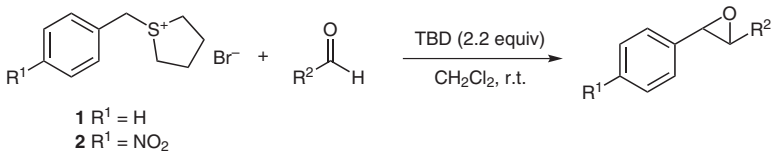
Entry	Time	Base	Conversion (%)[a]
1	24 h	Et_3N	0
2	24 h	DBU	71
3	10 min	TBD	100
4	10 min	MTBD	100

[a] Determined by ^1H NMR analysis of the crude reaction mixture.

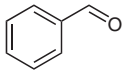
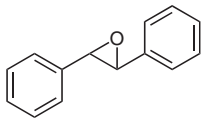
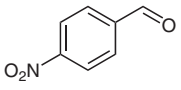
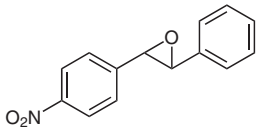
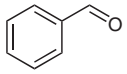
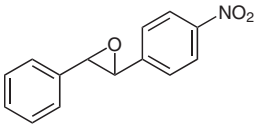
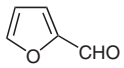
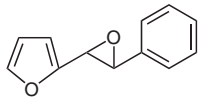
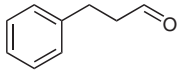
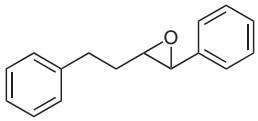
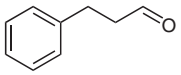
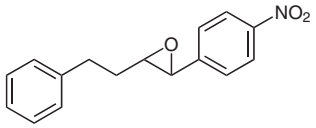
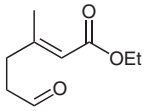
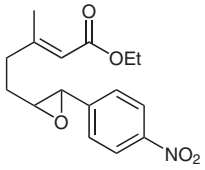
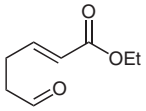
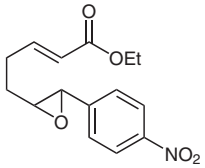
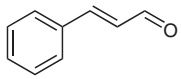
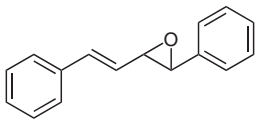
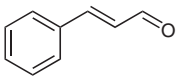
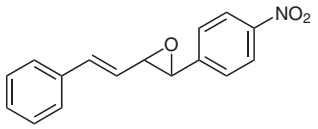
The scope and generality of this protocol was next investigated using sulfonium salts **1** and **2** and a range of structurally diverse aldehydes (Table 2). In general, the reaction between aldehydes and sulfonium ylides derived from **1** and **2** in the presence of an excess of TBD in dichloromethane resulted in excellent isolated yields of the corresponding epoxides with high selectivity observed for the *trans* isomer. In the case of *p*-nitrostilbene oxide, the reaction employing the unsubstituted sulfonium salt **1** and *p*-nitrobenzaldehyde led to an excellent yield of the epoxide with high selectivity for the *trans* product, typically in excess of 90% (entry 2). Interestingly, however, when the substituted sulfonium salt **2** is employed in the reaction with benzaldehyde (entry 3), the epoxide is again produced in excellent isolated yield, however, in this case, enhanced selectivity for the *trans* isomer is observed. This improvement in the *cis*/*trans* selectivity in the latter case probably reflects the increased stability of the sulfonium ylide derived from **2**. This ensures that *syn*-betaine formation is more reversible, so ensuring that the reaction proceeds through the more stable *anti*-betaine and hence produces the *trans* product.[10] Reaction of 2-furaldehyde and sulfonium salt **1** led to complete conversion of the aldehyde into the corresponding epoxide (entry 4), which was isolated in good recovered yield. Given the acid-sensitive nature of this material, and the low isolated yields commonly reported for this product, no further purification of the crude reaction mixture was attempted.[7b,11] Most gratifying was the observation that this protocol is compatible with enolizable aldehydes. The range of carbonyl substrates employed in ylide-mediated epoxidation reactions has traditionally been limited to nonenolizable aromatic aldehydes, since the basic reaction conditions required for ylide generation generally precludes the use of enolizable aldehydes, which are prone to enolization and subsequent aldol condensation or elimination reactions.[5a,12] We were therefore delighted to observe that 3-phenylpropionaldehyde is converted into the corresponding epoxide in reactions employing sulfonium salts **1** or **2** in high isolated yields (entries 5 and 6). This example clearly highlights the importance of electronic factors in ylide-mediated epoxidation reactions, as poor *cis*/*trans* selectivity is observed for the reaction employing sulfonium salt **1**. In contrast, reactions employing the more stable ylide produced from **2** provide the epoxide with excellent selectivity for the *trans* product. Finally, we considered the reaction of the α,β-unsaturated esters **3** and **4** that contain enolizable aldehydes which also undergo reaction to give the corresponding epoxides (entries 7 and 8). In the case of **3**, in which an alkene substituent is present, the reaction proceeds to give the epoxide as the only observable product in good yield and with high selectivity for the *trans* product.[10] In the case of aldehyde **4** and cinnamaldehyde (entry 9 and 10), however, the isolated yields of epoxide are limited by either a competing cyclopropanation reaction or by degradation of the product during purification.[7,10] The observed selectivity for the epoxide product in the case of **3** probably reflects preferential addition to the carbonyl functionality due to a sterically disfavored Michael addition.[10] Disappointingly, and in line with previous studies,[5e,6b] the reaction of ketone substrates, such as acetophenone and cyclohexanone, gave only trace quantities of the desired epoxide products and starting materials were isolated unchanged from these reactions.

We next explored the feasibility of employing alcohols as substrates and incorporating a manganese dioxide mediated oxidation step into the reaction sequence to produce the corresponding aldehydes in situ. One-pot preparative procedures offer significant potential advantages over linear sequences, and tandem oxidation protocols employing

Table 2 TBD-Mediated Sulfur Ylide Epoxidation Reactions of Aldehydes

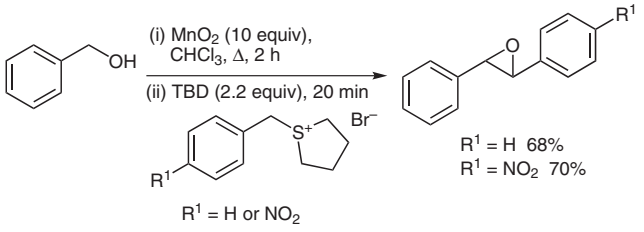


1 R^1 = H
2 R^1 = NO_2

Entry	Aldehyde	Salt	Product	Yield (%)[a]	*trans*/*cis*[b]
1		**1**		88	92:8
2		**1**		93	91:9
3		**2**		91	>98:2
4		**1**		100[c]	95:5
5		**1**		84	54:46
6		**2**		84	>98:2
7	 **3**	**2**		80	93:7
8	 **4**	**2**		35	95:5
9		**1**		100[c]	>98:2
10		**2**		38	>98:2

[a] All compounds gave satisfactory spectroscopic data.
[b] Determined by ^{1}H NMR analysis of the crude reaction mixture.
[c] Conversion based on consumption of the starting material.

manganese dioxide in particular are well documented, and take advantage of the mild, heterogeneous nature of this oxidant.[13] As we envisaged oxidizing only activated alcohols in these protocols, and since the oxidation step is the limiting factor in the reaction sequence, we employed activated MnO_2 as oxidant in contrast to our previous studies.[14] We chose to initially demonstrate the viability of such a sequential oxidation–epoxidation process using benzyl alcohol as a model substrate. In these reactions, the base and sulfonium salt are added on completion of the initial oxidation step, as in our experience, this strategy generally requires less perturbation of the original reaction conditions.[3,15] Thus, benzyl alcohol was subjected to an initial oxidation step performed using an excess of activated manganese dioxide (10 equiv) in chloroform at reflux. On completion of the oxidation step, the reaction mixture was cooled to room temperature and sulfonium salt **1** or **2** (2 equiv) and TBD (2.2 equiv) were added. We were highly gratified to observe that under these conditions, the corresponding stilbene oxides were produced in good isolated yields with high selectivity for the *trans* product again observed (Scheme 2).



Scheme 2 Sequential oxidation–epoxidation reactions of benzyl alcohol

In conclusion, we have demonstrated that guanidine bases, such as TBD and MTBD, are highly effective reagents for the generation of sulfonium ylides from sulfonium salts **1** and **2**. Importantly, when these ylides are generated in the presence of aldehydes, the corresponding epoxides are rapidly produced in excellent yields with high to excellent selectivity for the *trans* product. In contrast to previous approaches, this protocol is applicable to both nonenolizable and enolizable aldehydes and α,β-unsaturated aldehydes, considerably extending the scope of this widely used methodology. Furthermore, we have demonstrated that it is possible to generate sulfonium ylides in the presence of an oxidant, such as manganese dioxide, allowing for the development of an efficient sequential oxidation–epoxidation protocol. All of the reaction sequences described are tolerant of both moisture and aerobic conditions, greatly simplifying the synthetic protocol as no special precautions, such as the requirement for inert atmospheres, low temperatures, anhydrous solvents, or specialist equipment are required. The scope of this reagent combination for the generation of epoxides in sequential and tandem oxidation–epoxidation protocols is currently under investigation.

Typical Experimental Procedure for the Preparation of Sulfonium Salts 1 and 2

***S*-Benzyltetrahydrothiophenium Bromide (1)**

A mixture of tetrahydrothiophene (3.57 g, 40.6 mmol) and benzyl bromide (1 equiv, 6.94 g, 40.6 mmol) in acetone (20 mL) was stirred for 19 h at r.t. At this time, the resultant solid was collected in a Buchner funnel and washed with additional acetone (2 × 50 mL). The solid was dried overnight in a desiccator to give *S*-benzyltetrahydrothiophenium bromide (**1**, 7.51 g, 72%) as a white solid; mp 120–123 °C (lit.[6f] 119–121 °C).

IR (neat): ν_{max} = 3451, 770, 699, 586 cm^{-1}.

^1H NMR (400 MHz, D_2O): δ = 2.06–2.27 (4 H, m), 3.21–3.46 (4 H, m), 4.41 (2 H, s), 7.31–7.47 (5 H, m).

^{13}C NMR (100 MHz, D_2O): δ = 130.9, 130.6, 130.2, 128.8, 46.1, 43.0, 28.8.

MS (ES): *m/z* = 259 $[M]^+$, 179 $[M - Br]^+$.

HRMS (ES): *m/z* calcd for $C_{11}H_{15}S$ $[M - Br]^+$, 179.0889; found: 179.0888.

Typical Experimental Procedure for the Preparation of Epoxides from Sulfonium Salts 1 and 2 and Aldehydes

2,3-Diphenyl Oxirane

A mixture of benzaldehyde (76 mg, 0.72 mmol), *S*-benzyltetrahydrothiophenium bromide (**1**, 2 equiv, 0.37 g, 1.44 mmol) and TBD (2.2 equiv, 0.22 g, 1.58 mmol) in CH_2Cl_2 (10 mL) was stirred for 10 minutes at r.t. At this time, the reaction mixture was washed with H_2O (2 × 50 mL) and the aqueous layer extracted with CH_2Cl_2 (3 × 20 mL). The organic layers were combined, dried over $MgSO_4$ and the solvent removed to give a colorless oil which was purified by column chromatography (2% EtOAc–hexane) to give 2,3-diphenyl oxirane (*trans*/*cis* = 92:8, 124 mg, 88%) as a white solid; mp 68–70 °C (lit[4c] 66–67 °C).

IR (neat): ν_{max} = 1493, 1453, 846, 747, 696 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.98 (2 H, s), 7.42–7.52 (10 H, m).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 137.7, 129.1, 128.8, 126.1, 63.3.

MS (ES, NH_3): *m/z* = 214 $[M + NH_4]^+$, 197 $[M + H]^+$.

HRMS (ES, NH_3): *m/z* calcd for $C_{14}H_{16}ON$ $[M + NH_4]^+$: 214.1226; found $[M + NH_4]^+$: 214.1229.

Typical Experimental Procedure for the Preparation of Epoxides by a Sequential Oxidation–Epoxidation Process

2-(4-Nitrophenyl)-3-phenyl Oxirane

A mixture of benzyl alcohol (63 mg, 0.58 mmol) and MnO_2 (Aldrich activated, 10 equiv, 0.51 g, 5.80 mmol) in $CHCl_3$ (10 mL) was stirred for 2 h at reflux. At this time, the reaction was cooled to r.t. and TBD (2.2 equiv, 0.18 g, 1.28 mmol) and *S*-(4-nitrobenzyl) tetrahydrothiophenium bromide (2 equiv, 0.36 g, 1.16 mmol) were added. After stirring for a further 20 min, the MnO_2 was removed by filtration through a Celite pad, which was then washed with additional $CHCl_3$ (2 × 10 mL). The reaction mixture was then washed with H_2O (2 × 20 mL), the extracted layer was then washed with CH_2Cl_2 (3 × 20 mL). The organic layers were combined and dried over $MgSO_4$ and the solvent removed to give an orange oil which was purified by column chromatography (2% EtOAc–hexane) to give 2-(4-nitrophenyl)-3-phenyl oxirane (*trans*/*cis* = 100:0, 98 mg, 70%) as a pale yellow solid; mp 124–126 °C (lit[5e] 125–128 °C).

IR (neat): ν_{max} = 1600, 1513, 1340, 1106, 838 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.88 (1 H, d, *J* = 2 Hz), 4.00 (1 H, d, *J* = 2 Hz), 7.34–7.47 (5 H, m), 7.55 (2 H, dt, *J* = 9, 2 Hz), 8.28 (2 H, dt, *J* = 9, 2 Hz).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 148.3, 144.8, 136.5, 129.3, 129.2, 126.7, 126.0, 124.3, 63.8, 62.1.

MS (ES, NH_3): *m/z* = 259 $[M + NH_4]^+$, 242 $[M + H]^+$.

HRMS (ES, NH_3): *m/z* calcd for $C_{14}H_{15}O_3N_2$ $[M + NH_4]^+$: 259.1077; found: 259.1082.

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