



Sequential- and tandem-oxidation–epoxidation reactions employing guanidine bases



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ABSTRACT

1,5,7-Triazabicyclo[4.4.0]dec-1-ene (TBD) and 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-1-ene (MTBD) promote the efficient formation of sulfonium ylides from sulfonium salts in the Corey–Chaykovsky epoxidation of aldehydes and provide excellent yields of the corresponding epoxides. This reaction protocol can be further adapted to allow for the development of both sequential and tandem-oxidation–epoxidation protocols from aldehydes generated in situ by manganese dioxide (MnO₂) or barium manganate (BaMnO₄) mediated oxidation reactions.

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1. Introduction

Epoxides are highly versatile reagents, which undergo a range of synthetic transformations, including stereospecific nucleophilic ring-opening to yield bifunctional compounds, and rearrangement reactions to give cyclised products or carbonyl compounds.¹ Amongst the most effective and widely used non-oxidative route to epoxides developed to date has been by the reaction of sulfonium ylides generated in the presence of carbonyl compounds, the so-called Corey–Chaykovsky epoxidation.² Since its initial disclosure, this area has developed into a vibrant research field, with subsequent work leading to the development of effective protocols for the asymmetric synthesis of epoxides.³ While there have been some elegant strategies for the generation of the required sulfonium ylides,⁴ typical protocols rely on the use of basic reagents to generate the sulfonium ylide by deprotonation of a sulfonium salt. In general, this has meant employing bases, which are either air- and moisture-sensitive or inorganic in nature and, which require biphasic or aqueous conditions. It is surprising therefore that the use of moisture tolerant, non-ionic organic bases has received relatively little attention given their successful application in related synthetic transformations.⁵ Previous work has demonstrated that reagents, such as 1,8-diazabicyclo[5.4.1]undec-7-ene (DBU), 1,5,7-triazabicyclo[4.4.0]dec-1-ene (TBD), 7-methyl-1,5,7-triazabicyclo[4.4.0]dec-1-ene (MTBD) and tetramethyl guanidine are highly effective reagents for the generation of anions from a range of activated substrates,⁶ including phosphonium salts and phosphonates in olefination reactions,⁷ sulfoxonium salts in cyclopropanation reactions,⁸ nitroalkanes in Henry reactions⁹ and dialkyl phosphites

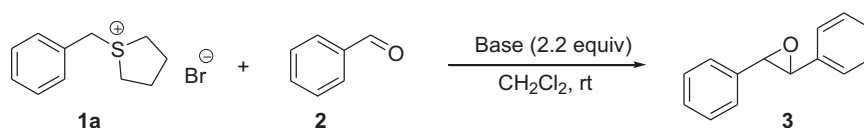
in Michael additions.¹⁰ We required an efficient method for the generation of sulfonium ylides for the synthesis of structurally diverse epoxides, and were attracted to the potential of extending the range of these organic bases to encompass sulfonium ylide-mediated epoxidation procedures. Herein we report the successful application of TBD and MTBD for the generation of sulfonium ylides in Corey–Chaykovsky epoxidation procedures, and the extension of this methodology to the development of sequential and tandem oxidation–epoxidation procedures.

2. Results and discussion

We initially assessed the ability of a range of organic bases to generate sulfonium ylides from sulfonium salt **1a** in the presence of benzaldehyde **2**, and were gratified to observe that both TBD and MTBD were highly effective promoters of the epoxidation reaction, providing high conversions to the epoxide product (Table 1, entries 3 and 4). These conversions could be improved to near quantitative by employing a two-fold excess of the base and sulfonium salt to provide stilbene oxide **3** as the only observable product in impressively short reaction times. Analysis of these crude reaction mixtures indicated that the epoxide was formed with high to excellent selectivity for the expected *trans* isomer.

The scope and generality of this protocol was next investigated using sulfonium salts **1a** and **1b** with a range of structurally diverse aldehydes. The reaction of the unsubstituted sulfonium salt **1a** with *para*-nitrobenzaldehyde led to an excellent yield of the epoxide with high selectivity for the *trans* product (Table 2, entry 2). Interestingly, when the substituted sulfonium salt **1b** is employed in the corresponding reaction with benzaldehyde (entry 3), the epoxide is again produced in excellent isolated yield but with enhanced selectivity for the *trans* isomer. Most gratifying and

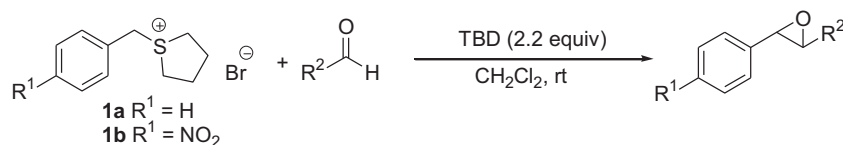
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Table 1
Optimisation of epoxidation protocol

Entry ^a	Time	Base	Conversion (%) ^b	<i>trans:cis</i> ^b
1	24 h	Et ₃ N	0	—
2	24 h	DBU	71	95:5
3	10 min	TBD	100	92:8
4	10 min	MTBD	100	94:6

^a Procedure: benzaldehyde (1 equiv), *S*-benzyltetrahydrothiophenium bromide **1a** (2 equiv) and TBD (2.2 equiv) in dichloromethane (10 mL) at room temperature.

^b Determined by ¹H NMR analysis of the crude reaction mixture.

Table 2
TBD-mediated Corey–Chaykovsky epoxidation

Entry	Aldehyde ^a	Salt	Product	Yield (%) ^b	<i>trans:cis</i> ^c
1	Ph-CHO 2	1a	Ph-epoxide 3	88	92:8
2	4-NO ₂ -Ph-CHO 4	1a	4-NO ₂ -Ph-epoxide 5	93	91:9
3	Ph-CHO 2	1b	4-NO ₂ -Ph-epoxide 5	91	>98:2
4	Ph-CH ₂ -CH ₂ -CHO 6	1a	Ph-CH ₂ -CH ₂ -epoxide 7	84	54:46
5	Ph-CH ₂ -CH ₂ -CHO 6	1b	4-NO ₂ -Ph-CH ₂ -CH ₂ -epoxide 8	84	>98:2
6	EtO ₂ C-CH=C(CH ₃)-CH ₂ -CH ₂ -CHO 9	1b	EtO ₂ C-CH=C(CH ₃)-CH ₂ -CH ₂ -epoxide 10	80	93:7
7	EtO ₂ C-CH=CH-CH ₂ -CH ₂ -CHO 11	1b	EtO ₂ C-CH=CH-CH ₂ -CH ₂ -epoxide 12	36	95:5
8	Ph-CH=CH-CHO 13	1a	Ph-CH=CH-epoxide 14	100 ^c	>98:2
9	Ph-CH=CH-CHO 13	1b	4-NO ₂ -Ph-CH=CH-epoxide 15	38	>98:2
10	Furan-2-CHO 16	1a	Furan-2-epoxide 17	68	95:5

^a Procedure: aldehyde (1 equiv), *S*-benzyltetrahydrothiophenium bromide **1a** (2 equiv) and TBD (2.2 equiv) in dichloromethane (10 mL) at room temperature.

^b All compounds gave satisfactory spectroscopic data.

^c Determined by ¹H NMR analysis of the crude reaction mixture.

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