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Published on Web 10/07/2003

Controllable Diastereoselective Cyclopropanation. Enantioselective Synthesis of Vinylcyclopropanes via Chiral Telluronium Ylides

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Compounds containing vinylcyclopropane fragments have received considerable attention because of their frequent occurrence in biologically active compounds,[1] as well as their utility as valuable synthetic intermediates.[2] Although many synthetic methods have been developed,[3] asymmetric synthesis of multisubstituted vinylcyclopropanes with high diastereoselectivities and enantioselectivities remains a challenging problem. One of the most common methods is the transition metal-catalyzed cyclopropanation[4] of α-diazo carbonyl compounds with electron-rich alkenes. Suzuki[5a] and Taylor[5b] found that these kinds of compounds could be prepared from optically pure homoallylic alcohol via several steps. The addition of allylic ylides $L_nM^+CH^-CH{=}CHX$ to Michael acceptors is also a convenient and attractive method because ylides are readily available and L_nM is easily recovered and reused. However, practical methods for the highly enantioselective synthesis of multisubstituted vinylcyclopropanes via an ylide remain undeveloped probably due to the difficulties associated with both enantioselectivity and diastereoselectivity. Hanessian et al.[6] described an efficient protocol for the preparation of these kinds of compounds with excellent diastereoselectivity using a phosphonic amide as a chiral auxiliary. Recently, Aggarwal et al.[7] reported the reaction of a chiral silylated allylic sulfur ylide with α-aminoacrylate to afford the desired vinylcyclopropane with 71% de and 75% ee. Very recently, our laboratory discovered an efficient method for the one-step enantioselective synthesis of 1,3-disubstituted-2-silylvinylcyclopropanes with high diastereoselectivity via a sulfur ylide.[8] However, this method is limited to the cyclopropanation of *β*-aryl-α,*β*-unsaturated esters, amides, ketones, and nitriles. For *β*-alkyl-α,*β*-unsaturated esters such as methyl crotonate, low yields are obtained due to the rearrangement of the sulfur ylide although the enantioselectivity is high. In addition, there is still lack of access to other optical isomers with different relative configurations. Despite their importance, few reports have appeared from the literature on catalytic asymmetric synthesis of 1,2,3-trisubstituted cyclopropanes with high enantioselectivity and diastereoselectivity via ylide routes. In this communication, we report an enantioselective synthesis of trisubstituted cyclopropanes with controllable diastereoselectivity and its catalytic version.

Metzner found that a C_2-symmetric sulfur ylide is a good reagent for the preparation of diarylepoxides with high enantioselectivities.[9a] Very recently, they reported that the sulfur ylide could react with aldehydes enantioselectively to afford vinylepoxides and the enantiomeric excess ranged from 37 to 90%.[9b] Considering that allylic telluronium ylides[10] are more reactive[11] than the corresponding sulfur ylides, we designed new telluronium salts **1** to start our study. These salts were readily prepared from (2*S*,5*S*)-(+)-2,5-hexanedioldimethanesulfonate.[9a,12] Gratifyingly, it was found that the salt **1a**, after deprotonation by LiTMP/HMPA in situ, could react with methyl cinnamate to afford vinlcyclopropane **3a** with high diastereoselectivity (96/4, **3**/**4**) and 96% ee in 95% yield (entry 1, Table 1). Encouraged by the high diastereoselectivity and excellent enantioselectivity, we evaluated a variety of α,*β*-unsaturated carbonyl compounds as substrates. As shown in Table 1, α,*β*-unsaturated esters, amides, ketones were suitable substrates for the reaction. The reactions afforded high diastereoselectivity and enantioselectivity for *β*-aryl- and *β*-heteroaryl unsaturated esters in high yields. This ylide also proved to be efficient for methyl crotonate, which gave 94% ee in moderate yield (entry 8). Noticeably, α,*β*-unsaturated ketones gave cyclopropanes in high regioselectivity (entries 9−13). No epoxides were detected in this reaction. Additionally, whatever *β*-aryl- or *β*-alkyl substituted ketones were employed, excellent ee (up to 99%) and high diastereoselectivities were obtained. α,*β*-Unsaturated amides are less effective substrates in this reaction. Although both the yield and enantioselectivity were high, the conversion of cinnamylamide was low for reasons that remain unclear (entry 14). Unlike the sulfur

Table 1. Enantioselective Cyclopropanation via Telluronium Ylides[13]

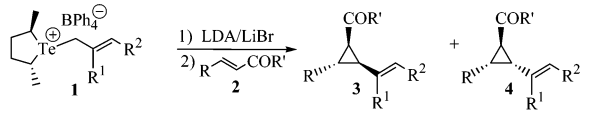
1a: R^1 = H ; R^2 = TMS; **1b**: R^1 = CH_3 ; R^2 = H; **1c**: R^1 = H ; R^2 = H;

Entry	Substrate	1	3/4[a]	Yield(%)[b]	Ee (%)[c]
1	Ph, CO_2Me	**1a**	96/4	95	96
2	Ph, CO_2Et	**1a**	98/2	97	97
3	*p*-$MeOC_6H_4$, CO_2Me	**1a**	97/3	63	94
4	*p*-MeC_6H_4, CO_2Me	**1a**	98/2	88	97
5	*p*-$F_3CC_6H_4$, CO_2Me	**1a**	88/12	99	96
6	*p*-BrC_6H_4, CO_2Me	**1a**	97/3	97	96[d]
7	2-furyl, CO_2Et	**1a**	94/6	81	97
8	CO_2Me	**1a**	92/8	57	94[e]
9	Ph, COPh	**1a**	98/2	95	95
10	*p*-BrC_6H_4, COPh	**1a**	99/1	94	99[d]
11	*p*-ClC_6H_4, COPh	**1a**	99/1	99	96
12	$H_3C(H_2C)_3$, $COBu^t$	**1a**	98/2[f]	78	99
13	$H_3C(H_2C)_3$, $CO(CH_2)_6CH_3$	**1a**	96/4[f]	49	98
14	Ph, $N(CH_2)_5$ (O)	**1a**	99/1	83(23[g])	93
15	*p*-BrC_6H_4, COPr	**1b**	97/3[f]	81	96
16	Ph, CO_2Me	**1c**	93/7	42	95
17[h]	Me, Ph, CO_2Et	**1a**	-	<1	-

[a] Determined by GC and/or ^{1}H NMR except noted. [b] Isolated yield. [c] Determined by HPLC using chiral stationary phases and for **3**. [d] The absolute configurations were determined by X-ray diffraction. [e] Determined by GC using chiral stationary phases. [f] Determined by GC−MS. [g] Conversion. [h] The ester recovered in 98% yield.

10.1021/ja036254c CCC: $25.00

Table 2. Controlled Reversal of Diastereoselectivities[13]

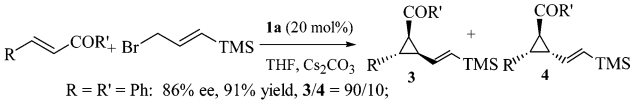


1a: R^1 = H ; R^2 = TMS; **1c**: R^1 = H ; R^2 = H;

Entry	Substrate	1	3/4[a]	Yield(%)[b]	Ee (%)[c]
1	Ph, CO_2Me	**1a**	4/96	98	81[d]
2	*p*-$MeOC_6H_4$, CO_2Me	**1a**	2/98	87	80
3	*p*-MeC_6H_4, CO_2Me	**1a**	3/97	98	83
4	*p*-$F_3CC_6H_4$, CO_2Me	**1a**	7/93	98	68
5	CO_2Me	**1a**	18/82	70	43[e]
6	Ph, O, $N(CH_2)_5$	**1a**	0/100	83	92
7	Ph, CO_2Me	**1c**	7/93	58	61

[a] Determined by GC and/or ^{1}H NMR except noted. [b] Isolated yield. [c] Determined by HPLC using chiral stationary phases and for **4**. [d] The absolute configuration was determined by comparing the optical rotation with that of the known compounds.[8] [e] Determined by GC using chiral stationary phases.

Scheme 1



R = R' = Ph: 86% ee, 91% yield, **3**/**4** = 90/10;
R = *p*-Cl-C_6H_4, R' = Ph: 89% ee, 94% yield, **3**/**4** = 91/9.

ylide in our previous report,[8] α-methyl allylic and simple allylic telluronium salts **1b** and **1c** also worked well (entries 15 and 16).

In our previous study on ylide chemistry, we found that the diastereoselectivity in the cyclopropanation of α,β-unsaturated esters and amides with telluronium allylide could be tuned by reaction conditions.[14] On the basis of this mechanistic insight, it is possible to tune the diastereoselectivity of this reaction, and thus, it provides a facile method for the synthesis of two optically pure isomers of trisubstituted cyclopropanes with high selectivity using the same chiral telluronium ylide, just by changing reaction conditions. As expected, by optimizing the reaction conditions, it was found that telluronium salt **1** could also react with α,β-unsaturated esters and amides in the presence of LDA/LiBr to afford the desired products, with different diastereoselectivities compared with using LiTMP/HMPA. In most cases, β-aryl esters and amides gave good to high diastereoselectivities and enantioselectivities. The reaction with methyl crotonate was less enantioselective, and only 43% ee was obtained. Optical purity of the product **(**up to 99% ee**)** could be enhanced by recrystallization in some cases.[13] Thus, *either one of the two diastereomers could be enantioselectively synthesized at will just by the choice of LiTMP/HMPA or LDA/LiBr*.Considering that the telluride will be regenerated during the cyclopropanation, we tried a catalytic process of this reaction. It was found that, in the presence of 20 mol % of salt **1** in THF, chalcones gave the desired cyclopropane with high diastereoselectivity in high yield with up to 89% ee (Scheme 1).

To summarize, we have developed an efficient method and the first example of catalytic ylide reaction for the enantioselective synthesis of 1,3-disubstituted 2-vinylcyclopropanes with high diastereoselectivity. Noticeably, two diastereomers could be obtained at will with high enantioselectivity in some cases. Compared with our previous report, both the yields and enantioselectivities are improved. The facile synthesis of telluride, controllable diastereoselectivity, and high enantioselectivity give this methodology high potential for practical use in organic synthesis.

Acknowledgment. We are grateful for financial support by the National Natural Sciences Foundation of China. This paper is dedicated to Professor Wei-Shan Zhou on the occasion of his 80th birthday.

Supporting Information Available: Synthesis and characterization of key compounds, GC and HPLC data of **3** and **4**, mechanistic model for diastereoselectivity (PDF). X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) For detailed procedures, please see Supporting Information. Compared with the corresponding bromide, the solubility of the salts using $[BPh_4]^-$ as the counterion in THF was much improved. Thus, higher yields (with similar selectivities) were observed when changing the counterion of the salt from bromide to BPh_4.

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JA036254C

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A facile tetrahydrothiophene-catalyzed ylide route to vinyloxiranes†

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Received (in Cambridge, UK) 24th April 2003, Accepted 30th June 2003
First published as an Advance Article on the web 10th July 2003

Access to vinyloxiranes using aldehydes and allylic bromides in the presence of 1–5 mol% tetrahydrothiophene is reported. Both aliphatic and aromatic aldehydes work well in this reaction and the catalyst loading could be reduced as low as 0.5 mol%.

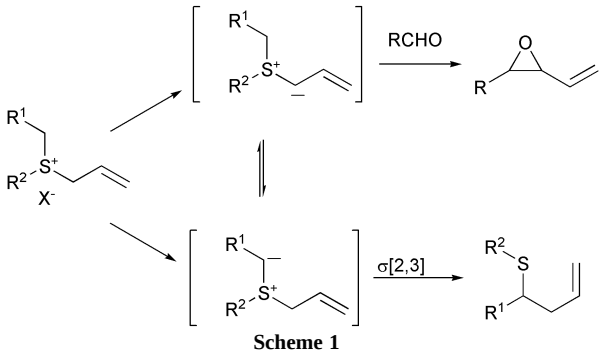
Sulfur ylides, particularly sulfur benzylides, have been developed as good reagents for the preparation of oxirane,[1] cyclopropane[2] and aziridine[3] derivatives since Johnson *et al.*[4] found the reaction of sulfur ylide with aldehydes in 1961. Although vinyloxiranes are versatile building blocks[5] and precursors of functionalized four-carbon sequences,[6] the reactions of allylic sulfur ylide with aldehydes, imines and electron-deficient alkenes were less explored than other ylide reactions, and it is still a challenging problem due to its easy [2,3][7] sigmatropic rearrangement. In order to obviate this rearrangement, typically, diphenyl sulfur ylide was used. Arsenic[8] or tellurium ylides[9] have been also employed to avoid the [2,3] sigmatropic rearrangement. In this way, the desired catalytic version[10] was realized by using 20 mol% diisobutyl telluride. Recently, Dai and Hou reported a one-pot strategy[11] for the synthesis of vinylaziridines and vinyl epoxides *via* sulfur ylides. In some cases, they found that the stereoselectivities of ylide expoxidation[11a] and/or aziridination[3a,11b,c,12] could be tuned by changing both the reaction conditions and the ligands of sulfur ylides. In our study of ylide chemistry,[13] we documented an enantioselective preparation of vinylcyclopropanes using stoichiometric chiral ylides.[14] Very recently, Metzner *et al.* described the first enantioselective synthesis of vinyl oxiranes from allylic chiral sulfur ylides.[15] To the best of our knowledge, no catalytic ylide epoxidation *via* allylic sulfur ylide has been reported, except that Aggarwal *et al.* reported that benzaldehyde reacted with (3,3-diphenyl)alkenyl sulfonyl hydrazone to afford diphenyl vinyl epoxide in the presence of 20 mol% tetrahydrothiophene.[1b] Here we report an efficient catalytic route to vinyloxiranes *via* allylic sulfur ylide.‡

By careful analysis of the reaction of allylic sulfur ylide in the presences of aldehyde (Scheme 1), we think that it is possible to realize catalytic ylide epoxidation when high concentrations of both aldehyde and allylic bromide are used in a one-pot reaction because the high concentration of allylic bromide is beneficial to the formation of sulfur salt and the high concentration of aldehyde could probably lead to the reaction of aldehydes with the sulfur ylide before the ylide rearranged. As alcoholic solvents were found to activate the aldehyde probably due to the formation of hydrogen bonds between solvent and aldehyde,[16] we chose *t*-BuOH as the solvent and used 5 mol% tetrahydrothiophene as the catalyst to start our study. As expected, this catalytic reaction proceeded very well. As shown in Table 1, the reaction of 4-chlorobenzaldehyde with allylbromide **2a** at reflux in the presence of 5 mol% tetrahydrothiophene gave the desired product in quantitative yield when either Cs_2CO_3 or K_2CO_3 was used as the base. This reaction could also be carried out without solvent, but the yield was lower than that when *t*-BuOH was used as the solvent (entry 4 in Table 1). Gratifyingly, the yield was still 83% even when the loading of tetrahydrothiophene was reduced to 0.5 mol% (entry 6).

Further studies showed that both aromatic and aliphatic aldehydes worked very well even on the gram-scale. As described in Table 2, both electron-rich and electron-deficient aromatic aldeydes gave the desired epoxides in excellent yields (entries 1–4). Compared with aromatic aldehydes, aliphatic aldehydes such as cyclohexanecarboxaldehyde and decyl aldehyde always are less active in catalytic ylide reactions. But under our conditions, they worked well (entries 5, 10 and 11). Although the stereoselectivity was not good, the isomers could be separated easily as a single *cis*- and/or *trans*-isomer by flash chromatography. Noticeably, β-trimethylsilylallyl bromide also participated in this reaction to give the corresponding epoxides in excellent yields using only 1 or 5 mol% of catalyst (entries 6–11).

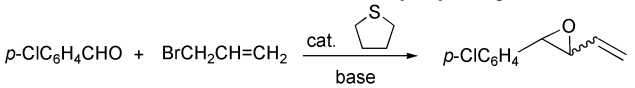
We also tried catalytic asymmetric ylide epoxidation by the use of chiral sulfides **4**, **5** and **6** as the catalyst. Only moderate yields were achieved in the presence of sulfide **4** or **6**. The enantioselectivities were low to moderate (entries 1 and 3 in Table 3). Sulfide **5** could not catalyze this reaction probably because the formation of salt is very difficult.

In conclusion, we have developed an efficient catalytic ylide route to vinyloxiranes *via* allylic sulfur ylides. The cheap and



Scheme 1

Table 1 Effects of reaction conditions on catalytic ylide epoxidation



1a 2a 3a

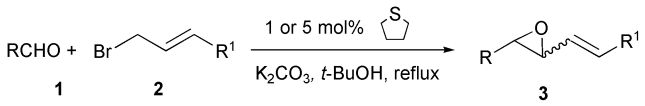
Entry	Solvent	Loading (mol%)[a]	Base	Yield[b]
1	*t*-BuOH	5	Cs_2CO_3	100
2	*t*-BuOH	5	K_2CO_3	100
3	*t*-BuOH	1	K_2CO_3	100
4	—	1	K_2CO_3	58
5	*t*-BuOH[c]	1	K_2CO_3	51
6	*t*-BuOH	0.5	K_2CO_3	83

[a] Tetrahydrothiophene loading. [b] Determined by GC. [c] Trace amount of water was added.

† Electronic supplementary information (ESI) available: preparation of vinyloxiranes and chiral catalysts. See http://www.rsc.org/suppdata/cc/b3/b304443b/

DOI: 10.1039/b304443b

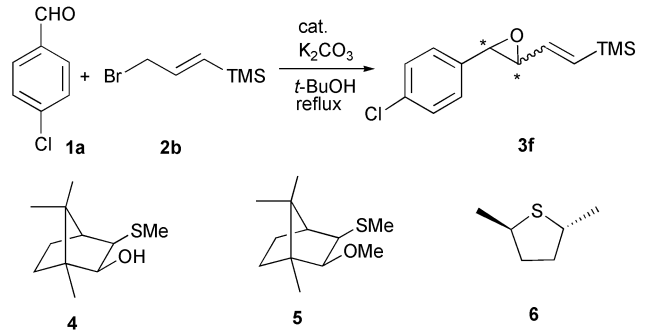
Table 2 Reactions of aldehydes with allylic bromides catalyzed by tetrahydrothiophene[a]



Entry	Loading[b]	R	R^1	*cis*/*trans*[c]	Yield (%)[d]
1	1	4-ClC_6H_4	H	36/64	94
2	1	C_6H_5	H	33/67	85
3	1	4-$NO_2C_6H_4$	H	38/62	96
4	5	4-$CH_3OC_6H_4$	H	30/70	85
5	5	*n*-C_9H_{19}	H	55/45	75
6	1	4-ClC_6H_4	TMS	25/75	83
7	1	C_6H_5	TMS	24/76	89
8	1	4-$NO_2C_6H_4$	TMS	30/70	85
9	1	2-ClC_6H_4	TMS	27/73	85
10	5	*n*-C_9H_{19}	TMS	42/58	88
11	5	*cyclo*-C_6H_{11}	TMS	50/50	78

[a] All reactions were carried out in one-pot at reflux using tetrahydrothiophene (0.06 mmol), β-trimethylsilylallyl bromide (9.75 mmol) [or allylbromide (19.4 mmol)], aldehyde (6.5 mmol), K_2CO_3 (7.8 mmol), *t*-BuOH (2 mL) under dry N_2 atmosphere. [b] mol%. [c] Determined by GC. [d] Isolated yield.

Table 3 Asymmetric ylide epoxidations of **1a**[a]



Entry	Cat.	Loading (mol%)	*cis*/*trans*[b]	ee (%)[c] for *trans*-**3f**	Yield (%)
1	**4**	20	40 : 60	37	40
2	**5**	20	—	—	0
3	**6**	5	34 : 60	25	51

[a] All reactions were carried out in one-pot at reflux using catalyst, β-trimethylsilylallyl bromide (0.6 mmol), aldehyde (0.5 mmol), K_2CO_3 (0.6 mmol), *t*-BuOH (0.5 mL) under dry N_2 atmosphere. [b] Determined by GC. [c] Determined by HPLC.

readily available catalyst, the simple procedure, the mild conditions and the high catalytic efficiency together with the easy separation of *cis*/*trans*-isomers, make this method potentially useful in organic synthesis.

This research was supported by the National Natural Sciences Foundation of China and 'The Talent Scientists Program' from Chinese Academy of Sciences.

Notes and references

‡ General procedure: To a Schlenk tube were added tetrahydrothiophene (5.7 mg, 0.06 mmol), allylbromide (1.68 mL, 19.4 mmol), 4-chlorobenzaldehyde (907 mg, 6.5 mmol), dry K_2CO_3 (powdered, 1.07 g, 7.8 mmol) and *t*-BuOH (2 mL, distilled over sodium) under N_2 atmosphere. The resulting mixture was refluxed for 12 h, and then filtered rapidly through a short silica gel column (ethyl acetate eluent). The filtrate was concentrated and the residue was purified by chromatography (hexane/ethyl acetate, 200/1, v/v) on silica gel to afford the desired product, 1.09 g (94%).

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