Cyclopropanation Reactions of Allylic Ylides with α,β-Unsaturated Esters and Amides: Tuning of Stereoselectivity and the Dramatic Effect of Lithium Salts

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The allylic telluronium ylides **2a**−**2c**, generated *in situ* from the corresponding telluronium salts **1a**−**1c** in the presence of a lithium salt, reacted with α,β-unsaturated esters or amides to afford *trans*-2-vinyl-*trans*-3-substituted cyclopropyl esters or amides, respectively, with high selectivity and generally excellent yields. In the absence of lithium salts, the stereoselectivity of these reactions changed to give *cis*-2-vinyl-*trans*-3-substituted cyclopropyl esters or amides. The ratio of the two isomers **4** and **5** can be tuned from 99:1 to 1:99. Other factors, such as temperature, solvents, and amounts of base, are also shown to influence the stereochemistry of this reaction. A possible mechanism for tuning of the reaction stereochemistry by simply varying reaction conditions is proposed.

Vinylcyclopropanes are important compounds not only because they are versatile intermediates in organic transformations and in the total synthesis of complex molecules,[1] but also because they are substructure of several biologically active natural compounds.[2] Most frequently, vinylcyclopropanes are prepared by indirect routes.[3] One direct method, involving the reaction of conjugated dienes with carbenes or carbenoids,[4] lacks generality and requires difficult manipulations. Another direct method—the addition of an activated allylic reagent, such as a vinyl-type carbene or carbenoid, to an alkene—is also limited by structural requirements, and only a few examples have appeared in the literature.[5] The addition of allylic ylides $L_nM^+CH^-CH{=}CHX$ to Michael acceptors is a convenient and attractive method because ylides are generally easily prepared and ML_n can be recovered and reused. However, practical methods for the synthesis of vinylcyclopropanes via allylides routes remain undeveloped.[6]

In the last 40 years, great interest in preferentially preparing one of several geometrical isomers has arisen. Although the syntheses of one of several geometrical isomers from the same starting materials with high stereoselectivity, using different reagents[7] or via multistep reactions,[8] have appeared in the literature, similar attempts varying only reaction conditions, using the same starting material and the same reagents,[9] remain a

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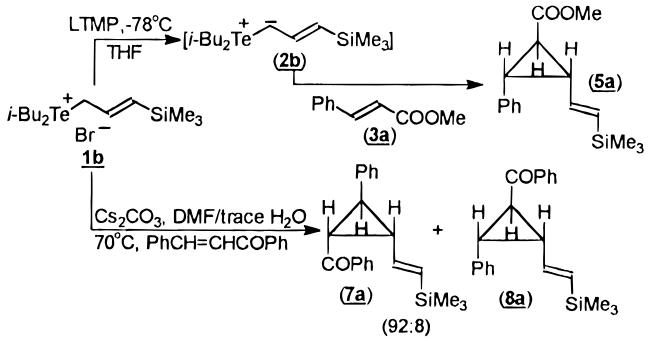
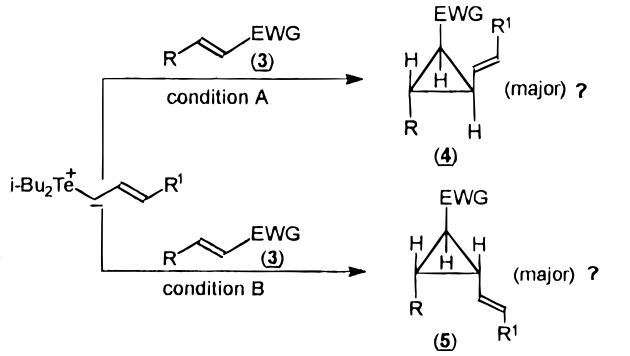
Scheme 1



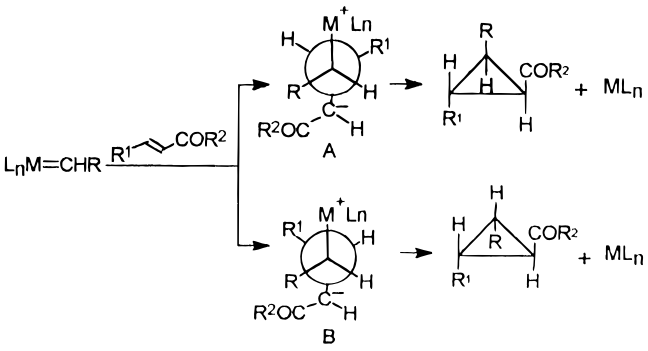
challenge. For example, although the stereochemistry of ylide olefination has been an area of extensive research,[10] the stereochemical tuning to furnish either the *Z* or *E* isomer under different conditions with high stereoselectivity has been realized with only a few ylides.[9] In ylide cyclopropanation, to our knowledge, there has been no stereoselectivity development of this sort.

In our continuing studies on the application of arsonium and telluronium ylides in organic synthesis,[11] we have focused on the cyclopropanation reaction of allylic ylides, especially on their stereochemistry. In our previous work, we found that silylated telluronium allylide **2b**, generated *in situ* from the [3-(trimethylsilyl)prop-2-enyl]diisobutyltelluronium bromide (**1b**) with lithium 2,2,6,6-tetramethylpiperidide (LTMP), reacted with methyl cinnamate to form exclusively *trans*-2-phenyl-*trans*-3-[2-(trimethylsilyl)vinyl]-1-(methoxycarbonyl)cyclopropane (**5a,** Scheme 1).[12] On the other hand, under solid−liquid phase-transfer conditions, a one-pot reaction of the same ylide **2b** with chalcone gave *trans*-2-phenyl-*cis*-3-[2-(trimethylsily)vinyl]-1-benzoylcyclopropane (**7a**) with

Scheme 2



Scheme 3



excellent stereoselectivity[13] (Scheme 1). The different stereochemistry in these two similar reactions suggests that reaction conditions may seriously influence the stereochemistry. Is it possible to tune the stereochemistry by varying the reaction conditions to obtain either one of the two geometrical isomers exclusively from methyl cinnamate (Scheme 2)? If this could be realized, it would provide the first efficient method for obtaining with high stereoselectivity two isomers of polyfunctionalized vinylcyclopropanes via an ylide route. We now report the full details of our efforts to develop this concept.

Results and Discussion

Effect of Lewis Acids on the Stereoselectivity of the Reaction of Silylated Telluronium Allylide with α,β-Unsaturated Esters. It is well accepted that the ylide cyclopropanation proceeds via two consecutive steps, the Michael addition to the acceptor's double bond to form **A** or **B** and an elimination of ML_n to form the cyclopropane ring (Scheme 3). Two factors govern the ratio of the two isomers in this type of reaction: first, the relative initial concentration of **A** and **B** and second, the equilibrium between **A** and **B**. These factors are determined by the nature of the ylides and substrates and also the reaction media. Considering the effect of lithium salt on the stereochemistry of the ylide olefination reaction[14] and the possible role of LTMP in the reaction described in Scheme 1, we first turned our attention to the effect of Lewis acids, especially the effects of lithium salts on the reaction stereoselectivity. Thus, we used $NaN(SiMe_3)_2$ or LiBr + $NaN(SiMe_3)_2$ instead of LTMP as the base to generate ylide **2b**, which reacted in methyl cinnamate to form 2-[2-(trimethylsilyl)vinyl]-3-phenyl-1-(methoxy-

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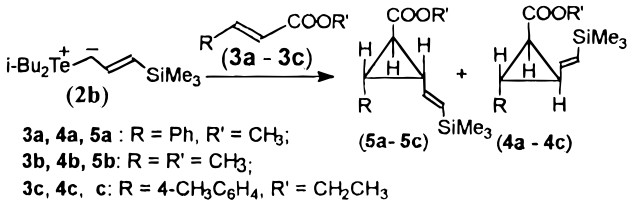
Table 1. Effect of Lewis Acids on the Stereochemistry of the Reaction of Ylide 2b with α,β-Unsaturated Esters[a]



3a, 4a, 5a : R = Ph, R' = CH_3;
3b, 4b, 5b: R = R' = CH_3;
3c, 4c, c: R = 4-$CH_3C_6H_4$, R' = CH_2CH_3

entry	ylide	substrate	base (ratio of **1** and base)[b]	ratio (**5:4**)[c]	yield (%)[d]
1	**2b**	**3a**	$NaN(SiMe_3)_2$	54:46 (**5a:4a**)	91
2	**2b**	**3a**	LiBr + $NaN(SiMe_3)_2$	>99:1 (**5a:4a**)	93
3	**2b**	**3a**	$KN(SiMe_3)_2$	<1:99 (**5a:4a**)	87
4	**2b**	**3a**	LiCl + $KN(SiMe_3)_2$	82:18 (**5a:4a**)	85
5	**2b**	**3a**	$LiN(SiMe_3)_2$	97:3 (**5a:4a**)	41
6	**2b**	**3a**	$MgBr_2$ + $KN(SiMe_3)_2$	90:10 (**4a:5a**)	73
7	**2b**	**3b**	$KN(SiMe_3)_2$	26:74 (**5a:4a**)	67
8	**2b**	**3b**	LiCl + $KN(SiMe_3)_2$	55:45 (**5b:4b**)	71
9	**2b**	**3b**	LiBr + $KN(SiMe_3)_2$	71:29 (**5b:4b**)	70
10	**2b**	**3b**	LiBr + $NaN(SiMe_3)_2$	70:30 (**5b:4b**)	76
11	**2b**	**3b**	LiCl (5 equiv) + $KN(SiMe_3)_2$	59:41 (**5b:4b**)	65
12	**2b**	**3c**	$KN(SiMe_3)_2$ (1 equiv)	2:98 (**5c:4c**)	80
13	**2b**	**3c**	$KN(SiMe_3)_2$ (1:1.5)	25:75 (**5c:4c**)	68
14	**2b**	**3c**	$KN(SiMe_3)_2$ (1:2.0)	40:60 (**5c:4c**)	18
15	**2b**	**3c**	$KN(SiMe_3)_2$ (1:3.0)		0
16	**2b**	**3a**	LiBr + $NaN(SiMe_3)_2$ (1:2.0)	98:2 (**5a:4a**)	87

[a] The configurations of **4** and **5** were determined by 300 MHz ^{1}H NMR. [b] THF was the solvent. The ratio of salt **1** base, except as mentioned, is 1:1. [c] The ratio of stereoisomers was determined by ^{1}H NMR and/or GC. [d] Isolated yields based on α,β-unsaturated esters.

carbonyl)cyclopropane with excellent yield but with different stereochemistry (entries 1, 2 in Table 1). In the presence of LiBr, the reaction was almost stereospecific, and the configuration of the product **5a** is the same as that when LTMP is used as the base to produce ylide **2b**. The same is found when $LiN(SiMe_2)_3$ is used as the base (entry 5 in Table 1). However, in the absence of lithium salt, the stereoselectivity of this reaction was very poor, and the ratio of the two isomers (**5a**:**4a**) was nearly 1:1 (entry 1 in Table 1). These results convinced us that the lithium salt was one of the main factors governing the stereoselectivity and encouraged us to attempt to produce the other isomer by lowering the acidity of the Lewis acid or removing it from the reaction system. In view of the lower Lewis acidity of potassium ion relative to that of sodium ion, we exploited $KN(SiMe_3)_2$ as a base in the above-described reaction. As expected, a dramatic effect on the stereochemistry of the product was observed. Isomer **4a** was the sole product, with totally different stereochemistry from that obtained in the presence of LiBr. The yield was still very high (entry 3 in Table 1).

Further studies showed that the effect of Lewis acids on the stereochemistry of ylide cyclopropanation also held when methyl crotonate (**3b**) was used as the substrate. Although the trends for tuning the stereochemistry are the same as those for substrate **3a**, the propensity for the formation of **5b** is not overwhelmingly preferred over that of **5a** (entries 2, 10, 11 in Table 1). Magnesium bromide and a variety of lithium salts, such as LiCl and LiBr, were effective additives to change the stereochemistry of the product in favor of the formation of **5**. Some detailed results are summarized in Table 1. The presence of excess LiCl (5 equiv) did not improve the stereoselectivity of this reaction (entry 11 in Table 1). Interestingly, an increase in the amount of base $KN(SiMe_3)_2$ used decreased greatly the yield of the product and also the stereoselectivity (entries 12−15 in Table 1). Therefore, to prepare **4** in high yield and high selectivity, the 1 equiv of $KN(SiMe_3)_2$ is crucial. Otherwise, a mixture of **4** and **5** would be obtained.

However, in the presence of lithium bromide, an excess amount of $NaN(SiMe_3)_2$ did not affect the yield and stereoselectivity. For instance, when we added 2 equiv of $NaN(SiMe_3)_2$ to 1 equiv of salt **1b** in THF to produce the ylide **2b** and later added methyl cinnamate to the reaction mixture, the yield and stereoselectivity of **5a** changed as little as compared with the result when an equivalent amount of $NaN(SiMe_3)_2$ was used (entries 2, 16 in Table 1).

The above results demonstrate that the acidity of the Lewis acid (the cation of the base) plays an important role in the stereochemistry of this reaction. Either *trans*-2-[2-(trimethylsilyl)vinyl]-*trans*-1-phenylcyclopropyl ester or *cis*-2-[2-(trimethylsilyl)vinyl]-*trans*-3-phenylcyclopropyl ester can be easily synthesized with high stereospecificity, depending on the choice of reaction conditions.

Effects of Temperature and Solvent on the Stereochemistry. The effects of solvent and reaction temperature were investigated in more detail with methyl cinnamate and methyl crotonate as reactants. The results are listed in Table 2. From entries 1 and 2 in Table 2, it can be seen that, besides the Lewis acid,

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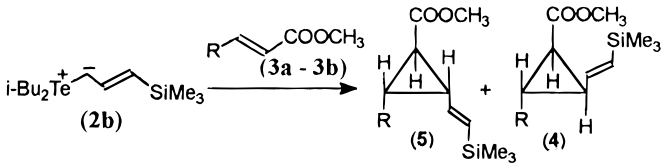
Table 2. Effects of Solvent and Temperature on the Stereochemistry of the Reaction of Ylide 2b with Methyl Crotonate and Methyl Cinnamate[a]



3a, 4a, 5a : R = Ph; **3b, 4b, 5b**: R = CH_3

entry	substrate	solvent, temp (°C), base	ratio (**5:4**)[b]	yield (%)[c]
1	**3a**	THF, 0, LTMP	<1:99 (**5a:4a**)	20[d]
2	**3a**	THF, −78, LTMP	>99:1 (**5a:4a**)	93
3	**3b**	hexane + THF (10:1), −78, $KN(SiMe_3)_2$	17:83 (**5b:4b**)	57
4	**3b**	DME + THF (10:1), −78, $KN(SiMe_3)_2$	5:95 (**5b:4b**)	64
5	**3b**	DMF + THF (10:1), −78, $KN(SiMe_3)_2$		0
6	**3b**	ether + THF (10:1), −78, $KN(SiMe_3)_2$	5:95 (**5b:4b**)	70
7	**3b**	toluene + THF (10:1), −78, $KN(SiMe_3)_2$	4:96 (**5b:4b**)	76
8	**3b**	THF, −78, LiBr + $NaN(SiMe_3)_2$	70:30 (**5b:4b**)	76
9	**3b**	toluene + THF (10:1), −78, LiBr + NaN $(SiMe_3)_2$	80:20 (**5b:4b**)	80
10	**3b**	toluene + THF (trace), −78, LiBr + NaN $(SiMe_3)_2$	65:35 (**5b:4b**)	70
11	**3b**	THF, −78, $KN(SiMe_3)_2$	26:74 (**5b:4b**)	67
12	**3b**	THF, −110, $KN(SiMe_3)_2$	43:57 (**5b:4b**)	56
13	**3b**	THF, −40, $KN(SiMe_3)_2$	22:78 (**5b:4b**)	70
14	**3b**	THF, 0, $KN(SiMe_3)_2$	21:79 (**5b:4b**)	20[e]

[a] The configuration was determined by 300 MHz ^1H NMR. [b] The ratio of stereoisomers was determined by ^1H NMR or/and GC. [c] Isolated yields based on α, β - unsaturated esters. [d] 75% of methyl cinnamate was recovered. [e] 73% of methyl cinnamate was recovered.

temperature is a governing factor in the stereoselectivity of this reaction. In the presence of lithium salts (entries 1, 2) or without their addition (entries 11−14 in Table 2), a great change in the ratio of the products **4b** and **5b** was observed as the temperature was changed. Higher temperature is beneficial to the stereoselectivity of **4a**,**b,** but it lowers the yield of **4a**,**b** greatly (entries 1**,** 14). It is clearly shown in Table 2 that the reaction could give reasonable yields in various solvents, from oxygenated solvents to nonpolar solvents (entries 3−4, 6−10 in Table 2). The solvent can also influence the stereoselectivity but less effectively than do lithium salts. In DMF, no product was isolated.

Tuning of the Stereochemistry of the Reaction of Allylic Telluronium Ylides with α,β-Unsaturated Esters and Amides. After studying the above effects, we examined the reaction of allylic telluronium ylides with a variety of α,β-unsaturated esters and amides. Some experimental results pertinent to tuning the stereochemistry are shown in Table 3. Ylides **2a**−**c** can react with β-aryl or methyl α,β-unsaturated esters and amides to form vinylcyclopropane derivatives. Not only the trimethylsilylated allylide but also the unsubstituted allylide gave good results. Moreover, either isomer **4** or **5** could be obtained with high stereoselectivity in good to excellent yields by the proper choice of base and solvent.

Thus, effective stereocontrol for the synthesis of either one of geometrical isomers of vinylcyclopropyl esters and amides is achieved by varying the reaction conditions. These results illustrate the efficiency, applicability, and generality of the present method.

Determination of the Configuration of Cyclopropane Derivatives. The configuration of the cyclopropane derivatives was determined by ^1H NMR, $^1H-^1H$ NOESY, and chemical transformation. First, we determined the configuration of **5b** according to ^1H NMR: the ^1H NMR spectrum of **5b** showed chemical shifts at 1.48, 1.66, and 2.15 ppm, which were assigned to the three cyclopropane protons Hc, Ha, and Hb, respectively (Chart 1). On the basis of coupling patterns and coupling constants, we easily ascertained that the methoxycarbonyl group is oriented *trans* to both the (trimethylsilyl)vinyl group and the methyl group. Shen et al.[15] had shown that proton chemical shifts are strongly influenced by the nature of the substituents on the ring in the trisubstituted cyclopropane system and that the substituent with higher electronegativity causes a downfield chemical shift. Based on these results, we assigned the most upfield doublet of doublets cyclopropane proton in **5a** to Hc′ and the most downfield doublet of doublets to Ha′ (Chart 1). According to its coupling constants, we concluded that both the phenyl and (trimethylsilyl)vinyl groups are oriented *trans* to the methoxycarbonyl group. This determination is consistent with $^1H-^1H$ NOESY of **5a** (Scheme 4). There are strong NOE effects between Ha′ and Hb′, Hc′ and Hd′, Hb′ and He′ and the proton attached to the phenyl group and Hc′. By comparing the coupling patterns and constants of **4a** and **5a**, the configuration of **4a** was also ascertained. The ketone **8a** can be obtained from ester **5a** (Scheme 5): compound **5a** could be hydrolyzed easily to acid with 5% $NaOH-CH_3OH$, the acid reacting with phenyllithium to form **8a** instead of **7a.**

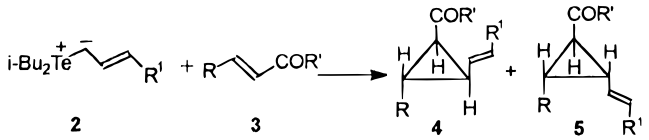
Mechanism

The results presented in the previous sections indicate that we are now able to control the stereochemical course of the ylide cyclopropanation reaction. By proper choice of base or by adjusting the reaction conditions, we can obtain either geometrical isomer **4** or **5**. For several different types of substrates, we realized the tuning of the stereochemistry. The ratio of the two isomers may be tuned from 99:1 to 1:99.

Before discussing the possible mechanism, we will qualitatively examine the relative reaction rate of the two

(15) Shen, Y. C.; Huang, Y. Z.; Xin, Y. K.; Xu, G. J. *Acta Chim. Sinica* **1981**, *39*, 243.

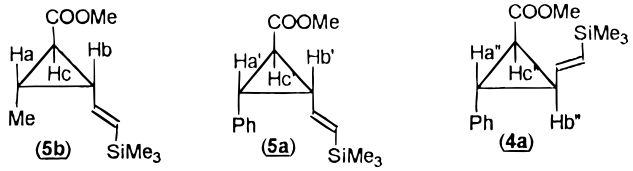
Table 3. Stereochemical Tuning of the Reaction of Allylic Telluronium Ylides 2 with α,β-Unsaturated Esters and Amides under Different Conditions[a]



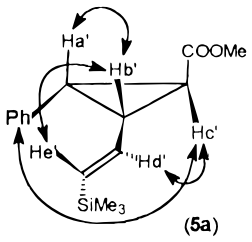
entry	R^1	R and R′	base, solvent	ratio (**5:4**)[b]	yield (%)[c]
1	$SiMe_3$ (**2a**)	R = Ph; R′ = OCH_3	$KN(SiMe_3)_2$, THF	<1:99 (**5a:4a**)	87
2			LiBr + $NaN(SiMe_3)_2$, THF	>99:1 (**5a:4a**)	93
3	$SiMe_3$ (**2a**)	R = CH_3; R′ = OCH_3	$KN(SiMe_3)_2$, toluene + THF (10:1)	4:96 (**5b:4b**)	76
4			LiBr + $NaN(SiMe_3)_2$, toluene + THF (10:1)	80:20 (**5b:4b**)	80
5	$SiMe_3$ (**2a**)	R = *p*-$CH_3OC_6H_4$; R′ = OCH_2CH_3	$KN(SiMe_3)_2$, THF	2:98 (**5c:4c**)	80
6			LiBr + $NaN(SiMe_3)_2$,THF	>99:1 (**5c:4c**)	93
7	$SiMe_3$ (**2a**)	R = furyl; R′ = OCH_2CH_3	$KN(SiMe_3)_2$, THF	<1:99(**5d:4d**)	90
8			LiBr + $NaN(SiMe_3)_2$, THF	>99:1(**5d:4d**)	93
9	$SiMe_3$ (**2a**)	R = Ph; R′ = 	$KN(SiMe_3)_2$, THF	<1:99 (**5e:4e**)	96
10			LiBr + $NaN(SiMe_3)_2$, THF	>99:1 (**5e:4e**)	94
11	H (**2b**)	R = Ph; R′ = OCH_3	$KN(SiMe_3)_2$, THF	4:96 (**5f:4f**)	76
12			LiBr + $NaN(SiMe_3)_2$, THF	98:2 (**5f:4f**)	85
13	H (**2b**)	R = furyl; R′ = OCH_2CH_3	$KN(SiMe_3)_2$, toluene + THF (10:1)	5:95 (**5g:4g**)	88
14			LiBr + $NaN(SiMe_3)_2$, THF	95:5 (**5g:4g**)	76
15	H (**2b**)	R = Ph; R′ = 	$KN(SiMe_3)_2$, toluene + THF (10:1)	<1:99(**5h:4h**)	94[d]
16			LiBr + $NaN(SiMe_3)_2$, toluene + THF (10:1)	>99:1(**5h:4h**)	91
17	CH_3 (**2c**)	R = Ph; R′ = OCH_3	$KN(SiMe_3)_2$, THF	12:88 (**5i:4i**)	74
18			LiBr + $NaN(SiMe_3)_2$, toluene + THF (10:1)	86:14 (**5i:4i**)	80
19	CH_3 (**2c**)	R = Ph; R′ = 	$KN(SiMe_3)_2$, toluene + THF (10:1)	3:97 (**5j:4j**)	92[e]
20			LiBr + $NaN(SiMe_3)_2$, toluene + THF (10:1)	98:2 (**5j:4j**)	88[f]

[a] All the products gave satisfactory elemental analysis and/or high-resolution mass spectrometry. ^1H NMR, MS, IR spectra. The configuration was determined by 300 MHz ^1H NMR. [b] The ratio of stereoisomers was determined by ^1H NMR and/or GC. [c] Isolated yields based on α,β-unsaturated esters. [d] 22% of amide was recovered. [e] 21% of amide was recovered. [f] 25% of amide was recovered.

Chart 1



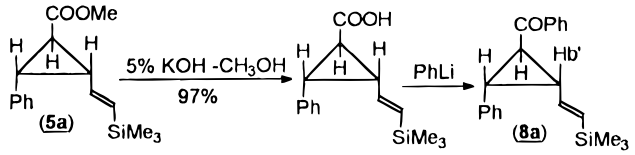
Scheme 4



consecutive steps, i.e., the Michael addition and the elimination reaction.

In our experiments, we found that the deep red color of ylide **2b**, generated *in situ* from salt **1b** with $KN(SiMe)_3$, faded very slowly after addition of 1 equiv of methyl cinnamate. Subsequent quenching at −78 °C just after the complete disappearance of the ylide color gave **4a** in 64% yield. When we repeated the above reaction but quenched it after the reaction mixture was slowly warmed to room temperature, we isolated **4a** in 66% yield. These two experiments qualitatively showed that

Scheme 5

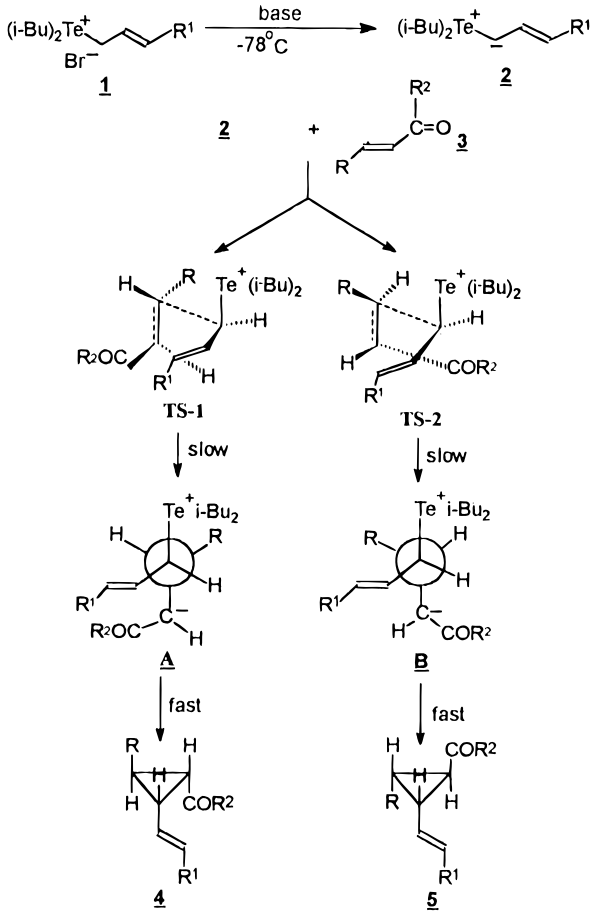


the elimination reaction might be the fast reaction and the first step, while the Michael addition might be a rate-determining step. Thus, the ratio of isomers **4** and **5** will depend solely on the ratio of **A** and **B** formed in the initial condensation.

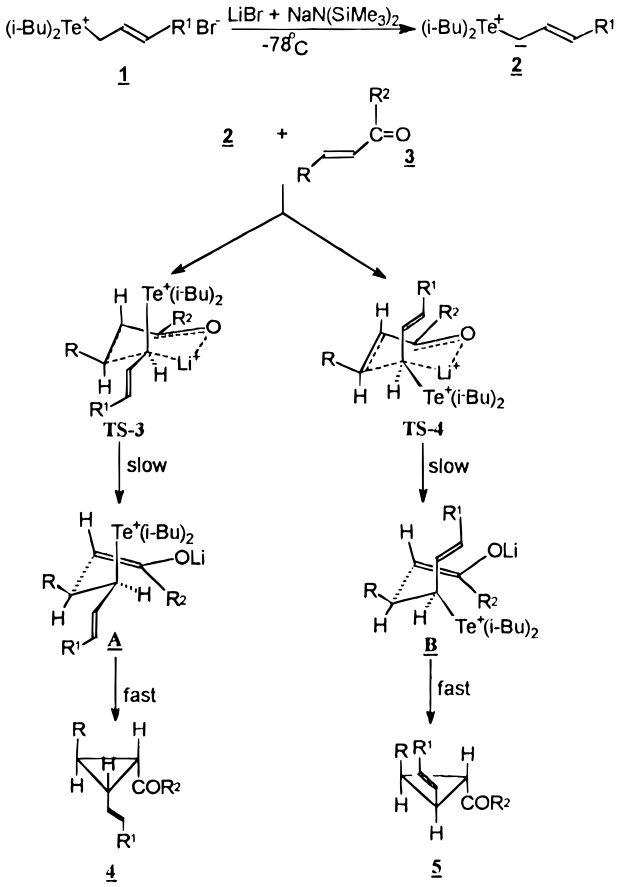
By changing the base from $NaN(SiMe_3)_2$ to $KN(SiMe_3)_2$, we were able to shift the ratio of **5**:**4** from 54:46 to 1:99 (entries 1, 3 in Table 1). Potassium ion is thought to be a less coordinated species. In light of the well-accepted mechanism for the ylides of other atoms (S, As) with α,β-unsaturated compounds,[16] a possible mechanism for the reaction between ylide **2** and α,β-unsaturated esters or amides using $KN(SiMe_3)_2$ as the base is depicted in Scheme 6. It is obvious that transition state 1 (**TS-1**) is more stable than transition state 2 (**TS-2**). In **TS-2**, all the sterically demanding groups are crowded at one side (as shown in the Newman projection formula **B** (Scheme 6). Thus, **4a** is certainly the major product, because the stable intermediate **A** formed preferentially over intermediate **B**, and it is difficult to shift to unstable intermediate **B** during the subsequent elimination reaction.

(16) (a) Huang, Y. Z.; Shen Y. C. *Adv. Organomet. Chem.* **1982**, *20*. (b) Bestmann, H. J.; Seng, D.-C. F. *Angew. Chem.* **1962**, *74*, 154. (c) Tsuge, O.; Shinkai, P. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3514. (d) Greenberg, F. H.; Schulman, E. *J. Org. Chem.* **1993**, *58*, 5853. (e) Trost, B. M. *J. Am. Chem. Soc.* **1967**, *89*, 138.

Scheme 6



Scheme 7



In contrast to the use of $KN(SiMe_3)_2$, the use of LiBr + $NaN(SiMe_3)_2$ can reverse the ratio of **4**:**5** from 1:99 to 99:1. The coordination of the lithium salt might be an important factor. It has been demonstrated by Vedejs et al.[17b] and by Schmidbauer[17a] that some Lewis acids, such as $MgBr_2$ amd LiX, can coordinate with $R_3P{=}CH_2$.[17] Recently, Armstrong et al.[18] reported the structure of a single crystal of $[Ph_3P{=}CH_2{-}LiN(CH_2Ph)_2]_2$, showing the coordination of methylene phosphorane with lithium, and proposed that other heteroatom ylides might also be potential Lewis base donors to alkali metal cations. Similarly, we think that the lithium ion may coordinate with the ylidic carbon of ylide **2**. The coordination of LiBr with the carbonyl oxygen of ester or amide is obviously possible. Thus, a possible mechanism could be envisioned to proceed via a chelating six-membered ring transition state, which is formed by coordination of lithium ion with carbonyl oxygen and ylidic carbanion simultaneously. Transition state **TS-4** might be anticipated to be more stable than **TS-3** because the Te(*i*-Bu)$_2$ group is more sterically demanding than the vinyl group (Scheme 7); thus, the formation of **B** in the initial condensation is favored over that of **A**.

When methyl cinnamate was added to the ylide **2b** solution, produced *in situ* from the salt **1b** with LTMP, the color of the ylide faded slowly, and quenching just after the complete disappearance of the ylide color gave **5a** in 89% yield, as did quenching at room temperature.

This experiment showed that the initial step, i.e., in the presence of lithium bromide, Michael addition of ylide **2** to α,*β*-unsaturated esters and amides, is a slow step and that the second step is fast. Thus, the mechanism of the reaction of ylide **2** with α,*β*-unsaturated esters and amides can be explained as shown in Scheme 7**.** Intermediate **B** formed in the first step is favored over intermediate **A** because of the formation of a chelating six-membered ring transition state in the presence of lithium ion. This, plus the fast elimination, leads to **5** as the major product.

Conclusions

The stereocontrolled method described in this paper provides a facile and general means for synthesis of vinylcyclopropane derivatives and also demonstrates that telluronium ylides might be excellent reagents for the preparation of these compounds. Another salient feature is that the stereochemistry of the resulting vinylcyclopropane derivatives can be tuned at will by proper choice of the reaction conditions. The role of lithium salts in the reactions of allylic ylides with α,*β*-unsaturated esters or amides is noteworthy. These features, together with the generality of this method and the easy preparation of ylides, make this reaction a valuable tool for organic synthesis. Applications of this method to the synthesis of some natural products are now in progress in our laboratory.

Experimental Section

All reactions were carried out under N_2. All solvents for the reactions were purified before use. Sodium bis(trimethylsilyl)amide and potassium hydride were purchased from

(17) (a) Schmidbaur, H. *Acc. Chem. Res.* **1975**, *8*, 62 and references cited therein. (b) Vedejs, E.; Meier, G. P.; Snoble, K. A. J. *J. Am. Chem. Soc.* **1981**, *103*, 2823.

(18) Armstrong, D. R.; Davidson, M. G.; Moncrieff, D. *Angew. Chem., Int. Ed. Engl.* **1995**, 478.

Aldrich and Fluka, respectively, and were used directly without further purification. Potassium bis(trimethylsilyl)-amide,[19] allyldiisobutyltelluronium bromide (**1a**), [3-(trimethylsilyl)prop-2-enyl]diisobutyltelluronium bromide (**1b**), and crotyldiisobutyltelluronium bromide (**1c**), were prepared as described in ref 20.

General Procedures: Condition A. A solution of sodium bis(trimethylsilyl)amide (0.75 mmol) in THF (0.75 mL) was added dropwise to a solution of telluronium salt (0.75 mmol) and LiBr (0.75 mmol) in 6.5 mL of solvent at −78°C under N_2. The mixture was stirred for 5 min, and then α,β-unsaturated compound (0.5 mmol) in solvent (1 mL) was added. The reaction mixture was then allowed to warm to room temperature after the reaction was completed. Usual workup and flash chromatography gave the pure product.

Condition B is similar to condition A, except $KN(SiMe_3)_2$ was used instead of $NaN(SiMe_3)_2$ and no lithium salt was added.

***trans*-2-Phenyl-*trans*-3-[2-(trimethylsilyl)vinyl]-1-(methoxycarbonyl)cyclopropane (5a).** Condition A, 93%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 0.02 (s, 9 H), 2.36 (dd, J = 5.2, 5.3 Hz, 1 H), 2.58 (ddd, J = 5.3, 8.8, 9.5 Hz, 1 H), 3.06 (dd, J = 5.2, 9.5 Hz, 1 H), 3.84 (s, 3 H), 5.42 (dd, J = 8.8, 19 Hz, 1 H), 6.01 (d, J = 19 Hz, 1 H), 7.34 (m, 5 H); MS m/z (relative intensity) 274 (1), 259 (7), 243 (3), 215 (6), 73 (100), 45 (11). Anal. Calcd for $C_{16}H_{22}O_2Si$: C, 70.03; H, 8.08. Found: C, 70.20; H, 8.33.

***trans*-2-Phenyl-*cis*-3-[2-(trimethylsilyl)vinyl]-1-(methoxycarbonyl)cyclopropane (4a).** Condition B, 87%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 0.08 (s, 9 H), 2.28 (m, 2 H), 2.80 (dd, J = 6.0, 6.1 Hz, 1 H), 3.71 (s, 3 H), 5.88 (d, J = 18.5 Hz, 1 H), 6.12 (ddd, J = 4, 8.5, 18.5 Hz, 1 H), 7.20 (m, 5 H); ^{1}H NMR (C_6D_6/TMS, 300 MHz) δ 0.20 (s, 9 H), 2.23 (ddd, J = 5.5, 8.7, 9.0 Hz, 1 H), 2.35 (dd, J = 5.5, 9.0 Hz, 1 H), 3.40 (t, J = 6.0 Hz, 1H), 3.42 (s, 3 H), 6.04 (d, J = 18.5 Hz, 1 H), 6.65 (dd, J = 8.7, 18.5 Hz, 1 H), 6.90 (dd, J = 1.7, 7.1 Hz, 2 H), 7.11 (m, 3 H).

***trans*-2-Methyl-*trans*-3-[2-(trimethylsilyl)vinyl]-1-(methoxycarbonyl)cyclopropane (5b).** Condition A, 80%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 0.08 (s, 9 H), 1.14 (d, J = 6.2 Hz, 3 H), 1.48 (dd, J = 4.6, 4.7 Hz, 1 H), 1.66 (m, 1 H), 2.15 (ddd, J = 4.6, 8.2, 8.5 Hz, 1 H), 3.65 (s, 3 H), 5.70 (dd, J = 8.2, 18.5 Hz, 1 H), 5.89 (d, J = 18.5 Hz, 1H); MS m/z (relative intensity) 212 (2), 197 (20), 181 (10), 165 (52), 139 (10), 123 (18), 89 (60), 73 (100). Anal. Calcd for $C_{11}H_{20}O_2Si$: C, 62.21; H, 9.49. Found: C, 61.99; H, 9.95.

***trans*-2-Methyl-*cis*-3-[2-(trimethylsilyl)vinyl]-1-(methoxycarbonyl)cyclopropane (4b).** Condition B, 76%; ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 0.03 (s, 9 H), 1.05 (d, J = 5.4 Hz, 3 H), 1.66 (m, 3 H), 3.61 (s, 3 H), 5.94 (d, J = 18.6 Hz, 1 H), 6.00 (dd, J = 8.1, 18.6 Hz, 1 H).

***trans*-2-(4-Methoxylphenyl)-*trans*-3-[2-(trimethylsilyl)-vinyl]-1-(ethoxycarbonyl)cyclopropane (5c).** Condition A, 93%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 0.06 (s, 9 H), 1.30 (t, J = 7.2 Hz, 3 H), 2.16 (dd, J = 4.8, 5.0 Hz, 1 H), 2.44 (ddd, J = 4.5, 8.8, 9.1 Hz, 1 H), 2.86 (dd, J = 5.0, 9.5 Hz, 1 H), 3.80 (s, 3 H), 4.14 (q, J = 7.2 Hz, 2 H), 5.32 (dd, J = 8.8, 18.4 Hz, 1 H), 5.86 (d, J = 18.4 Hz, 1 H), 6.82 (d, J = 8.6 Hz, 2 H), 7.13 (d, J = 9 Hz, 2 H); MS m/z (relative intensity) 318 (6), 303 (18), 273 (27), 245 (33), 73 (100), 43 (4). Anal. Calcd for $C_{18}H_{26}O_3Si$: C, 67.90; H, 8.23. Found: C, 68.15; H, 8.67.

***trans*-2-(4-Methoxylphenyl)-*cis*-3-[2-(trimethylsilyl)-vinyl]-1-(ethoxycarbonyl)cyclopropane (4c).** Condition B, 80%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 0.10 (s, 9 H), 1.25 (t, J = 7.1 Hz, 3 H), 2.18 (m, 2 H), 2.73 (dd, J = 6.0, 5.9 Hz, 1 H), 3.77 (s, 3 H), 4.18 (q, J = 7.0 Hz, 2 H), 5.98 (d, J = 18.5 Hz, 1 H), 6.10 (ddd, J = 4.7, 8.3, 18.5 Hz, 1 H), 6.76 (d, J = 8.4 Hz, 2 H), 7.02 (d, J = 8.4 Hz, 2 H).

***trans*-2-Furyl-*trans*-3-[2-(trimethylsilyl)vinyl]-1-(ethoxycarbonyl)cyclopropane (5d).** Condition A, 93%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 0.04 (s, 9 H), 1.28 (t, J = 7.3 Hz, 3 H), 2.29 (dd, J = 5.1, 5.2 Hz, 1 H), 2.40 (ddd, J = 5.1, 8.8, 9.0 Hz, 1 H), 2.82 (dd, J = 5.2, 9.2 Hz, 1 H), 4.18 (q, J = 7.3 Hz, 2 H), 5.60 (dd, J = 18.6, 8.8 Hz, 1 H), 5.94 (d, J = 18.6 Hz, 1 H), 6.11 (d, J = 3.2 Hz, 1 H), 6.3 (dd, J = 1.8, 3.1 Hz, 1 H), 7.24 (dd, J = 0.9, 1.4 Hz, 1 H); MS m/z (relative intensity) 278 (3), 263 (2), 160 (33), 73 (100), 59 (10). Anal. Calcd for $C_{15}H_{22}O_3Si$: C, 64.70; H, 7.96. Found: C, 64.72; H, 8.14.

***trans*-2-Furyl-*cis*-3-[2-(trimethylsilyl)vinyl]-1-(ethoxycarbonyl)cyclopropane (4d).** Condition B, 90%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 0.10 (s, 9 H), 1.13 (t, J = 7.1 Hz, 3 H), 2.33 (m, 2 H), 2.68 (dd, J = 5.8 Hz, 5.9 Hz, 1 H), 4.02 (q, J = 7.1 Hz, 2 H), 5.90 (d, J = 18.6 Hz, 1 H), 6.01 (m, 2 H), 6.31 (dd, J = 1.8, 3.0 Hz, 1 H), 7.02 (m, 1 H).

***trans*-2-Phenyl-*trans*-3-[2-(trimethylsilyl)vinyl]-1-(piperidinocarbonyl)cyclopropane (5e).** Condition A, 94%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 0.02 (s, 9 H), 1.59 (m, 6 H), 2.32 (dd, J = 4.9, 5.2 Hz, 1 H), 2.50 (ddd, J = 4.7, 8.7, 9.1 Hz, 1 H), 2.91 (dd, J = 5.2, 9.4 Hz, 1 H), 3.58 (br s, 4 H), 5.43 (dd, J = 8.7, 8.5 Hz, 1 H), 5.84 (d, J = 18.5 Hz, 1 H), 7.21 (m, 5 H); MS m/z (relative intensity) 327 (5), 312 (2), 254 (9), 236 (33), 112 (100), 91 (3), 84 (11), 73 (36), 69 (39); Anal. Calcd for $C_{20}H_{29}NOSi$: C, 73.32; H, 8.92; N, 4.28. Found: C, 73.77; H, 9.36; N, 4.07.

***trans*-2-Phenyl-*cis*-3-[2-(trimethyl)silyl]vinyl-1-(piperidinocarbonyl)cyclopropane (4e).** Condition B, 96%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 0.02 (s, 9 H), 1.51 (m, 6 H), 2.20 (m, 1 H), 2.30 (dd, J = 5.5, 9.3 Hz, 1 H), 2.95 (dd, J = 5.5, 5.5 Hz, 1 H), 3.16 (br s, 1 H). 3.41 (br s, 1 H), 3.77 (br s, 1 H), 3.97 (br s, 1 H), 5.76 (dd, J = 8.5, 18.5 Hz, 1 H), 5.82 (d, J = 18.5 Hz, 1 H), 7.17 (m, 5 H).

***trans*-2-Phenyl-*trans*-3-vinyl-1-(methoxycarbonyl)cyclopropane (5f).** Condition A, 85%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 2.21 (dd, J = 5.0, 5.0 Hz, 1 H), 2.49 (ddd, J = 4.6, 8.5, 9.4 Hz, 1 H), 2.94 (dd, J = 5.3, 9.5 Hz, 1 H), 3.60 (s, 3 H), 5.00 (m, 1 H), 5.42 (m, 2 H), 7.20 (m, 5 H); MS m/z (relative intensity) 202 (5), 143 (100), 128 (90), 115 (40), 91 (15), 77 (9), 65 (7), 51 (6). Anal. Calcd for $C_{13}H_{14}O_2$: C, 77.20; H, 6.98. Found: C, 76.76; H, 7.12.

***trans*-2-Phenyl-*cis*-3-vinyl-1-(methoxycarbonyl)cyclopropane (4f).** Condition B, 76%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 2.25 (m, 2 H), 2.76 (dd, J = 5.9, 6.0 Hz, 1 H), 3.71 (s, 3 H), 5.12 (dd, J = 1.6, 10.3 Hz, 1 H), 5.28 (dd, J = 1.6, 15.6 Hz, 1 H), 5.95 (m, 1 H), 7.15 (m, 5 H).

***trans*-2-Furyl-*trans*-3-vinyl-1-(ethoxycarbonyl)cyclopropane (5g).** Condition A, 76%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 1.11 (t, J = 7.1 Hz, 3 H), 2.15 (dd, J = 5.1, 5.2 Hz, 1 H), 2.25 (ddd, J = 5.2, 9.2, 10.0 Hz, 1 H), 2.61 (dd, J = 5.2, 9.1 Hz, 1 H), 4.04 (q, J = 7.1 Hz, 2 H), 4.95 (dd, J = 1.7, 10.0 Hz, 1 H), 5.11 (dd, J = 1.8, 17.0 Hz, 1 H), 5.32 (m, 1 H), 5.95 (m, 1 H), 6.15 (m, 1 H), 7.13 (m, 1 H); MS m/z (relative intensity) 207 (12), 206 (14), 177 (7), 161 (24), 133 (100), 105 (30), 55 (7). Anal. Calcd for $C_{12}H_{14}O_3$: C, 69.89; H, 6.84. Found: C, 69.78; H, 6.76.

***trans*-2-Furyl-*cis*-3-vinyl-1-(ethoxycarbonyl)cyclopropane (4g).** Condition B, 88%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 1.19 (t, J = 6.9 Hz, 3 H), 2.32 (m, 2 H), 2.66 (dd, J = 5.9, 5.7 Hz, 1 H), 4.07 (q, J = 6.9 Hz, 2 H), 5.09 (dd, J = 1.6, 10.4 Hz, 1 H), 5.26 (dd, J = 1.7, 17.1 Hz, 1 H), 5.81 (m, 1 H), 6.04 (d, J = 3.2 Hz, 1 H), 6.22 (dd, J = 1.8, 3.2 Hz, 1 H), 7.18 (dd, J = 1.8, 2.2 Hz, 1 H).

***trans*-2-Phenyl-*trans*-3-vinyl-1-(piperidinocarbonyl)-cyclopropane (5h).** Condition A, 91: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 1.45 (m, 6 H), 2.17 (dd, J = 5.0, 5.3 Hz, 1 H), 2.34 (m, 1 H), 2.85 (dd, J = 5.3, 9.4 Hz, 1 H), 3.48 (m, 4 H), 4.85 (m, 1 H), 5.11 (m, 2 H), 7.15 (m, 5 H); MS m/z (relative intensity) 255 (11), 164 (15), 128 (23), 112 (100), 91 (8), 84 (17), 69 (50). Anal. Calcd for $C_{17}H_{21}NO$: C, 79.94; H, 8.29; N, 5.51. Found: C, 80.09; H, 8.45; N, 5.35.

***trans*-2-Phenyl-*cis*-3-vinyl-1-(piperidinocarbonyl)cyclopropane (4h).** Condition B, 94%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 1.50 (m, 6 H), 2.11 (m, 1 H), 2.16 (dd, J = 5.5, 9.3 Hz, 1 H), 2.81 (dd, J = 5.6, 5.6 Hz, 1 H), 3.44 (br s, 4 H), 4.93 (dd, J = 1.8, 10.3 Hz, 1 H), 5.15 (dd, J = 1.8, 17.1 Hz, 1 H), 5.54 (ddd, J = 1.8, 10.3, 17.1 Hz, 1 H), 7.45 (m, 5 H).

***trans*-2-Phenyl-*trans*-3-propenyl-1-(methoxycarbonyl-)cyclopropane (5i).** Condition A, 80%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 1.52 (dd, J = 1.4, 6.5, 3 H), 2.15 (dd, J =

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4.9, 5.0 Hz, 1 H), 2.39 (ddd, J = 4.7, 9.3, 9.6 Hz, 1 H), 2.92 (dd, J = 5.3, 9.6 Hz, 1 H), 3.70 (s, 3 H), 4.32 (m, 1 H), 5.62 (m, 1 H), 7.30 (m, 5 H); MS m/z (relative intensity) 216 (4), 157 (100), 141 (31), 129 (63),115 (32), 91 (24), 77 (14), 51 (5). Anal. Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.65; H, 7.50.

***trans*-2-Phenyl-*cis*-3-propenyl-1-(methoxycarbonyl)cyclopropane (4i).** Condition B, 74%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 1.75 (dd, J = 0.8, 5.9 Hz, 3 H), 2.25 (m, 2 H), 2.67 (dd, J = 5.9, 5.9 Hz, 1 H), 3.86 (s, 3 H), 5.65 (m, 2 H), 5.23 (m, 5 H).

***trans*-2-Phenyl-*trans*-3-propenyl-1-(piperidinocarbonyl)cyclopropane (5j).** Condition A, 88: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 1.21 (d, J = 6.6 Hz, 3 H), 1.51 (m, 6 H), 2.22 (dd, J = 5.0, 5.1 Hz, 1 H), 2.39 (ddd, J = 4.7, 9.3, 9.3 Hz, 1 H), 2.88 (dd, J = 5.1, 9.4 Hz, 1 H), 3.63 (m, 4 H), 4.91 (m, 1 H), 5.65 (m, 1 H), 7.26 (m, 5 H); MS m/z (relative intensity) 269 (9), 178 (22), 112 (100), 91 (11), 69 (48); HMRS calcd for $C_{18}H_{23}NO$ 269.1780, found 269.1743.

***trans*-2-Phenyl-*cis*-3-propenyl-1-(piperidinocarbonyl)cyclopropane (4j).** Condition B, 92%: ^{1}H NMR ($CDCl_3$/TMS, 300 MHz) δ 1.54 (m, 6 H), 1.61 (dd, J = 1.6, 6.5 Hz, 3 H), 2.15 (m, 1 H), 2.18 (dd, J = 5.4, 9.3 Hz, 1 H), 2.81 (dd, J = 5.6, 5.7 Hz, 1 H), 3.59 (m, 4 H), 5.32 (m, 1 H), 5.65 (m, 1 H), 7.25 (m, 5 H).

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