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Tetrahydrothiophene-Catalyzed Synthesis of Benzo[*n*.1.0] Bicycloalkanes

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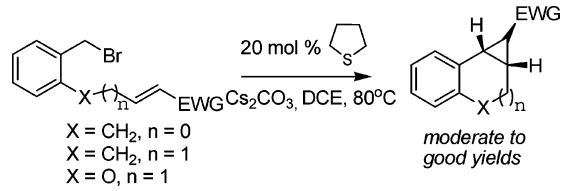

A catalytic intramolecular cyclopropanation for the preparation of benzobicyclic compounds with [*n*.1.0] units has been developed. In the presence of 20 mol % of tetrahydrothiophene, the reactions of compounds **2a**−**2h** afford versatile benzo[*n*.1.0]bicycloalkanes with excellent stereoselectivity in moderate to good isolated yields.

Introduction

[*n*.1.0] Bicycloalkanes have received considerable interest because of their frequent occurrence in biologically active natural and nonnatural products.[1,2] In addition, fused bicyclic compounds are important intermediates for the synthesis of some complex molecules because of their latent reactivity and highly stereoselective transformation.[3] Therefore, several strategies have been reported for the construction of this important structural motif.[4,5] Of the synthetic methods developed, most are involved in inter- or intramolecular cyclopropanation of electron-rich alkenes[5,3d] with metal carbenes. Recently, a tandem Michael addition−substitution of stabilized sulfur[6] and nitrogen[7] ylides to α,β-unsaturated compounds has been reported to produce such compounds, which complement metal-carbenoid methodologies and are often better suited to relatively electron-rich alkene substrates. In our recent study on ylide chemistry in organic synthesis,[8] we found that an intramolecular ylide Michael addition reaction of ester **1a** (using K_2CO_3 as base to generate ylide) afforded 2*H*-chromene **3a** in 85% yield, and the desired cyclopropane was not observed. Noticeably, using Cs_2CO_3 instead of K_2CO_3, **1a** gave 4*H*-chromene **4a** as a major product (Scheme 1). Thus, 2*H*-chromenes and 4*H*-chromenes could be synthesized controllably from the same starting material just by the choice of a base.[9] During the study on the mechanism of this reaction, we found that when the oxygen atom of the vinylogous ester **1a** was replaced by OCH_2 group, an ylide cyclopropanation[10] product **5a** was obtained in 76% yield under similar reaction conditions (Scheme 1), providing easy access to benzo[*n*.1.0] bicycloalkanes. In this paper, we wish to report this reaction in details.

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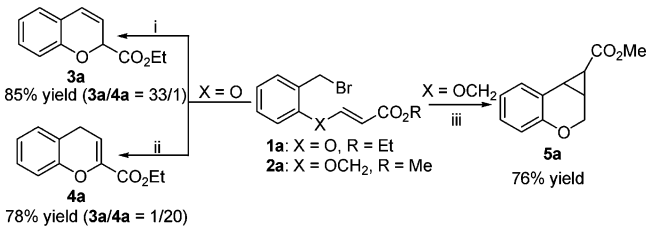
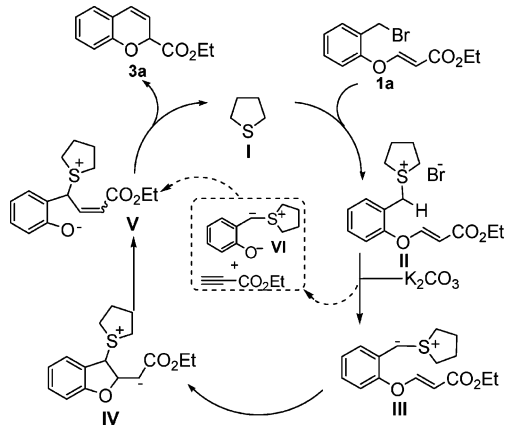
SCHEME 1. Substrate-Dependent Ylide Cyclization

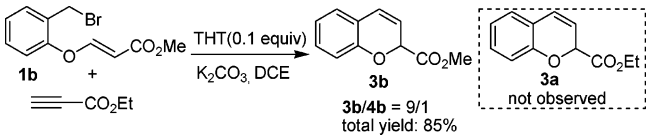


i) THT (10 mol %), DCE, K_2CO_3, 80 °C. *ii*) THT (100 mol %), DCE, Cs_2CO_3, 80 °C. *iii*) THT (20 mol %), DCE, Cs_2CO_3, 80 °C.

SCHEME 2. A Plausible Mechanism for the Annulation Reaction



SCHEME 3. Cross-Experiment

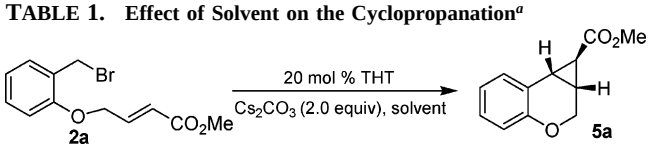


Results and Discussion

Initial Results. The mechanism for the formation of 2*H*-chromene **3a** from compound **1a** was proposed as follows (Scheme 2):[9] tetrahydrothiophene **I** reacted with bromide **1a** to form sulfonium salt **II**, which was deprotonated by K_2CO_3 to generate the corresponding sulfonium ylide **III** in situ. An intramolecular Michael addition of the ylide to acrylate, followed by a β-elimination,[11] produced intermediate **V**. An intramolecular S_N2' reaction of intermediate **V** afforded 2*H*-chromene **3a** and regenerated tetrahydrothiophene to finish a catalytic cycle. Alternatively, the intermediate **II** may also decompose into ylide **VI** and ynoate in the presence of K_2CO_3. Michael addition of the ylide **VI** into ynoate furnished **V**, which gave 2*H*-chromene **3a** as shown in Scheme 2. As a cross-experiment shown in Scheme 3 gave **3b** and **4b** (**3b**/**4b** = 9/1) in 85% total yields and 2*H*-chromene **3a** was not observed, we speculated that the latter pathway is much less possible.

On the basis of this mechanism, the C−O cleavage involving β-elimination is one of the key steps to form 2*H*-chromene **3**. It is envisioned that the annulation described above would be terminated when the oxygen atom is replaced by OCH_2 group.

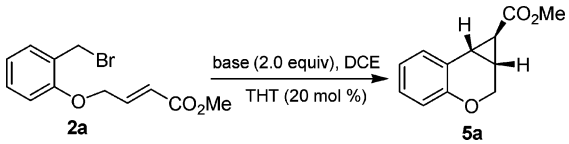
TABLE 1. Effect of Solvent on the Cyclopropanation[a]



entry	time (h)	solvent	yield (%)[b]
1	32	THF	32
2	16	Bu^tOH	<5[c]
3	14	CH_3CN	16
4	14	DMSO	<5[c]
5	22	DCE	56
6	32	CH_3Ph	15
7	18	DME	19
8	29	CH_2Cl_2[d]	49

[a] THT (20 mol %), **2a** in solvent (0.25 M), rt, 15 min, then Cs_2CO_3 (2.0 equiv), 80 °C. [b] Isolated yield. [c] Determined by ^1H NMR. [d] At 45 °C.

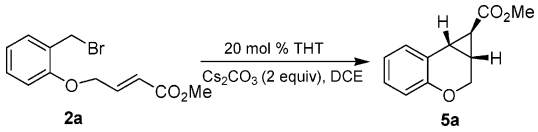
TABLE 2. Effects of Base and Additive[a]



entry	time (h)	additive	base	yield (%)[b]
1	24	/	Bu^tOK	<5[c]
2	58	/	K_2CO_3	8
3	14	/	DBU	<5[c]
4	22	/	Cs_2CO_3	56
5	34	20 uL H_2O	Cs_2CO_3	35
6	25	5 uL H_2O	Cs_2CO_3	44
7	34	KI (0.4 equiv)	Cs_2CO_3	29

[a] THT (20 mol %), **2a** in DCE (0.25 M), rt, 15 min, then additive, base (2.0 equiv), 80 °C. [b] Isolated yield. [c] Determined by ^1H NMR.

TABLE 3. Effects of Reaction Temperature and Substrate Concentration[a]



entry	time (h)	*c* (M)	*T* (°C)	yield (%)[b]
1	48	0.25	25	<10[c]
2	29	0.25	45	49
3	22	0.25	80	56
4[d]	12	0.25	80	59
5[e]	22	0.25	80	45
6	13	0.10	80	76
7	15	0.05	80	61

[a] THT (20 mol %), **2a** in DCE, rt, 15 min, then Cs_2CO_3 (2.0 equiv). [b] Isolated yield. [c] Determined by ^1H NMR. [d] 100 mol % of THT. [e] 10 mol % of THT.

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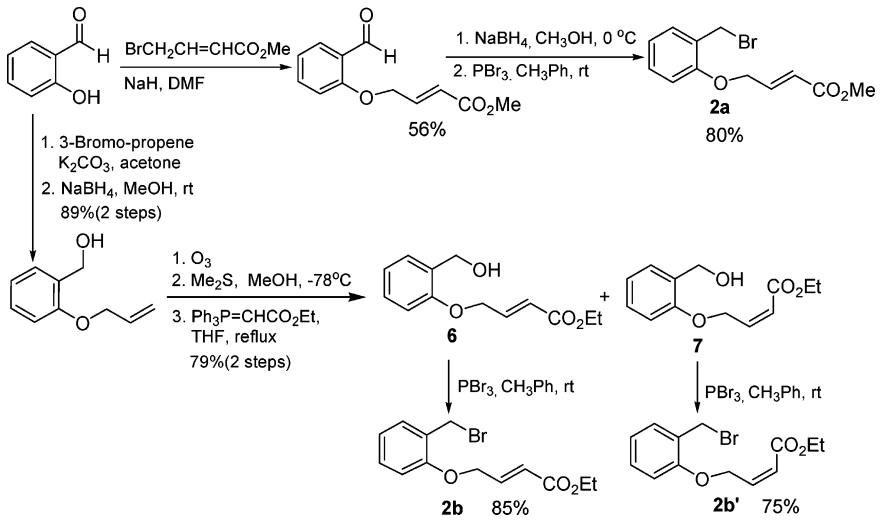
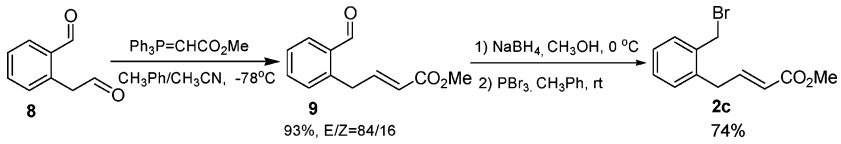
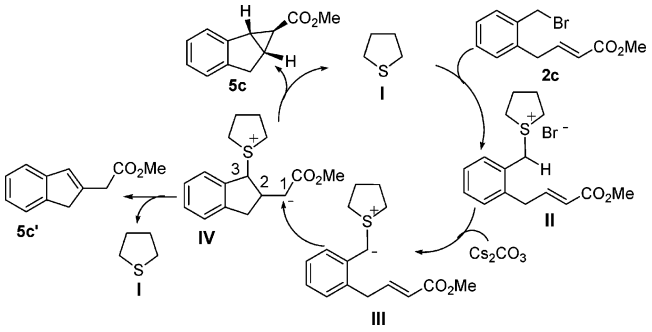
SCHEME 4. Synthesis of Substrates 2a, 2b, and 2b′



SCHEME 5. Synthesis of Substrate 2c



SCHEME 6. A Possible Mechanism for THT-Catalyzed Cyclopropanation Reaction



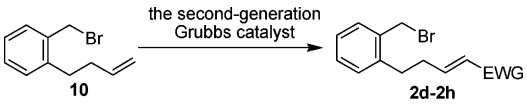
As expected, under a similar reaction condition using Cs_2CO_3 as a base, substrate **2a** (X = OCH_2) gave cyclopropane product **5a** in good yield.

Effects of Reaction Conditions on the Cyclopropanation Reaction. To optimize this intramolecular process, several reaction conditions were investigated using compound **2a** as a substrate. Initially, we examined the effect of solvents using 20 mol % of tetrahydrothiophene (THT) as catalyst and 2.0 equiv of cesium carbonate as a base. As shown in Table 1, the intramolecular cyclopropanation reaction usually proceeded better in halogenated solvents than in nonhalogenated solvents. Of the conditions screened, 1,2-dichloroethane (DCE) was the optimal solvent. Under this condition, 56% yield of **5a** was obtained (entry 5, Table 1).

We also investigated the base effects on this reaction. Although KOBu^t, K_2CO_3, and DBU gave the desired product, cesium carbonate was found to be the best one (entry 4, Table 2) under our screened conditions. As water could accelerate some ylide reactions,[12] a trace amount of water was added to further improve this reaction but resulted in a decrease of the yield (entries 5 and 6, Table 2). The addition of 40 mol % of KI was also found to decrease the yield (entry 7, Table 2).

Reaction temperature and concentration of the substrate proved to influence the yield of this reaction strongly. For

TABLE 4. Synthesis of Substrates 2d−2h[a]



entry	EWG	t (h)	yield(%)[b]
1	CO_2Et (**2d**)	12	98
2	$CO_2{}^tBu$ (**2e**)	12	98
3	CHO (**2f**)	12	74
4	COPh (**2g**)	32	89
5	$COCH_3$ (**2h**)	19	98

[a] Reactions were carried out with 1.5 equiv of alkene and 2.5 mol % of the second-generation Grubbs catalyst. [b] Isolated yield.

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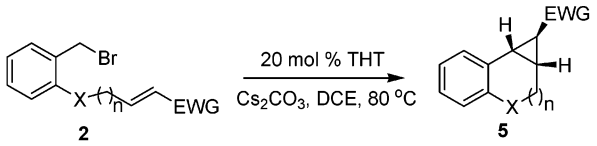
TABLE 5. Intramolecular Cyclopropanation[a]



entry	substrate	method[b]	product	yield (%)[c]
1	**2a**	A	**5a**	76
2	**2b**	A	**5b**	61
3	**2b'**	A	**5b**	48
4	**2c**	B	**5c**	53[de]
5	**2d**	A	**5d**	63
6	**2e**	A	**5e**	77 (86)[f]
7	**2f**	B	**5f**	64
8	**2g**	B	**5g**	64[d]
9	**2h**	A	**5h**	66 (80)[f]

[a] Reagents and conditions: 20 mol % of THT, 2.0 equiv of Cs_2CO_3, **2** in DCE (0.1 M), room temperature, 15 min, then 80 °C, 12−72 h. [b] Method A: O_3 was bubled into the crude product for a few minutes before chromatography; method B: purification by column chromatography. [c] Isolated yield. [d] At 45 °C. [e] 6% of 5c′ was isolated. [f] Conversion by ^{1}H NMR.

example, the conversion was very low at room temperature (entry 1, Table 3). However, when the temperature was increased from room temperature to 80 °C, 56% yield was obtained. At this temperature, even if 10% mol of THT was used, the desired product was given in 45% yield. Without THT, cyclopropanation product was not detected. We also investigated the concentration effect of the substrate and found that the yield was increased to 76% yield when 0.10 M of **2a** was used.

Reaction Scope. The generality of the intramolecular cyclopropanation was evaluated by employing a variety of α,β-unsaturated carbonyl compounds with different structures. Substrates **2a**, **2b**, and **2b′** are readily accessible from salicylaldehyde, as shown in Scheme 4.[13] Substrate **2c** was prepared from dialdehyde **8** by a selective Wittig reaction, followed bytreatment with $NaBH_4$ and PBr_3 as described in Scheme 5.

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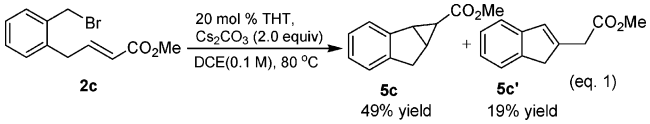
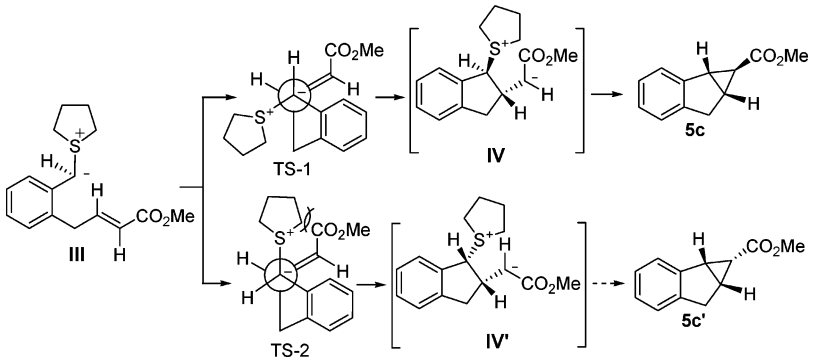
(15) In all cases except for substrates **2e** and **2f**, some byproducts were observed. The byproducts could not be separated by flash chromatography from the desired [*n*.1.0] bicyclic compounds in most cases, so they were not well characterized except for **5c′** isolated from the cyclopropanation reaction mixture of **2c** (eq 1). Fortunately, they could be readily removed by bubbling O_3 for a few minutes and, thus, the pure desired products could be obtained easily.



SCHEME 7. A Rationale for the High Diastereoselectivity



Substrates **2d**−**2h** were synthesized by a cross-metathesis reaction between the benzyl bromide **10** and an electron-deficient alkene using 2.5 mol % of the second-generation Grubbs catalyst in good to excellent yields (Table 4).[14]

As shown in Table 5, α,*β*-unsaturated esters, ketones, and aldehydes were good substrates for the intramolecular cyclopropanation to afford versatile benzo[*n*.1.0]bicycloalkanes with excellent stereoselectivity in moderate to good isolated yields.[15] Both *Z*- and *E*-α, *β*-unsaturated esters **2b** and **2b′** afforded the same product **5b**, and *E*-α,*β*-unsaturated esters **2b** gave higher yield than that of *Z*-α,*β*-unsaturated esters **2b′** (entries 2−3, Table 5). Noticeably, the diastereoselectivity of this reaction is excellent and only one diastereomer was observed in all cases as described in Table 5.

The products obtained here are synthetically useful. For example, product **5f** is a key intermediate for the synthesis of a potential antidepressant.[16] The structures of compounds **5a**−**5h** were determined by ^{1}H, ^{13}C NMR, and HRMS or elemental analysis. Compound **5g** was further confirmed by an X-ray crystallographic analysis.

A possible mechanism for the cyclopropanation is proposed as shown in Scheme 6 (substrate **2c** was used as an example). The reaction of tetrahydrothiophene with bromide **2c** produced sulfonium salt **II**. Deprotonation of salt **II**, followed by an intramolecular conjugate addition of ylide **III** and a 1,3-elimination, furnished bicycloalkane **5c** and regenerated tetrahydrothiophene to complete a catalytic cycle. Byproduct **5c′**[15] was probably formed from the intermediate **IV**, as shown in Scheme 6. A clear mechanism waits for further investigation.

The diastereoselectivity of the present reaction is excellent and only one diastereoisomer was observed in all cases we studied. As shown in Scheme 7, the origin of the selectivity, we proposed, is that transition-state TS-1 might be anticipated to be more stable than transition-state TS-2 because of the steric effects between tetrahydrothiophene group and ester group in TS-2. Thus, the formation of intermediate **IV** is favored over that of intermediate **IV′**, leading to compound **5c** as the major product.

Conclusions

In summary, we have developed a tandem ylide Michael addition−elimination− substitution reaction for the controllable synthesis of 2*H*-chromenes and 4*H*-chromenes, and we also reported a catalytic intramolecular cyclopropanation reaction for the preparation of benzobicyclic compounds with [*n*.1.0] units. The cheap and readily available catalyst, the simple procedure, and the mild reaction condition make this method potentially useful in organic synthesis. Further investigation of the mechanism of the reaction and development of its asymmetric version are in progress in our laboratory.

Experimental Section

Representative Procedure of Method A: Preparation of 1,-1a,2,7b-Tetrahydrocyclopropa[*c*]chromene-1-carboxylic Acid, Methyl Ester (5a). Tetrahydrothiophene (8.8 μL, 0.1 mmol) was added to a stirred solution of substrate **2a** (0.5 mmol) in DCE (5 mL), and the resulting mixture was stirred at room temperature for 15 min. Cs_2CO_3 (1.0 mmol, 326 mg) was added and the reaction mixture was stirred at 80 °C for 13 h. After the reaction was complete, the resulting mixture was filtered rapidly through a funnel with a thin layer of silica gel and was eluted with ethyl acetate. The filtrate was concentrated and the residue was dissolved in CH_2Cl_2. To this solution was bubbled O_3 at −78 °C for 10 min. The resulting mixture was concentrated and the residue was purified by chromatography on silica gel to afford the product **5a** (oil, 76% yield). ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.24 (dd, J = 1.8, 7.8 Hz, 1H), 7.10 (dt, J = 1.8, 7.8 Hz, 1H), 6.93 (dt, J = 0.9, 6.9 Hz, 1H), 6.80 (dd, J = 0.9, 7.8 Hz, 1H), 4.37 (ABd, J = 10.8 Hz, 1H), 3.92 (ABd, J = 10.8 Hz, 1H), 3.72 (s, 3H), 2.57−2.61 (m, 1H), 2.31−2.34 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.6, 152.6, 128.7, 127.3, 123.9, 121.8, 117.3, 61.5, 51.9, 26.9, 24.1, 22.8. IR (υ/cm^{-1}) 2952 (w), 1722 (s), 1582 (m), 1491 (m), 1439 (m), 757 (m); MS (EI, *m*/*z*, rel. intensity) 204 (86.07, M^+), 115 (100). Anal. calcd for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.48; H, 6.04.

Representative Procedure of Method B (for 1,1a,6,6a-Tetrahydro-cyclopropa[*a*]indene-1-carboxylic Acid, Ethyl Ester, 5c).[17] Tetrahydrothiophene (8.8 μL, 0.1 mmol) was added to a stirred solution of substrate **2c** (0.5 mmol) in DCE (5 mL), and the resulting mixture was stirred at room temperature for 15 min. Cs_2CO_3 (1.0 mmol, 326 mg) was added and the reaction mixture was stirred at 80 °C for 62 h. After the reaction was complete, the resulting mixture was filtered rapidly through a funnel with a thin layer of silica gel and was eluted with ethyl acetate. The filtrate was concentrated and the residue was purified by chromatography on silica gel to afford the product **5c** (oil, 49% yield); ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ 7.33−7.35 (m, 1H), 7.12−7.15 (m, 3H), 3.70 (s, 3H), 3.24−3.32 (m, 1H), 2.95−3.07 (m, 2H), 2.42−

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2.48 (m, 1H), 1.22−1.25 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.2, 143.5, 141.7, 126.4, 126.3, 125.2, 123.9, 51.8, 35.3, 34.4, 30.5, 26.5.

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Supporting Information Available: General synthetic procedures and characterization and spectral data for key compounds, CIF for compound **5g**. This material is available free of charge via the Internet at http://pubs.acs.org.

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