JOC Article

Catalytic Intramolecular Formal [3 + 2] Cycloaddition for the Synthesis of Benzobicyclo[4.3.0] Compounds

Xun Han,† Long-Wu Ye,† Xiu-Li Sun, and Yong Tang*

State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, 354 Fenglin Lu, Shanghai 200032, China

tangy@mail.sioc.ac.cn

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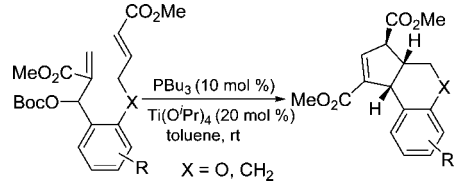

In the presence of 20 mol % of tributylphosphine, *tert*-butyl carbonate substrate **3a** undergoes smoothly an intramolecular formal [3 + 2] cycloaddition reaction at room temperature to give benzobicyclo[4.3.0] compounds in 99% yield with a 19/81 ratio of **2a** and **2a′**. The mechanism of the isomerization of the product **2a** into **2a′** has been investigated in detail. On the basis of this mechanism, two strategies, using 20 mol % of triphenylphosphine or 10 mol % of tributylphosphine in the presence of 20 mol % of $Ti(O^iPr)_4$, have been established for the selective construction of benzobicyclo[4.3.0] compounds. Under neutral conditions, the reactions of compounds **3a**−**g** afford benzobicyclo[4.3.0] compounds **2a**−**g** with high selectivities in good to excellent yields. In addition, α-methyl α,β-unsaturated ester **3h** also works well to give the corresponding product **2h** with one quaternary carbon center in 99% yield under neutral and room temperature conditions.

Introduction

Recently, much attention has been paid to tandem ylide reactions for the construction of cyclic and heterocyclic compounds.[1−8] For instance, Lu and his co-workers reported a phosphorus ylide cyclization for the synthesis of cyclopentenes in a number of elegant studies.[1] Krische et al. documented the first intramolecular variant of the cycloaddition.[2] Kwon et al. developed a facile method for the preparation of functionalized piperidines via [4 + 2] annulation of imines with allenes.[3] Recently, elegant works on the catalytic asymmetric versions have also been reported.[4−8] In a previous study on ylide chemistry,[9] we documented that cyclization precursor allylic bromides **1** underwent readily a formal [3 + 2] cycloaddition at 80 °C in the presence of PPh_3 and base, affording benzobicyclo[4.3.0] compounds diastereoselectively in good to excellent yields (Scheme 1).[10] Under neutral conditions at room temperature, very recently, we found that triphenylphosphine initiates the same formal [3 + 2] cycloaddition of the corresponding *tert*-butyl carbonate substrates **3** smoothly to give **2** in a

† Han and Ye made an equal contribution to this paper.

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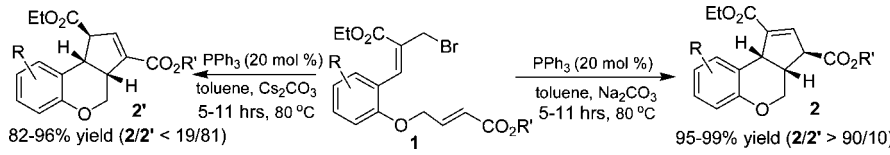
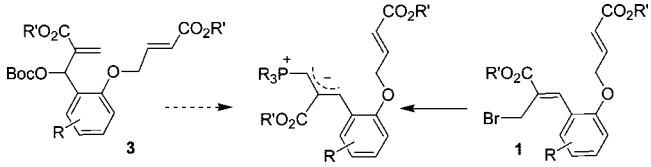
SCHEME 1. Base Effects for Phosphine-Catalyzed Formal [3 + 2] Cycloaddition



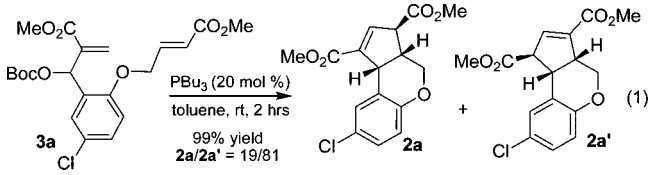
SCHEME 2. Possible Reaction Intermediate



selectivity of >95/5. Furthermore, the reaction proves phosphine-dependent. Compared with triphenylphosphine, tributylphosphine[11,12] can accelerate the reaction greatly but gave a mixture of **2** and **2′** with a ratio of 19/81 as the products, in which most of **2** is isomerized into **2′**. In this paper, results with the OBoc derivative **3** will be presented.

Results and Discussion

Modification of the Intramolecular [3 + 2] Cycloaddition and Isomerization Mechanisms of 2a. Since the reaction of bromide **1** with triphenylphosphine was very slow, the [3 + 2] cycloaddition shown in Scheme 1 was conducted at 80 °C. Considering that *tert*-butyl carbonate substrate **3** might also furnish a similar intermediate of this annulation in the presence of tributylphosphine (Scheme 2),[1d,10a] our further efforts focused on the improvement of the annulation by employing **3** as substrates. In the presence of 20 mol % of tributylphosphine, to our delight, it was found that the reaction of *tert*-butyl carbonate substrate **3a** underwent smoothly the same intramolecular annulation under neutral conditions and 99% yield was obtained at room temperature in 2 h. Unfortunately, the product was obtained as a mixture of **2a** and the isomerized product **2a′** with a ratio of 19/81 (eq 1).



To inhibit the isomerization of product **2a** and to make the current reaction useful, we investigated the mechanism of the isomerization in detail. Initially, an isomerization proceeded through phosphine-initiated Michael addition/proton transfer/elimination was proposed as depicted in Scheme 3 (path A). However, it was found that the PBu_3-catalyzed isomerization reaction proceeded very slowly under the reaction conditions. In the presence of 20 mol % of tributylphosphine, for example, it would take 72 h to switch the molar ratio of **2a** and **2a′** from 83/17 to 24/76 (entry 1, Table 1), which sharply contrasts with the fact that the intramolecular annulation took 2 h to give products **2a** and **2a′** with a ratio of 19/81 in 99% yield (eq 1).

SCHEME 3. Effects of Phosphine Catalysts on the [3 + 2] Cycloaddition

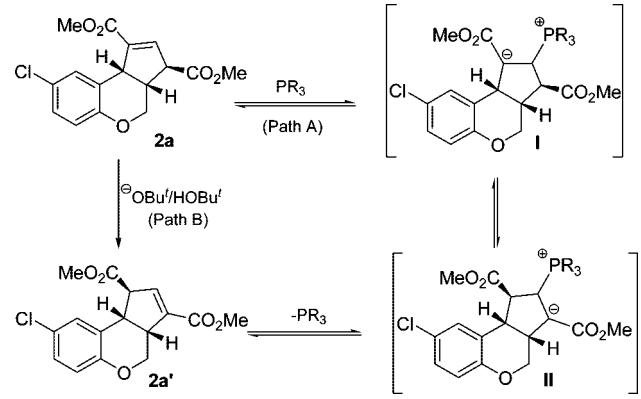
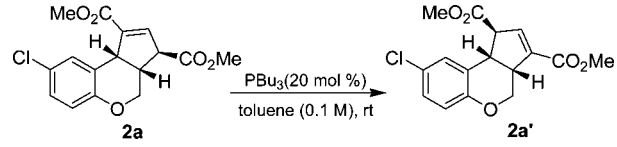


TABLE 1. PBu_3-Promoted Isomerization[a]



			reaction times (h) =				
entry		additive	0	2	6	24	72
1	**2a/2a′**		83/17	79/21	78/22	57/43	24/76
2	**2a/2a′**	^{t}BuOH[b]	83/17	82/18	80/20	72/28	25/75

[a] Conditions: PBu_3 (10.1 mg, 20 mol %), **2a** (80.7 mg, 0.25 mmol) in toluene (2.5 mL), rt. The ratio was determined by ^{1}H NMR. [b] 1.0 equiv of ^{t}BuOH was added.

Considering that the annulation reaction in eq 1 will release 1.0 equiv of ^{t}BuOH that might act as a proton shuttle to accelerate the isomerization, 1.0 equiv of ^{t}BuOH was added to a mixture of **2a** and tributylphosphine in toluene. However, it almost did not speed up the isomerization (entry 2, Table 1). These results suggested that **2a′** was formed only partially through PBu_3-promoted isomerization from **2a** and there is another decisive pathway to govern this isomerization.

In our previous study, we found that base could accelerate the isomerization of **2a** to **2a′**.[10b] In this annulation, the initial step is the attack of phosphine to *tert*-butyl carbonate, which will produce 1.0 equiv of ^{t}BuO$^-$ (eq 2). It is envisioned that the in situ generated ^{t}BuO$^-$ will result in the isomerization of **2a** to **2a′** (path B in Scheme 3). To demonstrate this assumption, 20 mol % of $Ti(O^iPr)_4$ was added to the reaction mixture to reduce the trends of the isomerization by modulating the concentration of ^{t}BuO$^-$. We are pleased to find that the molar ratio of produced **2a** and **2a′** was improved from 19/81 to 91/9 in the presence of 20 mol % of $Ti(O^iPr)_4$ (entry 1 vs. entry 2, Table 2). The ratio was further improved to 98/2 when the tributylphosphine loading decreased from 20 mol % to 10 mol % (entry 3, Table 2). All of these results indicated clearly

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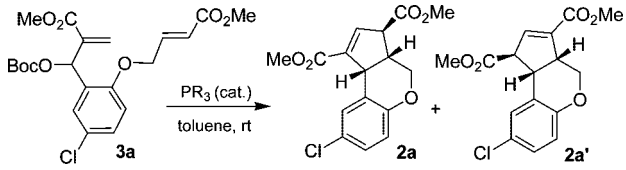
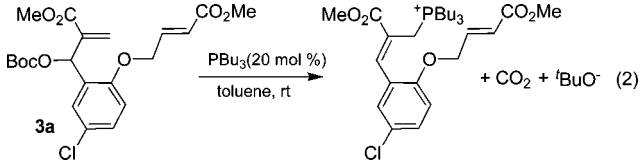
TABLE 2. Effects of Additive and Catalyst on the Annulation[a]



entry	catalyst (mol %)	additive (mol %)	yield (%)[b]	2a/2a′[c]
1	PBu_3 (20)		99	19/81
2	PBu_3 (20)	Ti(^{i}OPr) (20)	99	91/9
3	PBu_3 (10)	Ti(^{i}OPr) (20)	95	98/2
4	PPh_3 (20)		95	95/5

[a] Conditions: **3a** (110 mg, 0.25 mmol) in toluene (2.5 mL), rt, 0.25−32 h. [b] Isolated yield. [c] Determined by ^{1}H NMR.

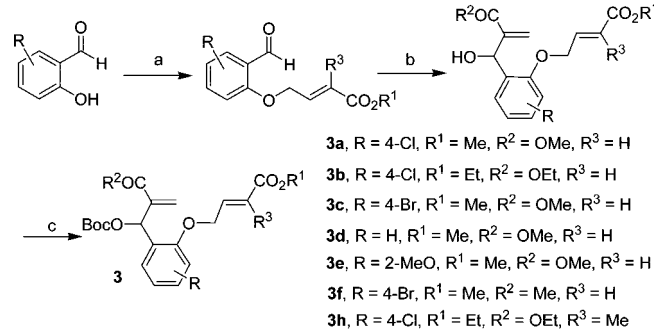
product **2a′**, is formed through both paths A and B as shown in Scheme 3 and path B is dominant.



On the basis of above mechanistic discussions, it is envisioned that the isomerization could also be blocked by employing weakly nucleophilic arylphosphine as catalyst to reduce the generation rates of ^{t}BuO$^-$. As we have speculated, using 20 mol % of PPh_3[13] as catalyst and without the addition of Ti(O^iPr)$_4$, the annulation also proceeded well to give benzobicyclo[4.3.0] compounds **2a** and **2a′** with a ratio of 95/5 under similar reaction conditions (entry 4, Table 2).

Reaction Scope. The generality of this intramolecular annualtion reaction was studied by investigating a variety of α,β-unsaturated carbonyl compounds. Substrates **3a**−**f** and **3h** are readily accessible from the corresponding salicylaldehydes, as shown in Scheme 4. γ-Bromocrotonate reacted with the salicylaldehydes,[14] followed by the Baylis−Hillman reaction[15] and esterification with di-*tert*-butyl dicarbonate,[16] affording the corresponding cyclization precursors *tert*-butyl carbonate **3a**−**f** and **3h**.

SCHEME 4. Synthesis of Substrates 3a−f and 3h[a]



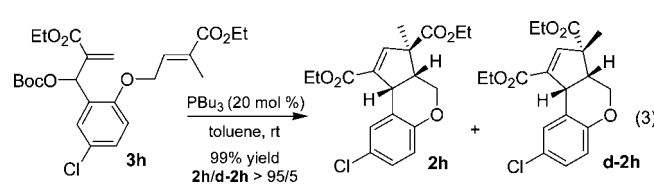
[a] Reagents and conditions: (a) $BrCH_2CH{=}C(R^3)CO_2R^1$, NaH, DMF, rt, 56−88%. (b) $CH_2{=}CHCOR^2$, DABCO or quinuclidine, rt, 29−71%. (c) $(Boc)_2O$, DMAP, CH_2Cl_2rt, 45−70%.

The *tert*-butyl carbonate **3g** was synthesized by cross-metathesis between 2-but-3-enylbenzaldehyde and acrylic acid methyl ester by using 2.5 mol % of the second-generation Grubbs catalyst,[17] followed by similar Baylis−Hillman reaction[18] and esterification as described in Scheme 5.

As shown in Table 3, under the optimal conditions, products **2a**−**g** were obtained as major ones with excellent selectivities. The substituents, such as Cl, Br, and OMe, on the benzene ring had slight effects on the yields (entries 1−7, Table 3). All of the substrates examined gave high to excellent yields. Noticeably, the diastereoselectivity of the current reaction is excellent and only one diastereomer was observed in all cases described in Table 3.

By using 20 mol % of PPh_3 as the catalyst, benzobicyclo[4.3.0] compounds **2a**−**g** could also be synthesized as major products with excellent diastereoselectivities in good to excellent yields, as shown in Table 4. The substituents on the benzene ring had also a slight effect on the yields (entries 1−7, Table 4). In addition, the reaction could also be performed well when 10 mol % of PPh_3 was used as catalyst (entry 1, Table 4). Thus, the present reaction provided a facile and an efficient method for the synthesis of functionalized benzobicyclo[4.3.0] compounds in a high-yielding and stereocontrolled manner.

In addition, by using 20 mol % of tributylphosphine as catalyst, α-methyl α,β-unsaturated ester *tert*-butyl carbonate substrate **3h** could also furnish the corresponding benzobicyclo[4.3.0] compound **2h** with a quaternary carbon as the product (eq 3). It is worth noting that, under this neutral and room temperature condition, the reaction yield was greatly improved compared with that of the bromide substrate in our previous report (99% vs. 78%).[10b]



Conclusions

In summary, we have developed a phosphine-catalyzed intramolecular ylide annulation under neutral conditions at room temperature. The isomerization mechanism of product **2** under the reaction conditions is studied. On the basis of this mechanism, we established two strategies for the efficient construction of benzobicyclo[4.3.0] compounds **2**. In addition, we also reported a phosphine-catalyzed ylide annulation for the facile

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SCHEME 5. Synthesis of Substrate 3g

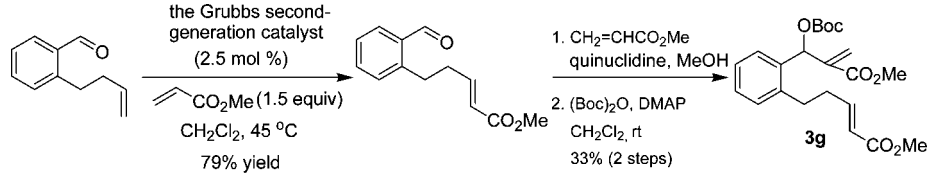
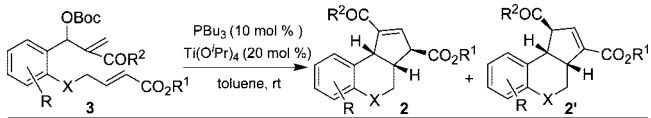


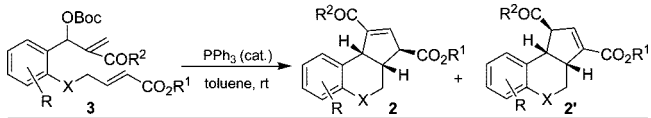
TABLE 3. Tributylphosphine-Catalyzed Highly Diastereoselective Synthesis of Benzobicyclo[4.3.0] Compounds 2[a]



entry	3	R	R^1	R^2	X	2 (2/2′)[b]	yield (%)[c]
1	**3a**	4-Cl	Me	OMe	O	**2a** (>97/3)	99
2	**3b**	4-Cl	Et	OEt	O	**2b** (>97/3)	99
3	**3c**	4-Br	Me	OMe	O	**2c** (>97/3)	99
4	**3d**	H	Me	OMe	O	**2d** (>95/5)	94
5	**3e**	2-OMe	Me	OMe	O	**2e** (93/7)	75
6	**3f**	4-Br	Me	Me	O	**2f** (>98/2)	95
7	**3g**	H	Me	OMe	C	**2g** (>97/3)	93

[a] Reagents and conditions: PBu_3 (5.1 mg, 10 mol %), $Ti(O^iPr)_4$ (14.2 mg, 20 mol %), **3** (0.25 mmol) in toluene (2.5 mL), rt, 1−2.5 h. [b] Determined by 300 MHz ^{1}H NMR. [c] Isolated yield for **2** + **2′**.

TABLE 4. Triphenylphosphine-Catalyzed Highly Diastereoselective Synthesis of Benzobicyclo[4.3.0] Compounds 2[a]



entry	3	R	R^1	R^2	X	2 (2/2′)[b]	yield (%)[c]
1	**3a**	4-Cl	Me	OMe	O	**2a** (>95/5)	95 (90)[d]
2	**3b**	4-Cl	Et	OEt	O	**2b** (>95/5)	99
3	**3c**	4-Br	Me	OMe	O	**2c** (>95/5)	99
4	**3d**	H	Me	OMe	O	**2d** (94/6)	86
5	**3e**	2-OMe	Me	OMe	O	**2e** (93/7)	82
6	**3f**	4-Br	Me	Me	O	**2f** (>96/4)	93
7	**3g**	H	Me	OMe	C	**2g** (93/7)	78

[a] Reagents and conditions: PPh_3 (13.1 mg, 20 mol %), **3** (0.25 mmol) in toluene (2.5 mL), rt, 32−120 h. [b] Determined by 300 MHz ^{1}H NMR. [c] Isolated yield for **2** + **2′**. [d] 10 mol % of PPh_3 was used.

preparation of benzobicyclo[4.3.0] compound with one quaternary carbon center in excellent yield. The simple procedure, mild conditions, high diastereoselectivity, excellent yields, and metal-free catalyzed processes make this method potentially useful in organic synthesis. Further investigations into the synthetic application of the current reaction and the development of its asymmetric version are in progress in our laboratory.

Experimental Section

Representative Procedure for the Tributylphosphine-Catalyzed Synthesis of Benzobicyclo[4.3.0] Compounds 2: Preparation of 8-Chloro-3,3a,4,9b-tetrahydrocyclopenta[*c*]chromene-1,3-dicarboxylic Acid Dimethyl Ester 2a. To a solution of substrate **3a** (110 mg, 0.25 mmol) in toluene (2.5 mL) was added $Ti(O^iPr)_4$ (14.2 mg, 0.050 mmol) and tributylphosphine (5.1 mg, 0.025 mmol) at room temperature. The resulting mixture was further stirred for 1 h. After the reaction was complete, the mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with ethyl acetate (50 mL). Next 20% aqueous H_2O_2 (0.3 mL) solution was added and the resultant mixture was stirred for another 2 h at room temperature, then saturated Na_2SO_3 (0.5 mL) was added. After the resulting mixture was stirred for 1 h, the residue was dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by flash chromatography on silica gel to afford the desired products **2a** as white solid. Mp 82−83 °C; yield 80 mg (99%); ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.56 (d, J = 2.1 Hz, 1H), 7.05 (dd, J = 8.7 and 2.4 Hz, 1H), 6.80−6.77 (m, 2H), 4.40−4.31 (m, 2H), 4.05−3.97 (m, 2H), 3.81 (s, 3H), 3.78 (s, 3H), 3.23−3.16 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 172.3, 164.8, 153.6, 141.2, 139.8, 129.7, 127.7, 126.4, 125.3, 119.1, 66.2, 52.4, 52.0, 50.6, 43.4, 42.2. IR ν/cm^{-1} 2982 (m), 2935 (m), 1734 (s), 1714 (s), 1628 (m), 1485 (m), 1242 (m), 821 (m), 735 (m), 639 (m); MS (ESI, positive mode, m/z) 377 (M + MeOH + Na^+), 345 (M + Na^+); HRMS (EI) calcd for $C_{16}H_{15}O_5Cl$ (M^+) 322.0608, found 322.0607.

Representative Procedure for the PPh_3-Catalyzed Synthesis of Benzobicyclo[4.3.0] Compounds 2: Preparation of 8-Chloro-3,3a,4,9b-tetrahydrocyclopenta[*c*]chromene-1,3-dicarboxylic Acid Dimethyl Ester 2a. To a solution of substrate **3a** (110 mg, 0.25 mmol) in toluene (2.5 mL) was added triphenylphosphine (13.1 mg, 0.050 mmol). The resulting mixture was stirred at room temperature for 32 h. After the reaction was complete, the mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with ethyl acetate. The filtrate was concentrated and the residue was purified by chromatography on silica gel to afford the desired product **2a** in 95% yield (76.3 mg).

Preparation of 8-Chloro-3-methyl-3,3a,4,9b-tetrahydrocyclopenta[*c*]chromene-1,3-dicarboxylic Acid Diethyl Ester 2h..[10b] To a solution of substrate **3h** (121 mg, 0.25 mmol) in toluene (2.5 mL) was added tributylphosphine (10.1 mg, 0.050 mmol). The resulting mixture was stirred at room temperature for 2 h. After the reaction was complete, the mixture was filtered rapidly through a funnel with a thin layer of silica gel and eluted with ethyl acetate. The filtrate was concentrated and the residue was purified by chromatography on silica gel to afford 90.5 mg (99%) of the desired product **2h**. ^{1}H NMR (300 MHz, $CDCl_3$, TMS) δ 7.62 (d, J = 2.1 Hz, 1H), 7.03 (dd, J = 9.0 and 2.4 Hz, 1H), 6.74 (t, J = 8.7 Hz, 2H), 4.46−4.14 (m, 7H), 3.08 (dt, J = 8.4 and 3.0 Hz, 1H), 1.41 (s, 3H), 1.36 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H).

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

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