Stannylcupration of Acetylenes Followed by Reaction with Epoxides: A Novel Annulation Strategy for the Synthesis of Cyclobutenes

Asunción Barbero, Purificación Cuadrado, Carlos García, Juan A. Rincón, and Francisco J. Pulido*

Departamento de Química Orgánica, Facultad de Ciencias, Universidad de Valladolid, Valladolid 47011, Spain

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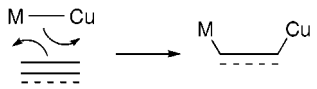
The metallocupration of allenes and acetylenes is a powerful and synthetically useful reaction because it generates two adjacent and usually well differentiated carbon atoms that react sequentially with a wide range of electrophiles (Scheme 1).

Our results in this area have been extensively published in the past years.[1,2] Other examples of stoichiometric[3] or catalytic[4] metallometalations of unactivated C=C π bonds have been reported recently, including the addition of silicon−magnesium,[5] silicon-aluminum,[5] and silicon−zinc[5] bonds to allenes.

The stannylcupration of acetylenes has been widely studied in our group,[6] and it is a particular example of the general reaction. It provides an easy entry to the synthesis of potentially useful small tin-synthons of wide synthetic applicability. In this paper, we report the stannyl cupration of acetylenes followed by reaction with epoxides as a simple and efficient route to the synthesis of cyclobutenes.

Scheme 1



Several strategies have been reported in the literature for the synthesis of cyclobutenes. The most available route to cyclobutenes is the photochemical[7] or thermal[8] [2 + 2] cycloaddition between an alkyne and an alkene. These methods have been thoroughly reviewed.[9] Extrusion of sulfur dioxide from appropriate cyclic sulfones leads to the formation of cyclobutenes. This reaction, known as the Ramberg−Bäcklund rearrangement, has been used widely in synthesis.[10] A third approach involves the introduction of a double bond into a preformed cyclobutane ring, typically via an elimination reaction.[11] A number of less general routes for making cyclobutenes have also been described.[12−15]

Some time ago, we reported in a short paper[16] two examples of cyclobutene ring formation from vinylstannanes initiated by treatment with butyllithium.

We now report in full an apparently general method for the synthesis of 1- and 3-substituted cyclobutenes from acetylenes and epoxides using our stannylcupration methodology. Reaction of acetylenes **1a**−**c** with lithium methyl(tributylstannyl)cuprate[6b] or lithium bis(tributylstannyl)cuprate,[6b] in THF at −78 °C, leads to *cis*-2-(tributylstannyl)vinyl cuprates **2a**−**c**, which are synthetically equivalent to *cis*-1,2-ethylene dianions (Scheme 2). Addition of the tin−copper pair across the triple bond occurs syn-stereospecifically, thus providing an easy entry to the synthesis of *Z*-vinylstannanes.[6] As we noted previously,[6] phenylacetylene (**1b**) reacts with our tin cuprate with regiochemistry opposite to that of 1-decyne (**1c**). The intermediate cuprates **2** react well with ethylene oxide at low temperature (−78 to 0 °C), giving the

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Scheme 2

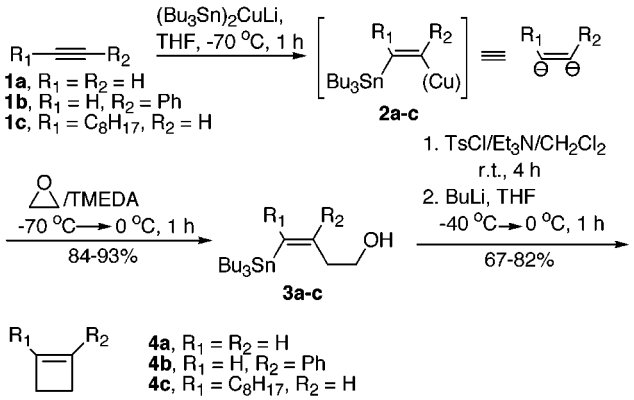
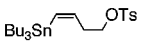
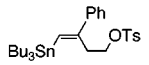
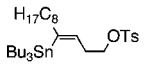
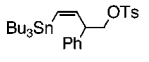
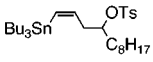
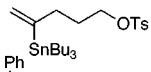
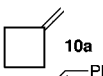
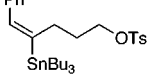
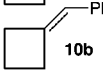


Table 1. Synthesis of Cyclobutenes 4a−c and 7a,b and Cyclobutanes 10a,b

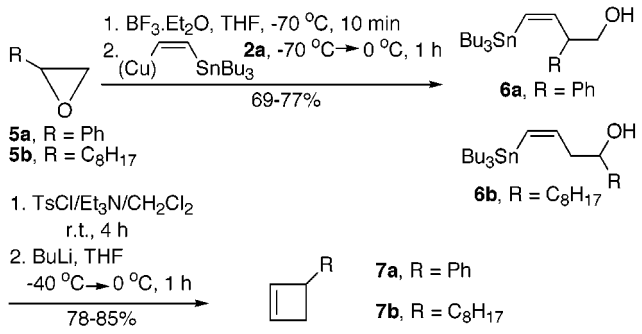
substrate	conditions	product	yield[a]
	BuLi/THF/-40 °C	 **4a**	72%[b]
	BuLi/THF/-40 °C	 **4b**	67%
	BuLi/THF/-40 °C	 **4c**	82%
	BuLi/THF/-40 °C	 **7a**	78%
	BuLi/THF/-40 °C	 **7b**	85%
	BuLi/THF/-70 °C	 **10a**	57%[c]
	BuLi/THF/-70 °C	 **10b**	83%

[a] Isolated yields. [b] Isolated as the dibromo derivative (bp 66−69 °C/22 mmHg). [c] Isolated as the dibromo derivative (bp 82−87 °C/20 mmHg).

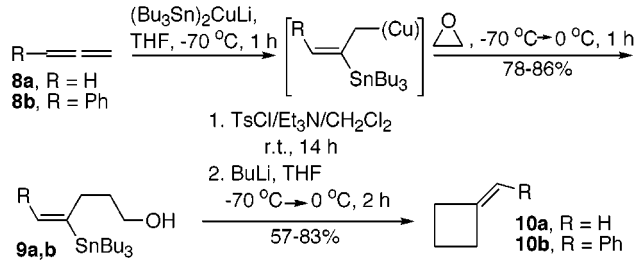
primary alcohols **3a**−**c** (Scheme 2). The use of TMEDA increases yields significantly. We prepared the *p*-toluenesulfonates of alcohols **3a**−**c** by standard procedures. When we treated the former *p*-toluenesulfonates with butyllithium (THF, −40 to 0 °C, 1 h), the major products were the 1-substituted cyclobutenes **4a**−**c** (Scheme 2, Table 1). It should be noted that the tin−lithium exchange takes place faster than the attack of butyllithium to the tosylate group.

The same methodology but using a different strategy enabled us to prepare 3-substituted cyclobutenes. Therefore, substituted epoxides **5a**,**b** react with the *cis*-2-(tributylstannyl)vinyl cuprate **2a** resulting from the stannylcupration of acetylene **1a**, in the presence of BF_3·Et_2O, to give the alcohols **6a**,**b**[17] (Scheme 3). Tosylation of **6a**,**b** followed by intramolecular nucleophilic displacement initiated by treatment with BuLi affords the 3-substituted cyclobutenes **7a**,**b** (Scheme 3, Table 1). Cyclobutenes **4a**−**c** and **7a**,**b** are quite stable. They can be distilled under reduced pressure and stored for a long time in the refrigerator. However, after 2 weeks at room

Scheme 3



Scheme 4



temperature, **4b** undergoes electrocyclic ring opening to a considerable extent. Yields of cyclobutenes **4** and **7** refer to isolated pure compounds; however, conversion of tosylated alcohols into cyclobutenes seems to be complete as was shown by GC and NMR analysis of the crude product.

Although 1,2-disubstituted cyclobutenes could be obtained starting from disubstituted acetylenes, we reported previously[6] that the intermediate cuprates derived from disubstituted acetylenes show a low reactivity toward electrophiles, including ethylene oxide, and therefore, yields of 1,2-disubstituted cyclobutenes are poor.[18]

The procedure herein described is highly versatile. Thus, through the choice of allenes **8a**,**b** as starting materials and our usual cuprate, it is possible to prepare the alcohols **9a**,**b** regioselectively (Scheme 4). Following the same protocol as before (TsCl, rt, and BuLi, −78 °C) alcohols **9** are converted into methylenecyclobutanes **10a**,**b** in very acceptable yields (Scheme 4, Table 1).

In summary, we report a new [2 + 2] annulation strategy for the synthesis of cyclobutenes by coupling of a C_2 acetylenic synthon and a C_2 epoxide synthon, where the key step for the success of the synthesis is the syn addition of the tincuprate to the acetylene that controls the cis stereochemistry required for the final cyclization step.

Experimental Section

All boiling points are uncorrected. All reagents were of commercial quality from freshly opened containers or were purified before use. THF was distilled under N_2 from purple solutions of sodium benzophenone ketyl. Acetylene **1a** (99.6%), allene **8a** (97%), and ethylene oxide (99.9%) were supplied by Air-Products in lecture bottles. Commercial reagents **1b**,**c** and **5a**,**b** were purchased from Aldrich. Preparation of allene **8b** was reported in a previous paper.[1c] IR spectra were recorded on a FT/IR spectrophotometer as neat liquid films. ^1H and ^{13}C NMR spectra were taken at 200 and 50 MHz, respectively. GC/MS were recorded operating either in CI mode or EI mode (70 eV).

(17) Alcohol **6b** is obtained along with a small amount (11%) of the regioisomeric alcohol resulting from attack of **2a** to the substituted end of the epoxide. In the absence of BF_3·Et_2O, the reaction gives poor yields.

(18) A typical reaction using diphenylacetylene led to only a 15% of 1,2-diphenylcyclobutene.

Purification of products were performed by flash chromatography on silica gel 60 (Merck, 230−400 mesh). Lithium bis(tributylstannyl)cuprate was prepared and used as reported in our original work.[6b] Nonaqueous reactions were carried out under nitrogen atmosphere. Compounds **3a**,**b** and **9a** were described in previous papers.[2b,6b] The very well-known compounds **4a** and **10a** were isolated as 1,2-dibromo derivatives, due to their low boiling point. Unless otherwise noted, yields of all compounds are of purified material.

General Procedure for the Preparation of Alcohols 3. Typically, a solution of the acetylene **1** (4 mmol) in THF (4 mL) was added dropwise to the lithium bis(tributylstannyl)cuprate[6b] reagent (4 mmol) cooled with a solid carbon dioxide−acetone bath, and the mixture was stirred for 1 h. TMEDA (4.5 mmol) was added to the stannylcupration mixture at −70 °C. After 5 min, ethylene oxide (8 mmol) was added at −70 °C, and the resulting mixture was warmed to 0 °C for 1 h, with continuous stirring. Saturated aqueous ammonium chloride (10 mL) was added to the mixture. Extraction with diethyl ether, drying ($MgSO_4$), and chromatography (hexanes−EtOAc) gave the alcohols **3a**−**c** (Scheme 2). We described compounds **3a** (93%) and **3b** (84%) in a previous paper.[6b]

(*Z*)-4-(Tributylstannyl)dodec-3-en-1-ol (3c): colorless oil (87%); IR (neat) 3630, 3350 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.97 (t, 1H, J = 7.2 Hz, $^3J_{Sn-H}$ = 136 Hz), 3.63 (t, 2H, J = 6.9 Hz), 2.38 (dt, 2H, J = 7.2, 6.9 Hz), 2.17 (t, 2H, J = 6.7 Hz), 1.65 (broad s, 1H), 1.55−0.8 (m, 42H); ^{13}C NMR ($CDCl_3$) δ 147.8, 135.9, 62.1, 41.1, 37.7, 32.4, 31.1, 30.0, 29.6, 29.1, 28.7, 28.2, 23.5, 14.7, 14.2, 10.2; MS (CI) m/z 475 $(M + H)^+$, 247 (base). Anal. Calcd for $C_{24}H_{50}OSn$: C, 60.90; H, 10.65. Found: C, 61.18; H, 10.81.

General Procedure for the Preparation of Alcohols 6. A solution of $BF_3{\cdot}Et_2O$ (4 mmol) in THF (4 mL) was added dropwise to a THF solution (4 mL) of the epoxide **5** (4 mmol) at −70 °C, and the mixture was stirred for 10 min. Immediately, the cuprate **2a** (4 mmol), prepared as before, in THF (4 mL) was added from an adjacent flask, via cannula, at −70 °C, and the resulting mixture was warmed to 0 °C for 1 h. An aqueous workup using ammonium chloride, extraction with diethyl ether (2 × 15 mL), drying with magnesium sulfate, and chromatography (SiO_2, hexane/EtOAc) gave the alcohols **6a** (77%) and **6b** (69%) (Scheme 3).

(*Z*)-2-Phenyl-4-(tributylstannyl)but-3-en-1-ol (6a): colorless oil (77%); IR (neat) 3400 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.45−7.25 (m, 5H), 6.72 (dd, J = 12.3, 6.2 Hz, $^3J_{Sn-H}$ = 132 Hz, 1H), 6.18 (d, J = 12.3 Hz, $^2J_{Sn-H}$ = 55.5 Hz, 1H), 3.81−3.68 (m, 2H), 3.28 (q with fine couplings, J = 6.2 Hz, 1H), 1.61 (broad s, 1H), 1.45−0.9 (m, 27H); ^{13}C NMR ($CDCl_3$) δ 148.1, 140.5, 132.6, 128.1, 127.0, 126.2, 66.4, 55.8, 29.4, 27.3, 13.7, 9.1; MS (CI) m/z 439 $(M + H)^+$, 269 (base). Anal. Calcd for $C_{22}H_{38}OSn$: C, 60.43; H, 8.76. Found: C, 60.61; H, 8.89.

General Procedure for the Synthesis of Cyclobutenes 4 and 7. The alcohols **3** and **6** were tosylated by standard procedures (TsCl, Et_3N, CH_2Cl_2, rt, 4 h). The former tosylates (2.8 mmol) in THF (3 mL) were treated with BuLi (4.2 mmol, 1.6 M in hexane) at −40 °C, and the resulting solution was warmed to 0 °C for 1 h with continuous stirring. Brine was added (5 mL) and the mixture extracted with diethyl ether (2 × 10 mL) and dried with $MgSO_4$. Careful rotoevaporation of the solvent and microdistillation of the oily residue gave the final products **4** and **7** (Schemes 2 and 3, Table 1). The known compound **4a** (72%, bp 2 °C) was isolated as the 1,2-dibromo derivative by addition of bromine to the reaction mixture before the final workup (Table 1).

1-Phenylcyclobutene (4b): colorless liquid (67%); bp 62−65 °C/3 mmHg (lit.[19] bp 68−70 °C/3.5 mmHg); IR (neat) 1623 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.24−7.15 (m, 5H), 6.21 (s, 1H), 2.84 (m, 2H), 2.45 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 148.4, 134.8, 128.2, 127.9, 127.1, 126.4, 37.1, 30.9; MS (EI) m/z 130 (M^+), 51 (base).

1-Octylcyclobutene (4c): colorless liquid (82%); bp 45−48 °C/1.5 mmHg; IR (neat) 1642 cm^{-1}; ^1H NMR ($CDCl_3$) δ 5.67 (s with fine couplings, 1H), 2.38 (t, J = 2.8 Hz, 2H), 2.29 (t, J = 2.8 Hz, 2H), 1.97 (t, J = 7.5 Hz, 2H), 1.50−1.21 (m, 12H), 0.93 (t, J = 7.2 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 151.3, 128.6, 35.7, 32.9, 32.1, 31.7, 29.6, 29.5, 28.7, 28.1, 23.3, 14.2; MS (EI) m/z 166 (M^+), 68 (base). Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.98; H, 13.56

3-Phenylcyclobutene (7a): colorless liquid (78%); bp 48−51 °C/1 mmHg; IR (neat) 3050−3030, 1592 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.43−7.20 (m, 5H), 6.21 (d with fine couplings, J = 1.9 Hz, 1H), 6.02 (d, J = 1.9 Hz, 1H), 4.23 (dd, J = 5.4, 2.6 Hz, 1H), 3.19 (dd, J = 15.4, 5.2 Hz, 1H), 2.37 (dd, J = 15.4, 2.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 143.7, 135.5, 131.9, 128.3, 127.6, 126.8, 68.6, 59.21; MS (EI) m/z 130 (M^+), 129 (base). Anal. Calcd for $C_{10}H_{10}$: C, 92.26; H, 7.74. Found: C, 92.58; H, 7.85.

3-Octylcyclobutene (7b): colorless liquid (85%); bp 52−55 °C/1 mmHg; IR (neat) 3045 cm^{-1}; ^1H NMR ($CDCl_3$) δ 6.08 (d, J = 1.8 Hz, 1H), 5.96 (d with fine couplings, J = 1.8 Hz, 1H), 2.75 (m, 1H), 2.64 (dd, J = 11.2, 3.1 Hz, 1H), 2.03 (dd, J = 11.2, 1.1 Hz, 1H), 1.57−1.20 (m, 14H), 0.82 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$) δ 140.4, 135.9, 62.3, 53.8, 44.1, 38.5, 37.1, 35,3, 32,6, 26.14, 22.6, 14.6; MS (EI) m/z 166 (M^+), 54 (base). Anal. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.87; H, 13.50.

General Procedure for the Preparation of Alcohols 9. The allene **8**[1c] (4 mmol) in THF (4 mL) was added to the lithium bis(tributylstannyl)cuprate[6b] (4 mmol) at −70 °C, and the mixture was stirred for 1 h. Ethylene oxide (8 mmol) was added to the stannylcupration mixture at −70 °C, and the resulting mixture was warmed to 0 °C for 1 h. The usual workup and chromatography (hexane/EtOAc) gave the alcohols **9a,b** (Scheme 4). We described alcohol **9a** (78%) in a previous paper.[2b]

(*E*)-5-Phenyl-4-(tributylstannyl)pent-4-en-1-ol (9b): colorless oil (86%); IR (neat) 3350 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.31−7.18 (m, 5H), 6.53 (s with fine couplings, 1H), 3.62 (t, J = 7.1 Hz, 2H), 2.42 (t, J = 6.7 Hz, 2H), 1.87 (m, 2H), 1.69 (broad s, 1H), 1.65−0.78 (m, 27H); ^{13}C NMR ($CDCl_3$) δ 157.7, 146.2, 137.0, 129.2, 128.7, 127.3, 63.2, 45.1, 32.8, 29.1, 27.3, 14.5, 10.1; MS (CI) m/z 453 $(M + H)^+$, 395 (base). Anal. Calcd for $C_{23}H_{40}OSn$: C, 61.22; H, 8.94. Found: C, 61.35; H, 9.03.

General Procedure for the Preparation of Cyclobutanes 10. The alcohols **9a**,**b** (3 mmol) were stirred with tosyl chloride (4 mmol) and triethylamine (4 mmol) in dichloromethane (12 mL) at room temperature overnight. Hexane (3 mL) was added to precipitate the excess of tosyl chloride, and the solution was filtered and concentrated. The crude tosylate (94−97%, ^1H NMR δ 3.97−4.08, CH_2-OTs) was dissolved in THF (4 mL) and used without further purification for better yields. BuLi (4.5 mmmol, 1.6 M in hexane) was added at −70 °C, and the mixture was stirred at this temperature for a few minutes. Then, the resulting brownish solution was allowed to warm to 0 °C during 2 h. Brine was added (5 mL), and the mixture was extracted with Et_2O and dried ($MgSO_4$). Rotoevaporation of the solvent and Kugelrohr distillation of the residue gave **10b** (359 mg, 2.5 mmol, 83% from **9b**) (Scheme 4, Table 1). The known compound **10a** (57%, bp 42 °C, Aldrich) was isolated as the dibromo derivative by addition of bromine to the reaction mixture before the final workup (Table 1).

Benzylidenecyclobutane (10b): colorless liquid (83%); bp 67−72 °C/3 mmHg (lit.[20] bp 112−113 °C/15 mmHg); IR (neat) 1672 cm^{-1}; ^1H NMR ($CDCl_3$) δ 7.41−7.18 (m, 5H), 6.14 (m, 1H), 3.14−2.88 (m, 4H), 2.19 (quintet, J = 6 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 141.27, 132.7, 129.3, 128.6, 127.5, 115.9, 34.5, 30.5, 18.1; MS (EI) m/z 144 (M^+), 129 (base).

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Supporting Information Available: Full spectroscopic and analytical data for compound **6b**. Experimental procedure for the tosylation of alcohols **3** and **6**, as well as ^1H NMR characterization data of all tosylates (1 page). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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