3-(Tri-*n*-butylstannyl)-2-cyclobuten-1-one: Synthesis and Stille Cross-Coupling as a Route to 3-Substituted Cyclobutenones

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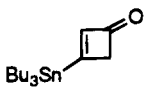
Introduction

Substituted cyclobutenones are versatile compounds for the synthesis of a variety of organic structures.[2-12] A few naturally occurring compounds bearing a cyclobutenone ring have even been described.[13] During the course of various studies of metal-mediated transformations based on cyclobutene systems,[4-6,14-18] the synthesis of 3-(tri-*n*-butylstannyl)-2-cyclobutenone (**1**) was desired. Its synthesis and conversion to 3-substituted cyclobutenones by palladium catalyzed cross-coupling with some organic halides are documented herein.



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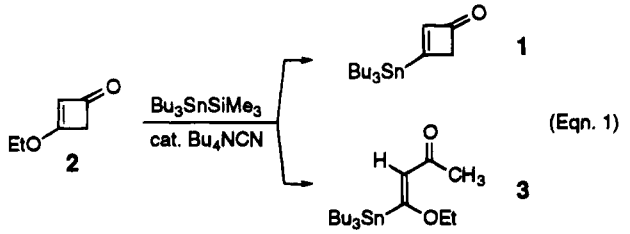
Results and Discussion

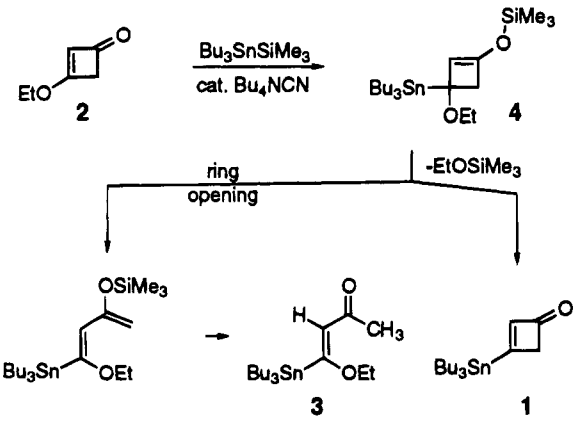
Following precedent established for the synthesis of (tri-*n*-butylstannyl)cyclobutenediones,[19] 3-ethoxy-2-cyclobuten-1-one[20,21] was treated with (tri-*n*-butylstannyl)-trimethylsilane and catalytic *n*-$Bu_4N^+CN^-$ in THF (eq 1). This established method for conjugate addition of a tri-*n*-butylstannyl moiety[22,23] did not reproducibly provide cyclobutenone, **1**. Rather, produced in addition to **1** were



(Eqn. 1)

variable amounts of the interesting functionalized organostannane, **3**, a molecule related to the β-stannylacrylates of Quayle.[24,25] Since the side product, **3**, probably resulted from a thermal ring-opening of the cyclobutene intermediate, **4** (Scheme 1), maintenance of low-tem-

Scheme 1



perature during the reaction and facilitation of OEt departure was attempted in order to maximize the formation of stannylcyclobutenone **1**. After some experimentation, it was discovered that addition of $AlCl_3$ to the low-temperature reaction mixture, *after consumption of starting material was indicated by TLC,* reproducibly provided good isolated yields of 3-(tri-*n*-butylstannyl)-2-cyclobutenone, **1**, on a multigram scale. Conversely, treatment of 3-ethoxycyclobutenone with (tri-*n*-butylstannyl)trimethylsilane and catalytic *n*-$Bu_4N^+CN^-$ in THF *with warming to room temperature* and direct chromatography of the crude reaction material led to an excellent yield of (*E*)-4-ethoxy-4-(tri-*n*-butylstannyl)-3-buten-2-one, **3**. It is presumed that protodesilylation of an intermediate trimethylsilylenol ether occurs during chromatography. The *E*-stereochemistry assigned to the β-stannylenone, **3**, was readily deduced from the magnitude of the 3-bond vinylic Sn-H coupling constant ($^3J_{SnH}$ = 75 Hz).[26,27]

Having established a dependable route to stannylcyclobutenone, **1**, Stille cross-coupling with a variety of unsaturated organic halides was investigated. Reasonable yields of 3-substituted cyclobutenones, **5**, were obtained by conducting the cross-coupling in CH_3CN at room temperature in the presence of 1.5 mol % $PhCH_2PdCl(PPh_3)_2$ (Table 1). The following points are note-

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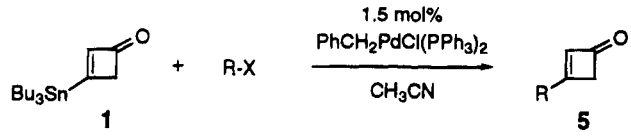
0022-3263/94/1959-7917$04.50/0

Table 1. Stille Cross-Coupling of 3-(Tri-*n*-butylstannyl)cyclobutenone



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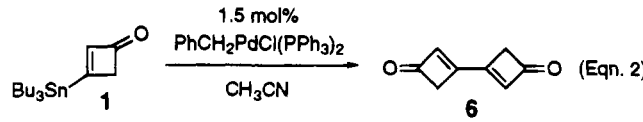
entry	RX	condns	product	yield (%)
1	PhCOCl	rt, 2 h	**5a**, R = PhCO	81
2	(*E*)-MeCH=CHCOCl	rt, 1.5 h	**5b**, R = (*E*)-COCH=CHMe	53
3	*i*-PrCOCl	rt, 1 h	**5c**, R = *i*-PrCO	55
4	PhI	rt, 2 h	**5d**, R = Ph	59
5	4-(MeO)C_6H_4I	rt, 5.75 h	**5e**, R = 4-(MeO)C_6H_4	52
6	2-(COOMe)C_6H_4I	65 °C, 2 h	**5f**, R = 2-(MeO_2C)C_6H_4	51
7	4-$NO_2C_6H_4$I	THF, rt, 22 h then 78 °C, 2 h	**5g**, R = 4-$NO_2C_6H_4$	50
8	2-iodothiophene	rt, 3 h	**5h**, R = 2-thienyl	52
9	2-bromopropene	rt, 1 h then 65 °C, 4 h with 4 mol % CuI	**5i**, R = 2-propenyl	47

worthy: (1) 3,3′-bi(2-cyclobutenone), **6**, a dimeric side-product, is formed (10−15%) under a variety of conditions contributing, in part, to the moderate isolated yields of the cross-coupling products, **5**; (2) stannylcyclobutenone, **1**, appears to be thermally unstable, discoloring on storage at room temperature; (3) best yields were obtained when the reaction was conducted at room temperature; (4) it is not necessary to run the cross-coupling reactions under an inert atmosphere; however, anhydrous conditions are required; (5) in a few cases the addition of cocatalytic CuI facilitated the cross-coupling reaction.[19,28−43] It is significant that simple cyclobutenones bearing electron-withdrawing groups are extremely rare.[44] The results documented in entries 1−3 of Table 1 demonstrate that the Stille cross-coupling of acid halides with 3-(tri-*n*-butylstannyl)cyclobutenone provides a simple and general entry to these potentially useful molecules.

3,3′-Bi(2-cyclobutenone), **6**, the dimeric compound mentioned above, is seen as a byproduct in all of the coupling reactions. A sample of the sensitive compound was obtained in low yield by conducting the palladium catalyzed reaction in the absence of an electrophile, allowing complete characterization of the material (eq 2).



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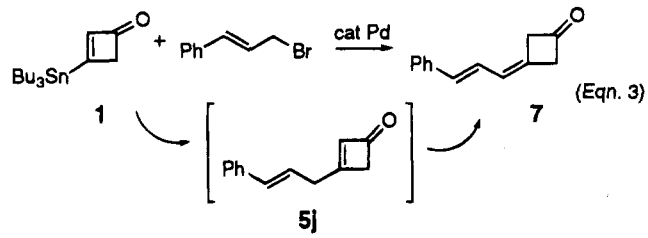
The palladium catalyzed cross-coupling of **1** with cinnamyl bromide did not produce the expected 2-cyclobutenone product, **5j**, rather, the tautomeric 3-[(*E*)-cinnamylidene]cyclobutanone, **7**, was obtained in 57% yield (eq 3).



Conclusions

Either 3-(tri-*n*-butylstannyl)-2-cyclobutenone or (*E*)-4-ethoxy-4-(tri-*n*-butylstannyl)-3-buten-2-one can be prepared in high yield from 3-ethoxy-2-cyclobutenone and (tri-*n*-butylstannyl)trimethylsilane/catalytic *n*-$Bu_4N^+CN^-$ in THF. Stille cross-coupling of 3-(tri-*n*-butylstannyl)-2-cyclobutenone with acid halides, aryl/heteroaryl iodides, and 2-bromopropene occurred in the presence of 1.5 mol % ($PhCH_2$)Pd(PPh_3)$_2$Cl and provided a novel route to 3-substituted 2-cyclobutenones.

Experimental Section

Materials and Methods. Purification by flash SiO_2 column chromatography was performed using 32−63 μm SiO_2 with compressed air as a source of positive pressure. Gas-liquid chromatography was performed on a Hewlett Packard 5890A GC with a 5% phenylmethylsilane crossed-linked capillary column with a film thickness of 0.33 microns and total length of 25 meters. All thin-layer chromatography was performed using Merck Kieselgel 60 F_{254} plates with visualization by UV and phosphomolybdic acid or *p*-anisaldehyde stain. Melting points are uncorrected and were determined either using recrystallized samples or samples which crystallized during concentration of the chromatography eluents. ^{1}H NMR spectra were recorded at 300 MHz or 360 MHz and were internally referenced to $CHCl_3$ (7.26 ppm) or CH_3CN (1.94 ppm). ^{13}C NMR spectra were recorded at 75.5 MHz and were referenced to $CDCl_3$ (77.0 ppm) or C_6H_6 (128.0 ppm). IR spectra were recorded in solution using KCl or NaCl cells.

THF and CH_3CN were dried by distillation over Na/benzophenone and CaH_2, respectively. Benzoyl, (*E*)-crotonoyl, and isobutyryl chloride were purchased from Aldrich and were distilled prior to use. Iodobenzene, 4-iodoanisole, 1-iodo-2-methylbenzoate, 1-iodo-4-nitrobenzene, 2-iodothiophene, cinnamyl bromide, 2-bromopropene, *trans*-benzyl(chloro)bis(triphenylphosphine)-palladium(II), anhydrous $AlCl_3$, and trifluoroacetic acid were

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purchased from Aldrich and used without purification. CuI was purified according to a literature procedure.[45] Tetra-*n*-butylammonium cyanide was purchased from Fluka Chemical Co. and was weighed out under a stream of nitrogen.

3-(Tri-*n*-butylstannyl)-2-cyclobutenone (1). 3-Ethoxy-2-cyclobutenone (**2**)[20,21] (4.50 g, 40.2 mmol, 1.0 equiv) and (tri-*n*-butylstannyl)trimethylsilane[22,23] (16.0 g, 44.1 mmol, 1.1 equiv) were dissolved in 300 mL of dry THF, placed in a dry 1 L round-bottomed flask equipped with a drying tube and cooled to −78 °C with stirring. *n*-Bu_4NCN (0.54 g, 2.01 mmol, 0.05 equiv) dissolved in 4 mL of dry THF was added slowly over 5 min as the reaction mixture turned a darker orange color. After 30 min at −78 °C, TLC (29% EtOAc in hexanes) indicated consumption of starting material. $AlCl_3$ (5.30 g, 40.2 mmol, 1.0 equiv) was added over 10 min under a flow of nitrogen resulting in a light yellow heterogeneous mixture which was stirred for 30 min at −78 °C and then warmed to room temperature over 1 h. Saturated aqueous $NaHCO_3$ (100 mL) was added with thorough mixing and the resulting slurry was extracted with 500 mL of ether and the ether layer was dried over $MgSO_4$. Solvent removal left an orange oil that was purified by flash chromatography (600 mL of hexanes followed by 6% EtOAc in hexanes) providing a yellow/orange band that left 10.2 g (28.6 mmol, 71%) of **1** as an orange oil after removal of solvents: R_f = 0.58 (10% EtOAc in hexanes); IR (CH_2Cl_2, cm^{-1}) 1740, 1645, 1510; ^1H NMR (300 MHz, $CDCl_3$) δ 6.55 (s, 1 H), 3.40 (s, 2 H), 1.55 (m, 6 H), 1.33 (m, 6 H), 1.07 (m, 6 H), 0.90 (t, J = 7.3 Hz, 9 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 189.9, 188.6, 151.6, 56.2, 28.4, 26.6, 13.0, 9.4. Anal. Calcd for $C_{16}H_{30}OSn$: C, 53.82; H, 8.47; Found: C, 53.93; H, 8.53.

(*E*)-4-Ethoxy-4-(tri-*n*-butylstannyl)-3-buten-2-one (3). 3-Ethoxy-2-cyclobuten-1-one (**2**) (4.05 g, 36.1 mmol, 1.0 equiv) and *n*-$Bu_3SnSiMe_3$ (13.1 g, 36.1 mmol, 1.0 equiv) were dissolved in 190 mL of dry THF and cooled to −22 °C while stirring under N_2. *n*-Bu_4NCN (0.24 g, 0.89 mmol, 0.025 equiv) in 2 mL of dry THF was added dropwise over 2 min as the reaction mixture turned a darker orange. After 1 h 3-ethoxycyclobutenone was consumed (TLC). The reaction mixture was warmed to room temperature over 2 h, solvent was removed, and the crude material was chromatographed (1 L of hexanes followed by 6% EtOAc in hexanes) producing a yellow band that provided 11.87 g (0.029 mol, 82%) of **3** as bright yellow oil: R_f = 0.56 (10% EtOAc in hexanes); IR (CH_2Cl_2, cm^{-1}) 1660, 1520; ^1H NMR (300 MHz, $CDCl_3$) δ 6.06 (s, 1 H), 3.82 (q, J = 7.0 Hz, 2 H), 2.13 (s, 3 H), 1.48 (m, 6 H), 1.32 (t, J = 7.0 Hz, 3 H), 1.27 (m, 6 H), 0.95 (m, 6 H), 0.85 (t, J = 7.3 Hz, 9 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 197.0, 195.7, 109.8, 64.6, 29.4, 28.4, 26.6, 13.5, 13.0, 10.6. Anal. Calcd for $C_{18}H_{36}O_2Sn$: C, 53.62; H, 9.00; Found: C, 53.52; H, 9.03.

Stille Cross-Coupling Experiments. General Procedure. In a dry round-bottomed flask equipped with a drying tube was added 1.0 molar equivalent of a 0.28 M CH_3CN solution of the stannylcyclobutenone **1** (THF was used for the experiment with 1-iodo-4-nitrobenzene which was insoluble in CH_3CN), 1.2 molar equiv of the respective electrophile and 1.5 mol % of Pd-($PhCH_2$)Cl(PPh_3)$_2$. The reaction was monitored by TLC and was terminated when all of the stannylcyclobutenone had been consumed (10% EtOAc in hexanes, R_f = 0.58). In some cases heat and/or addition of CuI was required to complete the reaction and these are mentioned where appropriate. When the reaction was complete (1 to 24 h), the reaction mixture was dissolved in about 100 mL of CH_3CN and washed 3 times with an equal volume of hexanes. Collection of the CH_3CN layer and removal of the solvent gave a dark oil that was purified by flash chromatography. Complete analysis (IR, ^1H and ^{13}C NMR, combustion analysis for C and H, and mp for solids) was obtained. A variety of conditions were explored for the coupling with each electrophile, however, only the optimum conditions are mentioned below.

3-Benzoyl-2-cyclobuten-1-one (5a). Stannylcyclobutenone **1** (0.54 g, 1.50 mmol) and distilled benzoyl chloride (0.42 g, 3.00 mmol) for 2 h at room temperature yielded 210 mg (1.22 mmol, 81%) of **5a** as a light yellow solid after chromatography (500 mL of hexanes followed by 6% EtOAc in hexanes): R_f = 0.20 (10% EtOAc in hexanes); mp 66−68 °C (hexane); IR (CH_2Cl_2, cm^{-1}) 1768, 1640, 1520; ^1H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J = 7.8 Hz, 2 H), 7.68 (t, J = 7.4 Hz, 1 H), 7.54 (dd, J = 7.8, 7.4 Hz, 2 H), 6.50 (s, 1 H), 3.75 (s, 2 H); ^{13}C NMR (75.5 MHz, C_6D_6) δ 188.6, 186.5, 164.5, 141.0, 136.0, 133.8, 129.1, 128.9, 51.3. Anal. Calcd for $C_{11}H_8O_2$: C, 76.73; H, 4.68. Found: C, 76.60; H, 4.71.

3-[1-[(*E*)-2-Butenoyl]]-2-cyclobuten-1-one (5b). Stannylcyclobutenone **1** (1.00 g, 2.80 mmol) and distilled crotonoyl chloride (0.35 g, 3.36 mmol) for 1.5 h at room temperature yielded 0.21 g (1.52 mmol, 53%) of **5b** as a bright yellow solid after chromatography (500 mL of hexanes followed by 6% EtOAc in hexanes): R_f = 0.19 (11% EtOAc in hexanes); mp 63−65 °C (hexane); IR (CH_2Cl_2, cm^{-1}) 1775, 1660, 1640, 1615; ^1H NMR (360 MHz, $CDCl_3$) δ 7.13 (dq, J = 15.6 and 7.0 Hz, 1 H), 6.59 (dq, J = 15.6 and 1.6 Hz, 1 H), 6.50 (s, 1 H), 3.51 (s, 2 H), 2.02 (dd, J = 7.0 and 1.6 Hz, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 187.3, 185.4, 165.3, 140.1, 138.6, 127.1, 49.3, 18.0. Anal. Calcd for $C_8H_8O_2$: C, 70.58; H, 5.92. Found: C, 70.35; H, 6.02.

3-(Isobutyryl)-2-cyclobuten-1-one (5c). Stannylcyclobutenone **1** (1.00 g, 2.80 mmol) and distilled isobutyryl chloride (0.36 g, 3.36 mmol) for 1 h at room temperature yielded 0.21 g (1.55 mmol, 55%) of **5c** as a yellow oil after chromatography (500 mL of hexanes followed by 6% EtOAc in hexanes): R_f = 0.65 (33% EtOAc in hexanes); IR (CH_2Cl_2, cm^{-1}) 1780 (br), 1680; ^1H NMR (360 MHz, $CDCl_3$) δ 6.49 (s, 1 H), 3.56 (s, 2 H), 3.18 (sept, J = 6.9 Hz, 1 H), 1.22 (d, J = 7.0 Hz, 6 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 200.3, 187.4, 164.0, 139.5, 49.0, 38.1, 17.6 (2C). Anal. Calcd for $C_8H_{10}O_2$: C, 69.55; H, 7.30. Found: C, 69.82; H, 7.30.

3-Phenyl-2-cyclobuten-1-one (5d). Stannylcyclobutenone **1** (0.18 g, 0.50 mmol) and iodobenzene (0.12 g, 0.61 mmol) for 2 h at room temperature yielded 40.3 mg (0.29 mmol, 59%) of **5d** as a light orange solid after chromatography (500 mL of hexanes followed by 6% EtOAc in hexanes): mp 50.1−51.4 °C (ether-hexane, lit.[21] 51−52 °C). Spectral data (IR and ^1H NMR) were consistent with those reported in the literature.[21]

3-(*p*-Methoxyphenyl)-2-cyclobuten-1-one (5e). Stannylcyclobutenone **1** (1.00 g, 2.80 mmol) and 4-iodoanisole (0.79 g, 3.36 mmol) for 5 h and 45 min at room temperature yielded 0.25 g (1.44 mmol, 52%) of **5e** as a light yellow solid after chromatography (500 mL of hexanes followed by 6% EtOAc in hexanes): mp 80.5−81.5 °C (hexane); R_f = 0.14 (12.5% EtOAc in hexanes); IR (CH_2Cl_2, cm^{-1}) 1745, 1600; ^1H NMR (300 MHz, $CDCl_3$) δ 7.58 (d, J = 8.7 Hz, 2 H), 7.00 (d, J = 8.8 Hz, 2 H), 6.23 (s, 1 H), 3.89 (s, 3 H), 3.49 (s, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 186.7, 169.9, 162.0, 130.4, 126.6, 123.8, 113.8, 54.9, 47.8. Anal. Calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79. Found: C, 76.03; H, 5.87.

3-(2-Carbomethoxyphenyl)-2-cyclobuten-1-one (5f). Stannylcyclobutenone **1** (0.80 g, 2.24 mmol) and methyl 2-iodobenzoate (0.71 g, 2.69 mmol) for 2 h at 65 °C yielded 0.23 g (1.14 mmol, 51%) of **5f** as a pale yellow solid after chromatography (600 mL of hexanes followed by 6% EtOAc in hexanes): mp 54−54.5 °C; R_f = 0.45 (33% EtOAc in hexanes); IR (CH_2Cl_2, cm^{-1}) 1770, 1740, 1600; ^1H NMR (360 MHz, $CDCl_3$) δ 7.69 (m, 1 H), 7.49 (m, 1 H), 7.42 (m, 2 H), 6.20 (s, 1 H), 3.80 (s, 3 H), 3.42 (s, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 187.0, 169.2, 167.1, 133.7, 130.8, 130.7, 130.4, 130.3, 129.8, 129.2, 52.0, 50.2. Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.14; H, 5.00.

3-(*p*-Nitrophenyl)-2-cyclobuten-1-one (5g). Stannylcyclobutenone **1** (0.75 g, 2.10 mmol) and 1-iodo-4-nitrobenzene (0.63 g, 2.52 mmol) (using THF instead of CH_3CN) for 22 h at room temperature then 2 h at 78 °C yielded 0.20 g (1.05 mmol, 50%) of **5g** as a light yellow solid after chromatography (500 mL of hexanes followed by 6% EtOAc in hexanes then 12.5% EtOAc in hexanes): mp 134−136 °C (hexanes); R_f = 0.15 (29% EtOAc in hexanes); IR (CH_2Cl_2, cm^{-1}) 1755, 1535; ^1H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, J = 8.5 Hz, 2 H), 7.80 (d, J = 8.5 Hz, 2 H), 6.60 (s, 1 H), 3.65 (s, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 185.6, 167.1, 148.6, 136.1, 133.1, 128.9, 123.6, 48.4. Anal. Calcd for $C_{10}H_7O_3N$: C, 63.49; H, 3.73. Found: C, 63.57; H, 3.69.

3-(2-Thienyl)-2-cyclobuten-1-one (5h). Stannylcyclobutenone **1** (0.87 g, 2.44 mmol) and 2-iodothiophene (0.61 g, 2.92 mmol) for 2 h at room temperature yielded 0.19 g (1.27 mmol, 52%) of **5h** as an orange oil after chromatography (600 mL of hexanes followed by 6% EtOAc in hexanes): R_f = 0.30 (25% EtOAc in hexanes); IR (CH_2Cl_2, cm^{-1}) 1760, 1610, 1580; ^1H NMR (360 MHz, $CDCl_3$) δ 7.65 (d, J = 4.6 Hz, 1 H), 7.30 (d, J = 3.7 Hz, 1 H), 7.11 (dd, J = 4.7 and 3.7 Hz, 1 H), 6.04 (s, 1 H), 3.46 (s, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 186.0, 161.9, 134.9, 134.0,

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131.2, 128.2, 127.4, 49.5. Anal. Calcd for C_8H_6OS: C, 63.98; H, 4.03. Found: C, 63.81; H, 4.08.

3-(2-Propenyl)-2-cyclobuten-1-one (5i). Stannylcyclobutenone **1** (0.714 g, 2.00 mmol) and 2-bromopropene (0.720 g, 6.00 mmol) for 1 h at room temperature then 3 h at 65 °C yielded 0.10 g (0.95 mmol, 47%) of **5i** as a yellow oil after chromatography (300 mL of hexanes followed by 100 mL of pentane then 20% Et_2O in pentane): R_f = 0.29 (10% EtOAc in hexanes); IR (CH_2Cl_2, cm^{-1}) 1760, 1650, 1600; ^1H NMR (300 MHz, $CDCl_3$) δ 6.02 (s, 1 H), 5.64 (br s, 1 H), 5.44 (br s, 1 H), 3.31 (s, 2 H), 2.05 (s, 3 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 187.5, 171.6, 137.2, 130.9, 125.1, 48.0, 17.7. Anal. Calcd for C_7H_8O: C, 77.75; H, 7.46. Found: C, 77.79; H, 7.48.

3,3'-Bi(2-cyclobutenone) (6). Stannylcyclobutenone **1** (1.00 g, 2.80 mmol) and $Pd(PhCH_2)Cl(PPh_3)_2$ (0.031 g, 0.04 mmol, 1.5 mol %) were dissolved in 10 mL of dry CH_3CN and heated to 50 °C for 28 h at which point **1** had been consumed (TLC). Addition of 80 mL of CH_3CN was followed by washing with an equal volume of hexanes (3×), removal of the CH_3CN, and chromatography (400 mL of hexanes followed by 10% EtOAc in hexanes then 500 mL of 25% EtOAc in hexanes) gave 67 mg (0.50 mmol, 18%) of **6** as a light yellow solid: mp 75–260 °C (slow dec, turned dark brown); R_f = 0.39 (33% EtOAc in hexanes); IR (CH_2Cl_2, cm^{-1}) 2980, 1760; ^1H NMR (300 MHz, $CDCl_3$) δ 6.41 (s, 1 H), 3.60 (s, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 185.6, 158.9, 140.3, 49.8. Anal. Calcd for $C_8H_6O_2$: C, 71.64; H, 4.51. Found: C, 71.57; H, 4.52.

3-((*E*)-Cinnamylidene)cyclobutanone (7). Stannylcyclobutenone **1** (1.00 g, 2.80 mmol) and cinnamyl bromide (0.66 g, 3.36 mmol) and $Pd(PhCH_2)Cl(PPh_3)_2$ (0.031 g, 0.04 mmol, 1.5 mol %) in 10 mL of dry CH_3CN for 5 h and 45 min at room temperature yielded 0.29 g (1.58 mmol, 57%) of **7** as an orange solid after chromatography (600 mL of hexanes followed by 6% EtOAc in hexanes): mp 69–71 °C (hexane); R_f = 0.47 (12.5% EtOAc in hexanes); IR (CH_2Cl_2, cm^{-1}) 3200, 2900, 1800, 1650, 1590, 1360; ^1H NMR (300 MHz, CD_3CN) δ 7.45 (apparent d, J = 7.4 Hz, 2 H), 7.33 (m, 2 H), 7.23 (m, 1 H), 6.83 (dd, J = 15.7 and 10.7 Hz, 1 H), 6.55 (d, J = 15.7 Hz, 1 H), 6.41 (dt, J = 10.7 and 2.3 Hz, 1 H), 3.76 (br s , 2 H), 3.70 (br s, 2 H); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 204.2, 136.5, 131.0, 128.0, 127.6, 127.1, 125.8, 125.1, 123.8, 54.1, 52.5. Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.57. Found: C, 84.68; H, 6.61. It is unclear if the double bond migrates during the reaction or on purification.

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