3-Stannylcyclobutenediones as Nucleophilic Cyclobutenedione Equivalents. Synthesis of Substituted Cyclobutenediones and Cyclobutenedione Monoacetals and the Beneficial Effect of Catalytic Copper Iodide on the Stille Reaction†

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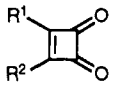
Treatment of 3,4-diisopropoxycyclobutenediones with *n*-$Bu_3SnSiMe_3$/catalytic CN^- furnished 3-isopropoxy-4-(tri-*n*-butylstannyl)cyclobutenedione in 65% yield. This compound cross-coupled with organic iodides attached to sp^2- and sp-hybridized carbon atoms and with vinyl trifluoromethanesulfonate esters under the influence of cocatalytic palladium/Cu species to provide 3-isopropoxy-4-substituted-cyclobutenediones in very good yields. Readily accessible 3-isopropoxy-4-methyl 3-cyclobutene-1,2-dione 2-(ethylene acetal) also reacts with *n*-$Bu_3SnSiMe_3$/catalytic CN^-, leading to 3-(tri-*n*-butylstannyl)-4-methyl-3-cyclobutene-1,2-dione 2-(ethylene acetal), which also undergoes the Pd/Cu-catalyzed cross-coupling reaction, allowing the construction of 3,4-disubstituted-cyclobutenedione monoacetals. Highly substituted and functionalized cyclobutenediones can be sythesized by virtue of the mild and neutral reaction conditions of this carbon–carbon bond forming reaction (Stille reaction).

Introduction

Substituted cyclobutenediones 1 are valuable precursors to substituted quinones and alkylidenecyclopentenone derivatives (Scheme I).[2] An essential aspect of the utility



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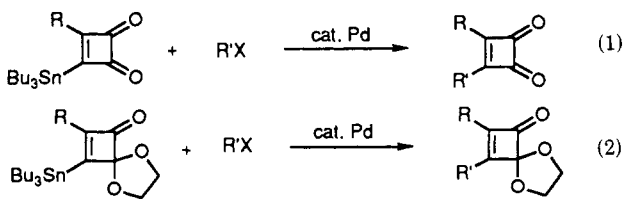
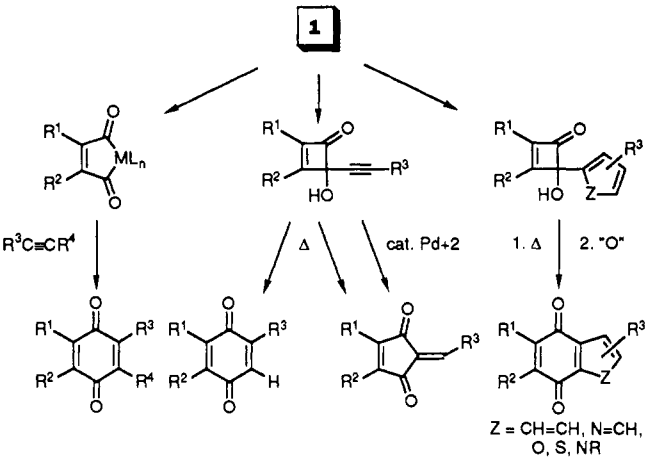
of cyclobutenediones as synthetic precursors to other molecules is the ready availability of generally substituted and functionalized cyclobutenediones. This issue has been addressed, in part, by the development of a method of substituted cyclobutenedione synthesis that relies on the introduction of substituents as organolithium nucleophiles.[3] Accordingly, the process, although fairly general, is restricted to substituents that are compatible with strongly basic and nucleophilic conditions. In an effort to extend and further generalize the range of molecules available from substituted cyclobutenediones, an alternate method of introduction of substituents was sought. We report herein that readily prepared and stable 3-stannylcyclobutenediones function as nucleophilic cyclobutenedione equivalents via palladium-catalyzed cross-coupling with a wide variety of organic substrates (eq 1). In addition, the stannylcyclobutenedione approach provides an alternate method for the regiospecific construction of cyclobutenedione monoacetals (eq 2),[4] substrates of use in the creation of highly substituted quinones.[5]



Results and Discussion

Introduction of a *n*-Bu_3Sn unit to an enone in a 1,4-fashion has been demonstrated by using *n*-$Bu_3SnSiMe_3$ in the presence of catalytic CN^-.[6] Application of this technology to 3,4-diisopropyl squarate provided 3-isopropoxy-4-(tri-*n*-butylstannyl)-3-cyclobutene-1,2-dione (**2**) in 65% yield, presumably via a 1,4-addition–elimination se-

Scheme I



† Dedicated to the memory of John Stille.

(1) Camille and Henry Dreyfus Foundation Teacher–Scholar, 1985–1990.

(2) Leading references from the Liebeskind group: (a) Liebeskind, L. S.; Jewell, C. F., Jr. *J. Organomet. Chem.* **1985**, *285*, 305. (b) Jewell, C. F., Jr.; Liebeskind, L. S; Williamson, M. *J. Am. Chem. Soc.* **1985**, *107*, 6715. (c) Liebeskind, L. S.; Baysdon, S. L.; South, M. S.; Iyer, S.; Leeds, J. P. *Tetrahedron* **1985**, *41*, 5839. (d) Liebeskind, L. S.; Iyer, S.; Jewell, C. F., Jr. *J. Org. Chem.* **1986**, *51*, 3065. (e) Iyer, S.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1987**, *109*, 2759. (f) Liebeskind, L. S; Mitchell, D.; Foster, B. *J. Am. Chem.* Soc. **1987**, *109*, 7908. (g) Liebeskind, L. S. *Tetrahedron* **1989**, *45*, 3053. (h) Mitchell, D.; Liebeskind, L. S. *J. Am. Chem. Soc.* **1990**, *112*, 291. Leading references from the Moore group: (i) Karlsson, J. O.; Nguyen, N. V.; Foland, L. D.; Moore, H. W. *J. Am. Chem. Soc.* **1985**, *107*, 3392. (j) Moore, H. W.; Decker, O. H. W. *Chem. Rev.* **1986**, *86*, 821. (k) Perri, S. T.; Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Org. Chem.* **1986**, *51*, 3067. (l) Decker, O. H. W.; Moore, H. W. *J. Org. Chem.* **1987**, *52*, 1174. (m) Reed, H. W.; Chow, K.; Nguyen, N. W. *J. Org. Chem.* **1987**, *52*, 3491. Perri, S.; Moore, H. W. *Tetrahedron Lett.* **1987**, 4507. (n) Perri, S.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 996. (o) Reed, M. W.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 4166. (p) Foland, L. D.; Karlsson, J. O.; Perri, S. T.; Schwabe, R.; Xu, S. L.; Patil, S.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 975. (q) Foland, L. D.; Decker, O. H. W.; Moore, H. W. *J. Am. Chem. Soc.* **1989**, *111*, 989. (r) Perri, S. T.; Dyke, H. J.; Moore, H. W. *J. Org. Chem.* **1989**, *54*, 2032. Other references: Selwood, D. L.; Jandu, K. S. *Heterocycles* **1988**, *27*, 1191.

(3) (a) Reed, M. W.; Perri, S. T.; Pollart, D. J.; Foland, L. D.; Moore, H. W. *J. Org. Chem.* **1988**, *53*, 2477. (b) Liebeskind, L. S.; Fengl, R. W.; Wirtz, K. R.; Shawe, T. T. *J. Org. Chem.* **1988**, *53*, 2482.

(4) Liebeskind, L. S.; Wirtz, K. R. *J. Org. Chem.*, preceding paper in this issue.

(5) Unpublished results of K. R. Wirtz.

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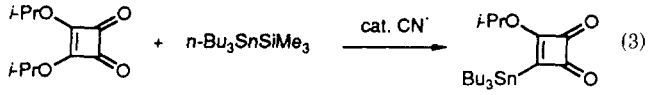
quence (eq 3). Alternative attempts to add R_3SnLi and other tin nucleophiles were unsuccessful. The stannyl-

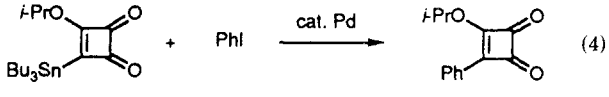


(3)

2

cyclobutenedione was stable to water, dilute HCl, and aqueous $NaHCO_3$. Purification was conveniently accomplished by using flash SiO_2 chromatography.

Initial attempts to cross-couple stannylcyclobutenedione **2** with iodobenzene were disappointing (eq 4). Various



(4)

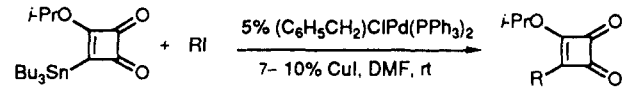
3

catalyst [$Pd(dibenzylideneacetone)_2$, $Cl_2Pd(PPh_3)_2$, $Cl_2Pd(CH_3CN)_2$, $Cl_2Pd(C_6H_5CN)_2$, and $Cl(C_6H_5CH_2)Pd(PPh_3)_2$] and solvent (THF, dichloroethane, benzene, toluene, HMPA, DMF, and $CHCl_3$) combinations were investigated, with little or no cross-coupled product formed. In DMF using 10% $Cl_2Pd(CH_3CN)_2$, a fair yield of **3** was obtained, but the reaction took over 2 days to reach completion. Product **3** was formed in 70% yield using $Pd(PPh_3)_4$ in toluene at 100 °C, but the search for milder reaction conditions was continued.

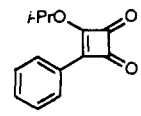
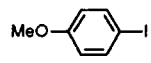
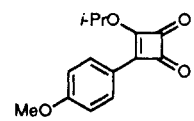
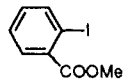
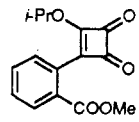
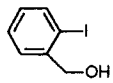
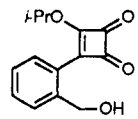
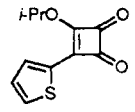
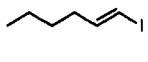
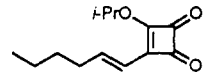
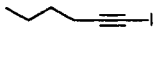
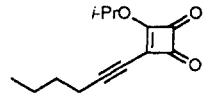
A dramatic improvement in the rate of the cross-coupling of stannylcyclobutenedione **2** with organic iodides was observed when CuI[7] was added as co-catalyst. Through the use of 5% $(C_6H_5CH_2)ClPd(PPh_3)_2$ and 7–10% CuI in DMF, stannylcyclobutenedione **2** efficiently cross-coupled at room temperature with the aryl, vinyl, and alkynyl iodides shown in Table I. In the presence of palladium alone, the reaction proceeded very slowly, giving ~50% of **3** after 3 days, while with CuI alone as catalyst, only minor decoposition of **2** was observed. Other sources of copper ($CuBr\cdot SMe_2$, CuCN, $CuBr_2$) were not as effective as CuI. Although Marino and Long documented the use of $PdCl_2(PPh_3)_2$/CuI (1/2 ratio) for the cross-coupling of a vinylstannane and a vinyl tosylate in a footnote in a recent communication,[8] the use of co-catalytic copper in the Stille reaction requires further emphasis.

The exact role of CuI in this reaction is not known; however, it is of interest that Campbell and Lipschutz have recently shown that efficient formation of vinylcuprates occurs by transmetalation between vinyltrialkylstannanes and higher order cuprates.[9] It is possible that the added copper facilitates the transmetalation step in our reactions (Sn → Cu → Pd) and thus speeds the cross-coupling. It is well-known that the palladium-catalyzed *alkynylation* of aryl and vinyl halides is co-catalyzed by CuI, but it has often been presumed that the role of the copper is to form a copper acetylide, a reaction that cannot intervene in the couplings shown in Table I.[10] More recently in a study

Table I. Palladium-Catalyzed Cross-Coupling of Stannylcyclobutenedione 2 with Organic Iodides



2 4

entry	RI	product	compd, %
1			**4a**, 99
2			**4b**, 80
3			**4c**, 68
4			**4d**, 57
5			**4e**, 75
6			**4f**, 66
7			**4g**, 57

of the alkynylation of iodonucleosides, Hobbs noted that alkynylation was most efficient when a catalyst system composed of tetrakis(triphenylphosphine)palladium(0) and copper(I) iodide in a palladium to copper ratio of 1:2 was used and suggested that the role of the copper might be to facilitate removal of triphenylphosphine from the palladium, providing a more reactive catlayst.[11] Similarly, Singh and Just studied the palladium-catalyzed alkynylation of bromo- and dibromobenzenes and noted a optimum catalysis at $Pd(PPh_3)_4/Cu_2Br_2$ ratios of 2/3.[12] Another interesting effect of copper on a palladium-catalyzed allylation was described recently by Moreno-Mañas.[13]

As demonstrated by the entries in Table I, the cross-coupling of stannylcyclobutenedione **2** was successfully achieved with a variety of C-sp^2 and C-sp-hybridized organic iodides, providing a direct method for the synthesis of cyclobutenediones bearing functionalized substituents, a process not feasible with the organolithiate method of introducing substituents onto the cyclobutenedione ring without resorting to a protection–deprotection sequence. It appears that the reaction of 1-iodohexyne (entry 7) represents the first example of the cross-coupling of an organostannane with an iodoalkyne.

Extension of the cross-coupling procedure to aryl triflates, organostannane coupling partners used successfully by others,[14] proved ineffective. However, vinyl triflates

(6) (a) Taborski, C.; Ford, F. E.; Soloski, E. J. *J. Org. Chem.* **1963**, *28*, 237. (b) Chenard, B. L.; Lagonis, E. D.; Davidson, F.; RajanBabu, T. V. *J. Org. Chem.* **1985**, *50*, 3666.

(7) Purified by the method of Teter, *J. Inorg. Synth.* **1967**, 9. The purified CuI was stored under argon and protected from light to avoid decomposition.

(8) Marino, J. P.; Long, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 7916.

(9) (a) Behling, J. B.; Babiak, K. A.; Campbell, A. L.; Moretti, R.; Koerner, M.; Lipschutz, B. H. *J. Am. Chem. Soc.* **1988**, *110*, 2641. (b) Behling, J. R.; Ng, J. S.; Babiak, K. A.; Campbell, A. L.; Elsworth, W.; Lipschutz, B. *Tetrahedron Lett.* **1989**, 27. (c) Lipschutz, B. H.; Ellsworth, E. L.; Dimcock, S. H.; Reuter, D. C. *Tetrahedron Lett.* **1989**, 2065.

(10) (a) Stephens, R. D.; Castro, C. E. *J. Org. Chem.* **1963**, *28*, 3313. (b) Edo, K.; Sakamoto, T.; Yamanaka, H. *Chem. Pharm. Bull.* **1978**, *26*, 2843. (c) Robins, M. J.; Barr, P. J. *Tetrahedron Lett.* **1981**, 421. (d) Robins, M. J.; Barr, P. J. *J. Org. Chem.* **1983**, *48*, 1854. (e) Beletskaya, I. P. *J. Organomet. Chem.* **1983**, *250*, 551.

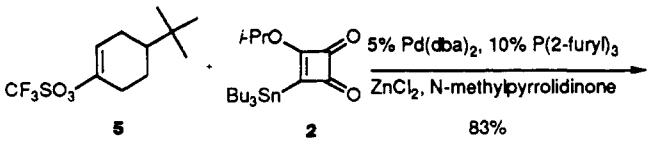
(11) Hobbs, F. W., Jr. *J. Org. Chem.* **1989**, *54*, 3420.

(12) Singh, R.; Just, G. *J. Org. Chem.* **1989**, *54*, 4453.

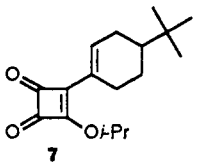
(13) Marquet, J.; Moreno-Mañas, M.; Prat, M. *Tetrahedron Lett.* **1989**, *30*, 3105.

(14) Echavarren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1988**, *110*, 1557.

coupled efficiently with stannylcyclobutenedione 2. Vinyl triflates 5 and 6 were prepared from the corresponding ketones, 4-*tert*-butylcyclohexanone and 4-cholesten-3-one, by the method of McMurry[15] and were cross-coupled with 2 in high yield, utilizing the tris(2-furyl)phosphine conditions of Farina et al. (eqs 5 and 6).[16]



5 2



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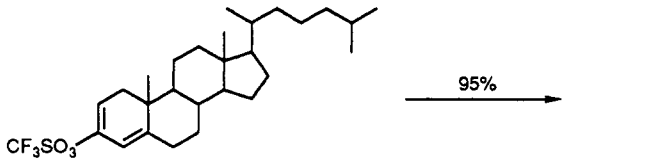

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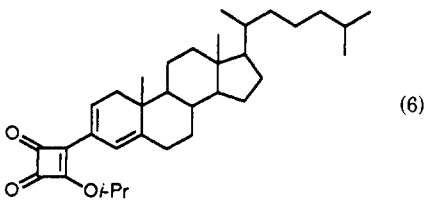
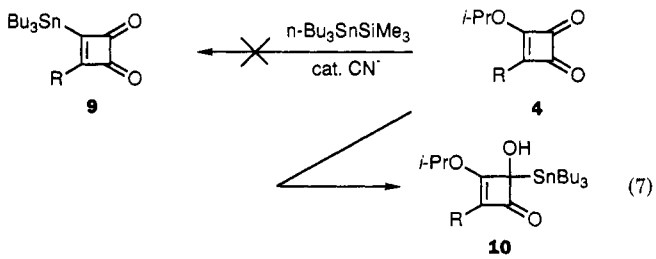


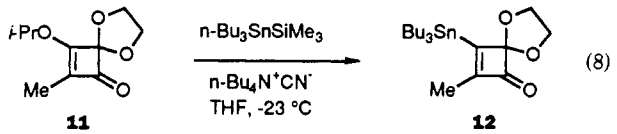
8 (6)

Application of the tin cross-coupling technology to the preparation of disubstituted cyclobutenediones was investigated next. On the basis of the successful introduction of the tri-*n*-butylstannyl group into the cyclobutenedione ring of diisopropyl squarate described above, the most obvious route to disubstituted cyclobutenediones would be treatment of 3-organyl-4-isopropoxy-3-cyclobutene-1,2-diones 4 with *n*-$Bu_3SnSiMe_3$ to prepare the stannylcyclobutenedione 9, followed by palladium-catalyzed cross-coupling. Unfortunately, reaction of 3-organyl-4-isopropoxycyclobutenediones with *n*-$Bu_3SnSiMe_3$ in the presence of catalytic cyanide did not lead to replacement of the isopropoxy group; rather, condensation at the more reactive enone moiety occurred providing compounds tentatively assigned structure 10 (eq 7).[17]



9 4 10 (7)

A simple solution to the problem was achieved through the use of the cyclobutenedione monoacetals described in the preceding article.[4] Addition of R^1Li to diisopropyl squarate, converson of the resulting alcohol to the trimethylsilyl ether, and reaction with ethylene glycol bis(trimethylsilyl ether)/trimethylsilyl triflate provided a general method for the synthesis of cyclobutenedione monoacetals 11. Treatment of monoacetal 11 with *n*-$Bu_3SnSiMe_3$ and catalytic cyanide generated the stannylcyclobutenedione monoacetal 12 in 72% yield (eq 8).

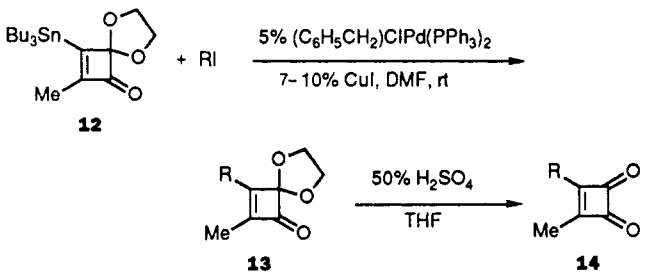


11 12 (8)

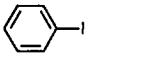
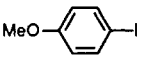
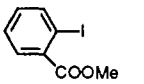
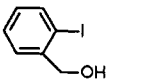
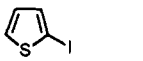
Cross-coupling of 12 with a variety of organic iodides was accomplished by utilizing the previously described Pd/Cu system, providing a second method for the regiospecific synthesis of monoacetals of disubstituted cyclobutenediones[4] and furnishing substrates that on hydrolysis provide the parent cyclobutenediones (Table II). A variety of conditions for the hydrolysis of cyclobutenedione monoacetals were explored, and rapid and clean conversion to the cyclobutenedione was achieved by dissolving the monoacetal in THF, adding one-half volume of 50% aqueous H_2SO_4, and stirring at room temperature.

In conclusion, the synthesis of substituted cyclobutenediones has been significantly generalized through the use of organotin technology. 3-Stannylcyclobutenediones, easily prepared by *n*-Bu_3Sn^- conjugate addition and *i*-PrO^- elimination on diisopropyl squarate, undergo efficient palladium-catalyzed cross-coupling with organic iodides (aryl, heteroaryl, vinyl, alkynyl) and vinyl triflates. The chemistry has also been extended to the preparation of cyclobutenedione monoacetals, which provide a general pathway for the synthesis of 3,4-diorganylcyclobutenediones, molecules of demonstrated utility in the synthesis of quinones and cyclopentenone derivatives. An interesting and useful effect of co-catalytic CuI on the palladium-catalyzed cross-couling reaction of organostannanes with organic halides and triflates has also been emphasized.

Table II. Palladium-Catalyzed Cross-Coupling of Stannylcyclobutenedione Monoacetal with Oganic Iodides



12 13 14

entry	RI	compd, %	compd, %
1		**13a**, 77	**14a**, 82
2		**13b**, 72	**14b**, 83
3		**13c**, 70	**14c**, 61
4		**13d**, 57	**14d**, 91
5		**13e**, 67	**14e**, 99
6		**13f**, 36	**14f**, 73

(15) McMurry, J. E.; Scott, W. J. *Tetrahedron Lett.* **1983**, 979.
(16) (a) Farina, V.; Baker, S. R.; Benigni, D. A.; Sapino, C., Jr. *Tetrahedron Lett.* **1988**, 5739. (b) Farina, V.; Baker, S. R.; Sapino, C., Jr. *Tetrahedron Lett.* **1988**, 6043.
(17) Low yields of 9 could be obtained under various conditions. Unpublished results of Dr. Jing Zhang.

Experimental Section

General Information. All reactions were performed under a nitrogen atmosphere. Squaric acid was purchased from Aldrich Chemical Company. Diisopropyl squarate [3,4-bis(1-methylethoxy)cyclobut-3-ene-1,2-dione] was prepared on a 50-g scale according to the published procedure.[3b] Radial chromatography was performed on a Model 7924 Chromatatron from Harrison Research with rotors (2.0 mm) coated with silica gel PF-254, type 60 (EM Science), with $CaSO_4 \cdot {}^1/_2H_2O$ as a binder.

4-(1-Methylethoxy)-3-(tri-*n*-butylstannyl)cyclobut-3-ene-1,2-dione (2). Diisopropyl squarate (6.54 g, 33.0 mmol) and n-$Bu_3SnSiMe_3$[6] (11.96 g, 33.0 mmol) were dissolved in 225 mL of distilled THF and the reaction mixture was cooled to −23 °C. A solution of n-$Bu_4N^+CN^-$ in THF (10.0 mL of 0.0704 M solution, 2 mol %) was added dropwise, and the clear solution quickly turned light yellow. After 1.5 h, TLC analysis (SiO_2, 25% Et_2O in hexanes) indicated that consumption of the diisopropyl squarate was complete (diisopropyl squarate R_f = 0.37, product R_f = 0.57). Removal of volatiles on a rotary evaporator and then on a vacuum pump left an orange oil that was purified by chromatography (flash-grade SiO_2, 3 in. × 11 in., 30% Et_2O in hexanes) to yield 9.21 g (65%) of **2** as a viscous oil: IR (CH_2Cl_2, cm^{-1}) 2960, 2930, 2880, 2860, 1775, 1740, 1640; ^1H NMR (300 MHz, $CDCl_3$) δ 5.41 (hept, J = 6.2 Hz, 1 H), 1.60–1.50 (m, 6 H), 1.44 (d, J = 6.3 Hz, 6 H), 1.40–1.25 (m, 6 H), 1.20–1.15 (m, 6 H), 0.90 (t, J = 7.2 Hz, 9 H). Anal. Calcd for $C_{19}H_{34}O_3Sn$: C, 53.18; H, 7.99. Found: C, 53.23; H, 8.00.

Typical Procedure for the Palladium-Catalyzed Cross-Coupling of 2 with Organic Iodides: 4-(1-Methylethoxy)-3-(4-methoxyphenyl)cyclobut-3-ene-1,2-dione (4b). Stannylcyclobuenedione **2** (0.345 g, 0.80 mmol) and *p*-iodoanisole (0.208 g, 0.89 mmol) were dissolved in 1.0 mL of DMF (sparged with N_2) under N_2 at room temperature. Benzylchlorobis(triphenylphosphine)palladium(II) (0.037 g, 6 mol %) and cuprous iodide (0.014 g, 9 mol %), purified according to the procedure of Teter,[9] were added, and the reaction was stirred at room temperature and monitored by TLC (SiO_2, 15% Et_2O in hexanes, stannylcyclobutenedione R_f = 0.37, product R_f = 0.08) for disappearance of starting cyclobutenedione (~45 min). The reaction was diluted with 15 mL of Et_2O and washed with saturated aqueous NH_4Cl (1 × 15 mL) and 10% aqueous KF (3 × 15 mL), and the resulting organic layer was filtered through a plug of SiO_2 (0.5 in. × 3 in.) with Et_2O. Removal of solvent left an organge solid that was purified by radial chromatography on a 2-mm SiO_2 rotor with 20% Et_2O in hexanes, yielding 0.156 g (80%) of **4b**: mp 99–101 °C (CH_2Cl_2/hexane); IR (CH_2Cl_2, cm^{-1}) 3040, 2930, 2870, 1780, 1740, 1620, 1570; ^1H NMR (300 MHz, $CDCl_3$) δ 8.04 (m, 2 H), 7.01 (m, 2 H), 5.60 (hept, J = 6.2 Hz, 1 H), 3.89 (s, 3 H), 1.55 (d, J = 6.2 Hz, 6 H). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.35; H, 5.75.

3-(1-Methylethoxy)-4-phenylcyclobut-3-ene-1,2-dione (4a): yellow solid, 0.258 g (99% yield) from 0.345 g of **2** and 0.182 g of iodobenzene; mp 113–114 °C (CH_2Cl_2/hexanes); IR (CH_2Cl_2, cm^{-1}) 3060, 2980, 1780, 1747, 1605, 1585, 1390; ^1H NMR (300 MHz, $CDCl_3$) δ 8.10–8.00 (m, 2 H), 7.60–7.45 (m, 3 H), 5.63 (hept, J = 6 Hz, 1 H), 1.57 (d, J = 6 Hz, 6 H). Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.10; H, 5.60.

4-(2-Carbomethoxyphenyl)-3-(1-methylethoxy)cyclobut-3-ene-1,2-dione (4c): yellow solid, 0.136 g (68% yield) from 0.347 g of **2** and 0.190 g of methyl 2-iodobenzoate; mp 63–64.5 °C (CH_2Cl_2/hexane); IR (CH_2Cl_2, cm^{-1}) 3060, 2990, 2958, 1790, 1758, 1728, 1592; ^1H NMR (300 MHz, $CDCl_3$) δ 7.93 (dd, J = 6.4 Hz, J = 1.4 Hz, 1 H), 7.75 (dd, J = 6.4 Hz, J = 1.4 Hz, 1 H), 7.64 (dt, J = 6.1 Hz, J = 1.4 Hz, 1 H), 7.55 (dt, J = 6.1 Hz, J = 1.4 Hz, 1 H), 5.58 (hept, J = 6.2 Hz, 1 H), 3.90 (s, 3 H), 1.52 (d, J = 6.2 Hz, 6 H). Anal. Calcd for $C_{15}H_{14}O_5$: C, 65.70; H, 5.15. Found: C, 65.57; H, 5.20.

2-(2-(Hydroxymethyl)phenyl)-3-(1-methylethoxy)cyclobut-3-ene-1,2-dione (4d): yellow solid, 0.096 g (57% yield) 0.343 g of **2** and 0.159 g of *o*-iodobenzyl alcohol; mp 93–94 °C (CH_2Cl_2/hexane); IR (CH_2Cl_2, cm^{-1}) 3500, 3040, 2980, 1780, 1745, 1580, 1560; ^1H NMR (300 MHz, $CDCl_3$) δ 7.8–7.4 (m, 4 H), 5.69 (hept, J = 6.2 Hz, 1 H), 4.73 (s, 2 H), 3.89 (s, 1 H), 1.57 (d, J = 6.2 Hz, 6 H). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.04; H, 5.75

3-(1-Methylethoxy)-4-(2-thienyl)cyclobut-3-ene-1,2-dione (4e): yellow solid, 0.122 g (75% yield) from 0.310 g of **2** and 0.182 g of 2-iodothiophene; mp 93–94.5 °C (CH_2Cl_2/hexanes); IR (CH_2Cl_2, cm^{-1}) 2990, 1790, 1738, 1600, 1505, 1420, 1395; ^1H NMR (300 MHz, $CDCl_3$) δ 7.90 (dd, J = 4 Hz, J = 1 Hz, 1 H), 7.80 (dd, J = 5 Hz, J = 1 Hz, 1 H), 7.30 (dd, J = 5 Hz, J = 4 Hz, 1 H), 5.60 (hept, J = 6 Hz, 1 H), 1.57 (d, J = 6 Hz, 6 H). Anal. Calcd for $C_{11}H_{10}O_3S$: C, 59.44; H, 4.54. Found: C, 59.52; H, 4.59.

4-(1-Hexenyl)-3-(1-methylethoxy)cyclobut-3-ene-1,2-dione (4f): yellow oil, 0.112 g (66% yield) from 0.343 g of **2** and 0.161 g of (*E*)-1-iodo-1-hexene;[18] IR (CH_2Cl_2, cm^{-1}) 2960, 2930, 2870, 1780, 1750, 1620, 1570; ^1H NMR (300 MHz, $CDCl_3$) δ 7.11 (dt, J = 15.8 Hz, J = 7.1 Hz, 1 H), 6.32 (dt, J = 15.8 Hz, J = 1.5 Hz, 1 H), 5.41 (hept, J = 6.2 Hz, 1 H), 2.26 (dq, J = 7.0 Hz, J = 1.5 Hz, 2 H), 1.44 (d, J = 6.2 Hz, 6 H), 1.33 (m, 4 H), 0.88 (t, J = 7.2 Hz, 3 H). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 70.07; H, 8.22.

4-(1-Hexynyl)-3-(1-methylethoxy)cyclobut-3-ene-1,2-dione (4g): yellow oil, 0.100 g (57% yield) from 0.345 g of **2** and 0.185 g of 1-iodo-1-hexyne;[19] IR(CH_2Cl_2, cm^{-1}) 2960, 2930, 2220, 1790, 1760, 1585, 1395; ^1H NMR (300 MHz, $CDCl_3$) δ 5.38 (hept, J = 6 Hz, 1 H), 2.62 (t, J = 7 Hz, 2 H), 1.63 (p, J = 7 Hz, 2 H), 1.51 (d, J = 6 Hz, 6 H), 1.50–1.40 (m, 2 H), 0.95 (t, J = 7 Hz, 3 H). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.96; H, 7.37.

4-(4-(1,1-Dimethylethyl)cyclohexen-1-yl)-3-(1-methylethoxy)cyclobut-3-ene-1,2-dione (7). Stannylcyclobutenedione **2** (0.427 g, 1.00 mmol) and **5** (0.288 g, 1.00 mmol), the vinyl triflate prepared from 4-*tert*-butylcyclohexanone,[13] were dissolved in 9.0 mL of N_2-sparged *N*-methylpyrrolidinone (NMP) in a reaction vessel maintained under a nitrogen atmosphere. Tris(2-furyl)-phosphine (0.025 g, 0.100 mmol)[14] was added followed by 0.276 g (2.00 mmol) of $ZnCl_2$ and 0.027 g (0.05 mmol) of bis(dibenzylideneacetone)palladium. The reaction vessel was heated to 65 °C and was monitored by TLC (SiO_2, 20% Et_2O in hexanes; stannylcyclobutenedione R_f = 0.42, product R_f = 0.30) for disappearance of starting material. After 45 min, the reaction mixture was cooled to room temperature, diluted with 25 mL of Et_2O, and washed with saturated aqueous NH_4Cl (3 × 20 mL), H_2O (1 × 25 mL), saturated aqueous NaCl (1 × 20 mL), and 10% KF (3 × 15 mL). The organic layer was dried (Na_2SO_4) and filtered, and the solvent was removed to yield a red-brown oil. Purification by radial chromatography using a 2-mm SiO_2 rotor (15% Et_2O in hexanes) yielded 0.229 g (83%) of **7** as a yellow solid: mp 73–75 °C (CH_2Cl_2/hexanes; IR (CH_2Cl_2 cm^{-1}) 2940, 2860, 1780, 1735, 1610, 1570, 1415; ^1H NMR (360 MHz, $CDCl_3$) δ 7.18 (m, 1 H), 5.49 (hept, J = 6.2 Hz, 1 H), 2.60 (m, 1 H), 2.34 (m, 2 H), 2.1–1.9 (m, 2 H), 1.46 (d, J = 6.2 Hz, 6 H), 1.4–1.1 (m, 3 H), 0.89 (s, 9 H). Anal. Calcd for $C_{17}H_{24}O_3$: C, 73.88; H, 8.75. Found: C, 73.94; H, 8.79.

Steroidal Cyclobutenedione 8. To 0.534 g of (5.25 mmol) of diisopropylamine in 15 mL o THF at 0 °C was added 2.20 mL of *n*-BuLi (5.50 mmol, 2.5 M in hexanes). The resulting solution of lithium diisopropylamide was cooled to −78 °C and 1.92 g (5.00 mmol) of 4-cholesten-3-one in 10 mL of THF was added dropwise. The enolate was generated at −78 °C for 2 h, 1.920 g (5.30 mmol) of *N*-phenyltrifluoromethanesulfonimide[13] was added, and the reaction mixture was allowed to warm slowly to room temperature overnight. Removal of the solvent left an orange oil, which was filtered through a silica gel plug (0.5 in. × 5 in.) with hexanes to yield an orange solid. Purification on SiO_2 (flash grade, 1.5 in. × 8 in.) with 5% Et_2O in hexanes as eluent gave 1.834 g (71%) of vinyl triflate **6** as a white solid: mp 94.5–96 °C (with darkening, CH_2Cl_2/hexanes); IR (CH_2Cl_2, cm^{-1}) 2940, 2870, 1418, 1217, 1141; ^1H NMR (360 MHz, $CDCl_3$) δ 5.5 (m, 1 H), 5.4 (m, 1 H), 2.4–2.2 (m, 2 H), 2.0 (m, 2 H), 0.99 (s, 3 H), 0.90 (d, J = 6.5 Hz, 3 H), 0.87 (d, J = 6.6 Hz, 3 H), 0.86 (d, J = 6.6 Hz, 3 H), 0.69 (s, 3 H), 1.8–0.8 (m, 22 H). Anal. Calcd for $C_{28}H_{43}F_3O_3S$: C, 65.09; H, 8.39. Found: C, 65.17; H, 8.43.

Treatment of vinyl triflate **6** (0.281 g) with stannylcyclobutenedione **2** (0.231 g) using the procedure described above for the preparation of **7** gave 0.260 g (95%) of **8** as a yellow solid: mp

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145–147 °C (CH_2Cl_2/hexanes); IR (CH_2Cl_2, cm^{-1}) 2920, 2860, 1778, 1735, 1577, 1421; ^1H NMR (300 MHz, $CDCl_3$) δ 7.05–6.98 (m, 1 H), 6.03 (s, 1 H), 5.51 (hept, J = 6.2 Hz, 1 H), 2.55 (dd, J = 19 Hz, J = 7 Hz, 1 H), 2.36–2.18 (m, 3 H), 2.06–1.98 (m, 1 H), 1.83–0.83 (m, 21 H), 1.49 (dd, J = 6.2 Hz, J = 1.5 Hz, 6 H), 0.95 (s, 3 H), 0.91 (d, J = 7 Hz, 3 H), 0.87 (dd, J = 7.8 Hz, J = 1.5 Hz, 6 H), 0.69 (s, 3 H). Anal. Calcd for $C_{34}H_{50}O_3$: C, 80.58; H, 9.94. Found: C, 80.49; H, 9.97.

4-Methyl-3-(1-methylethoxy)cyclobut-3-ene-1,2-dione 2-(Ethylene acetal) (11). Following the published procedure,[3b] MeLi was added to diisopropyl squarate to give 2,3-bis(1-methylethoxy)-4-hydroxy-4-methylcyclobut-2-enone, 10.90 g (50.87 mmol), which was combined with trimethylsilyl chloride (8.15 g, 75.02 mmol) in 200 mL of dry ether. After addition of triethylamine (21 mL, 3.0 equiv), the reaction mixture was stirred under a nitrogen atmosphere at room temperature for 12 h. Filtration of the solution through SiO_2 (2 in. × 5 in.) with Et_2O and removal of solvent on a rotary evaporator and then on a vacuum pump left 14.10 g (98%) of 2,3-bis(1-methylethoxy)-4-((trimethylsilyl)oxy)-4-methylcyclobut-2-enone as a clear oil: IR (CH_2Cl_2, cm^{-1}) 2990, 2938, 1770, 1628, 1388; ^1H NMR (300 MHz, $CDCl_3$) δ 4.91–4.83 (m, overlapping heptets, 2 H), 1.44 (s, 3 H), 1.41 (d, J = 6.2 Hz, 3 H), 1.38 (d, J = 6.2 Hz, 3 H), 1.29 (d, J = 6.2 Hz, 3 H), 1.25 (d, J = 6.2 Hz, 3 H), 0.14 (s, 9 H). Anal. Calcd for $C_{14}H_{26}O_4Si$: C, 58.70, H, 9.15. Found: C, 58.88; H, 9.09.

To 12.77 g (44.58 mmol) of the silyl ether prepared above and 1,2-bis((trimethylsilyl)oxy)ethane (9.22 g, 44.60 mmol) dissolved in 200 mL of THF at room temperature under a nitrogen atmosphere was added 100 μL (1.1 mol %) of trimethylsilyl trifluoromethanesulfonate. After 2 min, analysis by TLC showed consumption of starting material. The reaction mixture was filtered through a plug of SiO_2 (2 in. × 4 in.) with ether, and the solvent was removed to yield an orange oil. Purification on SiO_2 (flash grade, 3.5 in. × 12 in., 40% Et_2O in hexane) yielded 8.56 g (96%) of 11 as a colorless oil: IR (CH_2Cl_2, cm^{-1}) 2985, 2900, 1769, 1630, 1614, 1407; ^1H NMR (300 MHz, $CDCl_3$) δ 4.73 (hept, J = 6.2 Hz, 1 H), 4.21–4.02 (m, 4 H), 1.72 (s, 3 H), 1.41 (d, J = 6.2 Hz, 6 H); ^{13}C NMR (75.48 MHz, $CDCl_3$) δ 192.66, 181.39, 130.78, 116.94, 76.86, 65.92, 22.46, 6.75. Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.34; H, 7.05.

3-(Tri-*n*-butylstannyl)-4-(1-methylethoxy)cyclobut-3-ene-1,2-dione 2-(Ethylene acetal) (12). 4-Methyl-3-(1-methylethoxy)cyclobut-3-ene-1,2-dione 2-(ethylene acetal) (11) (3.97 g, 20.0 mmol) and (tri-*n*-butylstannyl)trimethylsilane (7.28 g, 20.0 mmol) were dissolved in 130 mL of distilled THF under N_2, and the reaction vessel was cooled to −23 °C. A solution of n-$Bu_4N^+CN^-$ in THF (5.40 mL, 0.074M, 2 mol %) was added dropwise, and the clear solution turned light yellow. After 1.5 h, monitoring by TLC (SiO_2, 50% Et_2O in hexanes, starting material R_f = 0.12, product R_f = 0.62) showed consumption of starting material. Removal of solvent left an orange oil that was purified by chromatography (flash SiO_2, 3 in. × 12 in., 40% Et_2O in hexanes) to yield 6.15 g (68%) of **12** as a light yellow oil: IR (CH_2Cl_2, cm^{-1}) 2960, 2920, 2860, 1750, 1245; ^1H NMR (300 MHz, $CDCl_3$) δ 4.14 (m, 2 H), 4.06 (m, 2 H), 1.91 (s, 3 H), 1.55 (m, 6 H), 1.34 (m, 6 H), 1.10 (m, 6 H), 0.90 (t, J = 7.0 Hz, 9 H). Anal. Calcd for $C_{19}H_{34}O_3Sn$: C, 53.18; H, 7.99. Found: C, 52.97; H, 8.02.

Typical Procedure for the Palladium-Catalyzed Cross-Coupling of 12 with Organic Iodides: 4-Methyl-3-phenylcyclobut-3-ene-1,2-dione 2-(Ethylene acetal) (13a). Into 2.0 mL of DMF (N_2 sparged) were dissolved stannylcyclobutenedione monoacetal **12** (0.389 g, 0.90 mmol) and iodobenzene (0.219 g, 1.07 mmol). After addition of CuI (0.014 g, 8 mol %) and benzylchlorobis(triphenylphosphine)palladium(II) (0.035 g, 5 mol %), the reaction mixture was stirred at room temperature for 8 h, at which point analysis by TLC showed consumption of starting material (SiO_2, 30% Et_2O in hexanes; starting material R_f = 0.50, product R_f = 0.18). The reaction mixture was diluted with 10 mL of ether and washed with saturated aqueous NH_4Cl (1 × 10 mL) and 10% aqueous KF (2 × 15 mL); then the organic layer was filtered through a plug of SiO_2 (1 in. × in.) with Et_2O. Removal of solvent left an orange oil that was purified by radial chromatography on a 2-mm SiO_2 rotor (25% Et_2O in hexanes) to yield 0.150 g (77%) of **13a** as a yellow solid: mp 85.5–87 °C (CH_2Cl_2/hexanes); IR (CH_2Cl_2, cm^{-1}) 3060, 2980, 2900, 1760, 1620, 1380; ^1H NMR (360 MHz, $CDCl_3$) δ 7.69 (m, 2 H), 7.50 (m, 3 H), 4.26 (s, 4 H), 2.12 (s, 3 H). Anal. Calcd for $C_{13}H_{12}O_3$: C, 72.21; H, 5.59. Found: C, 72.05; H, 5.63.

3-(4-Methoxyphenyl)-4-methylcyclobut-3-ene-1,2-dione 2-(ethylene acetal) (13b): yellow solid, 0.381 g (72% yield) from 0.939 g of **12** and 0.605 g of *p*-iodoanisole; mp 106–107.5 °C (CH_2Cl_2/hexane); IR (CH_2Cl_2, cm^{-1}) 3050, 3010, 2960, 2900, 2840, 1755, 1605, 1510; ^1H NMR (360 MHz, $CDCl_3$) δ 7.63 (apparent d, J = 9.0 Hz, 2 H), 6.99 (apparent d, J = 9.0 Hz, 2 H), 4.26 (m, 4 H), 3.87 (s, 3 H), 2.09 (s, 3 H). Anal. Calcd for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.62; H, 6.10.

3-(2-Carbomethoxyphenyl)-4-methylcyclobuten-3-ene-1,2-dione 2-(ethylene acetal) (13c): yellow solid, 0.450 g (70%) from 1.024 g of **12** and 0.736 g of methyl *o*-iodobenzoate; mp 82–84 °C (CH_2Cl_2/hexane); IR (CH_2Cl_2, cm^{-1}) 3040, 2980, 2950, 2890, 1770, 1725, 1660; ^1H NMR (300 MHz, $CDCl_3$) δ 7.97 (apparent d, J = 7.5 Hz, 1 H), 7.56 (m, 3 H), 4.16 (m, 2 H), 4.03 (m, 2 H), 3.86 (s, 3 H), 1.82 (s, 3 H). Anal. Calcd for $C_{15}H_{14}O_5$: C, 65.69; H, 5.15. Found: C, 65.78; H, 5.16.

3-(2-(Hydroxymethyl)phenyl)-4-methylcyclobut-3-ene-1,2-dione 2-(ethylene acetal) (13d): yellow solid, 0.300 g (57%) from 0.936 of **12** and 0.602 g of *o*-iodobenzyl alcohol; mp 126.5–128.5 °C (CH_2Cl_2/hexane); IR (CH_2Cl_2, cm^{-1}) 3600, 3500, 3040, 2950, 1770, 1620; ^1H NMR (300 MHz, $CDCl_3$) δ 7.60–7.30 (m, 4 H), 4.63 (s, 2 H), 4.35–4.15 (m, 2 H), 4.12–3.95 (m, 2 H), 2.80 (br s, 1 H), 1.93 (s, 3 H); high resolution mass spectrum calcd for $C_{14}H_{14}O_4$ 246.0892, found 246.0892.

3-(2-Thienyl)-4-methylcyclobut-3-ene-1,2-dione 2-(ethylene acetal) (13e): orange solid, 0.158 g (67%) from 0.468 g of **12** and 0.266 g of 2-iodothiophene: mp 128–131 °C (CH_2Cl_2/hexane); IR (CH_2Cl_2, cm^{-1}) 3050, 2980, 2960, 2900, 1765, 1615, 1420; ^1H NMR (360 MHz, $CDCl_3$) δ 7.73 (dd, J = 5.0 Hz, J = 0.7 Hz, 1 H), 7.48 (dd, J = 3.7 Hz, J = 0.7 Hz, 1 H), 7.22 (dd, J = 5.0 Hz, J = 3.7 Hz, 1 H), 4.27 (m, 4 H), 2.07 (s, 3 H). Anal. Calcd for $C_{11}H_{10}O_4S$: C, 59.44; H, 4.53. Found: C, 59.52; H, 4.59.

3-((*E*)-1-Hexenyl)-4-methylcyclobut-3-ene-1,2-dione 2-(ethylene acetal) (13f): orange oil, 0.087 g (36%) from 0.468 g of **12** and 0.272 g of (*E*)-1-iodo-1-hexane;[16] IR (CH_2Cl_2, cm^{-1}) 3040, 2950, 2920, 2880, 1755, 1635, 1380; ^1H NMR (300 MHz, $CDCl_3$) δ 6.54–6.31 (m, 2 H), 4.19 (m, 2 H), 4.14 (m, 2 H), 2.28 (apparent q, J = 6.8 Hz, 2 H), 1.84 (s, 3 H), 1.55–1.25 (m, 4 H), 0.93 (t, J = 7.2 Hz, 3 H). Anal. Calcd for $C_{13}H_{18}O_3$: C, 70.24; H, 8.16. Found: C, 69.97; H, 8.01.

Typical Procedure for Hydrolysis of the Cyclobutenedione Monoacetals to Disubstituted Cyclobutenediones: 3-Methyl-4-phenylcyclobutene-1,2-dione (14a). Cyclobutenedione monoacetal **13a** (0.026 g, 0.12 mmole) was dissolved in 5 mL of THF to which 2 mL of 50% aqueous H_2SO_4 was added, and the solution was stirred at room temperature. After 3 h, analysis by TLC (SiO_2, 30% Et_2O in hexanes) showed consumption of starting material and the reaction mixture was diluted with 10 mL of H_2O and 10 mL of Et_2O. The organic layer was separated, the aqueous layer was washed with Et_2O (2 × 10 mL), and the combined organic layers were dried over Na_2SO_4. Filtration, removal of solvent, and purification of the crude material by radial chromatography (1-mm SiO_2 rotor, 25% Et_2O in hexanes) yielded 0.017 g (82%) of **14a** as a yellow solid: mp 101.5–102 °C (CH_2Cl_2/hexane); IR (CH_2Cl_2, cm^{-1}) 3050, 2950, 1780, 1765, 1600, 1590, 1335; ^1H NMR (300 MHz, $CDCl_3$) δ 8.06–8.00 (m, 2 H), 7.68–7.50 (m, 3 H), 2.67 (s, 3 H); high resolution mass spectrum calcd for $C_{11}H_8O_2$ 172.0524, found 172.0524.

3-(4-Methoxyphenyl)-4-methylcyclobut-3-ene-1,2-dione (14b): yellow solid, 0.067 g (80%) from 0.103 g of **13b**; mp 148.5–150 °C (CH_2Cl_2/hexane); IR (CH_2Cl_2, cm^{-1}) 3050, 2970, 1780, 1765, 1600, 1510; ^1H NMR (360 MHz, $CDCl_3$) δ 8.02 (apparent d, J = 9.0 Hz, 2 H), 7.06 (apparent d, J = 9.0 Hz, 2 H), 3.92 (s, 3 H), 2.62 (s, 3 H). Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.35; H, 5.02.

3-(2-Carbomethoxyphenyl)-4-methylcyclobut-3-ene-1,2-dione (14c): yellow solid, 0.054 g (61%) from 0.105 g of **13c**; mp 77–79 °C (CH_2Cl_2/hexane); IR (CH_2Cl_2, cm^{-1}) 3050, 2950, 1790, 1775, 1725, 1610, 1435; ^1H NMR (360 MHz, $CDCl_3$) δ 8.10 (dd, J = 7.8 Hz, J = 1.0 Hz, 1 H), 7.70 (dt, J = 7.8 Hz, J = 1.2 Hz, 1 H), 7.62 (dt, J = 7.6 Hz, J = 1.2 Hz, 1 H), 7.42 (dd, J = 7.6 Hz, J = 1.0 Hz, 1 H), 3.88 (s, 3 H), 2.46 (s, 3 H). Anal. Calcd for $C_{13}H_{10}O_4$: C, 67.82; H, 4.38. Found: C, 67.55; H, 4.40.

3-(2-(Hydroxymethyl)phenyl)-4-methylcyclobut-3-ene-1,2-dione (14d): yellow solid, 0.099 g (90%) from 0.133 g of **13d**; mp 93–94 °C (CH_2Cl_2/hexane); IR (CH_2Cl_2, cm^{-1}) 3600, 3500, 3050, 2950, 2890, 1790, 1770, 1595, 1375; ^1H NMR (300 MHz $CDCl_3$) δ 7.65–7.38 (m, 4 H), 4.70 (s, 2 H), 3.59 (br s, 1 H), 2.58 (s, 3 H). Anal. Calcd for $C_{12}H_{10}O_3$: C, 71.28; H, 4.98. Found: C, 71.08; H, 5.01.

4-Methyl-3-(2-thienyl)cyclobut-3-ene-1,2-dione (14e): orange solid: 0.079 g (99%) from 0.101 g of **13e**; mp 128–130 °C (CH_2Cl_2/hexane); IR (CH_2Cl_2, cm^{-1}) 3110, 3060, 2930, 1785, 1770, 1600, 1415; ^1H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, J = 3.8 Hz, J = 1.0 Hz, 1 H), 7.94 (dd, J = 5.0 Hz, J = 1.0 Hz, 1 H), 7.35 (dd, J = 5.0 Hz, J = 3.8 Hz, 1 H), 2.58 (s, 3 H). Anal. Calcd for $C_9H_6O_2S$: C, 60.66; H, 3.39. Found: C, 60.63; H, 3.43.

3-((*E*)-1-Hexenyl)-4-methylcyclobut-3-ene-1,2-dione (14f): yellow oil, 0.033 g (73%) from 0.056 g of **13f**; IR (CH_2Cl_2, cm^{-1}) 3040, 2960, 2930, 2860, 1775, 1765, 1625, 1570, 1380; ^1H NMR (360 MHz, $CDCl_3$) δ 7.35 (dt, J = 15.7 Hz, J = 7.0 Hz, 1 H), 6.50 (dt, J = 15.7 Hz, J = 1.2 Hz, 1 H), 2.36 (s, 3 H), 2.40–2.32 (m, 2 H), 1.52 (m, 2 H), 1.39 (m, 2 H), 0.94 (t, J = 7.3 Hz, 3 H). Anal. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 74.04; H, 7.97.

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Generation and Electrophilic Reactions of the 2,2,2-Trifluoro-1-(phenylthio)ethyl Carbocation

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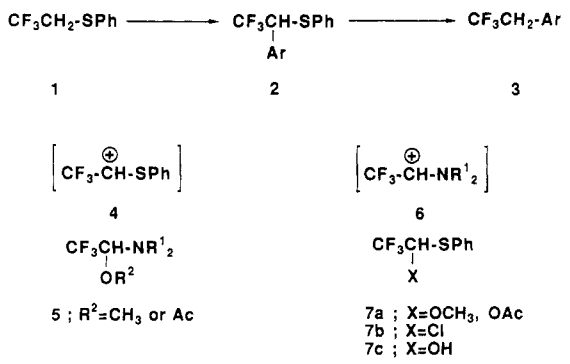
2,2,2-Trifluoro-1-(phenylthio)ethyl carbocation (**4**) has been generated by the reaction of 1-chloro-2,2,2-trifluoroethyl phenyl sulfide (**7b**) with $ZnCl_2$ in nitromethane or $SnCl_4$ in 1,2-dichloroethane. The carbocation **4** can be trapped with various aromatics bearing electron-donating groups, affording 1-aryl-2,2,2-trifluoroethyl phenyl sulfide **2** in 37–83% yields. Similarly, allyltrimethylsilane and various nitriles provided the corresponding allylated sulfide and amide sulfides, respectively. The reaction rate is affected by the electron-donor ability of the reactant aromatics. The optically active chloride **7b'** was prepared and subjected to a $ZnCl_2$-catalyzed reaction. Both product **2** and the recovered **7b'** were racemic, suggesting the formation of carbocation intermediate.

Because of increasing attention to organofluorine compounds in the medical and material sciences,[1] transformations to organofluorine compounds have been extensively studied in recent years. Trifluoroethylation, however, has been relatively unexplored. Trifluoroethyl aromatics have been of interest in agrochemistry, for example, as insecticides[2] and fungicides.[3] The Wurtz–Fittig reaction of 2,2,2-trifluoroethyl iodide with copper metal,[4] reduction of trifluoroacetyl aromatics prepared by an addition of aryl Grignard to trifluoroacetic acid,[5] and replacement of chlorine by fluorine of 2,2,2-trichloroethyl aromatics[6] have been proposed. However, these methods are limited because of vigorous conditions, low yields, or the use of expensive and hazardous reagents.

Carbon–carbon bond formation on the methylene carbon of 2,2,2-trifluoroethyl phenyl sulfide (**1**) and subsequent desulfurization would be a promising pathway. However, metalation of **1** followed by alkylation failed to yield alkylated compounds but led instead to defluorination.[7] This suggests that the 1-(phenylthio)-2,2,2-trifluoroethyl carbanion is very unstable, although a few successful alkylations on the carbon bearing the trifluoromethyl group have been reported.[8-10] On the other hand, the chemistry of the carbocation **4** has not been investigated, presumably due to the difficulty of its generation. Therefore, an electron-donating group must be introduced to the carbon attached to the trifluoromethyl group to compensate the deactivation by the trifluoromethyl group. Aryl group participation in the stabilization has been well demon-

Scheme I



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