Novel Cyclization by Stannyl Anion Generated from $Me_3SiSnBu_3$ and F^-. The Application to the Natural Product Synthesis

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Stannyl anion, generated from $Me_3SiSnBu_3$ and $(Et_2N)_3S^+TMSF_2^-$ (TASF) or CsF in DMF, was quite effective for generation of an aryl or vinyl anion, which reacted with a carbonyl group intramolecularly to provide the useful cyclized product in good yield.

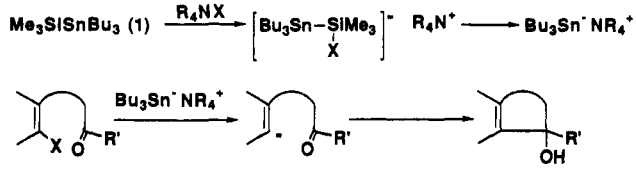
Introduction

In the field of modern synthetic organic chemistry, the stannyl anion is of growing importance.[1] The stannyl anion is usually prepared from organotin halides,[2a] hexaorganoditins,[2b,2c] and organotin hydrides.[2d] We have found that the stannyl anion can be generated from $Me_3SiSnBu_3$ (1) and R_4NX.[3] The generated stannyl anion reacts with an aryl or vinyl halide to produce an aryl or vinyl anion, *via* a halogen–metal exchange process, which reacts with a carbonyl group intramolecularly to give a cyclized product.[3] The first step of this reaction is the formation of a hypervalent silicate by coordination of X^- of R_4NX to $Me_3SiSnBu_3$. On the basis of the HSAB theory, the most suitable halide ion should be fluoride[4] because the harder silyl moiety of $Me_3SiSnBu_3$ is strongly coordinated by the harder fluoride ion. However, the use of Bu_4NF led to a poor result while the use of Bu_4NCl gave a good result.[3] Now we report the generation of the stannyl anion from $Me_3SiSnBu_3$ and TASF[5] [$(Et_2N)_3S^+TMSF_2^-$] or CsF and the utilization of the generated stannyl anion for natural product synthesis.

Results and Discussion

The reaction of **2a** with $Me_3SiSnBu_3$ in the presence of Bu_4NF at low temperature was reexamined because the most suitable halide ion was considered to be fluoride. When the reaction was carried out at −50 °C, the desired products, **3a** and **5a**, were obtained in 55 and 15% yields,

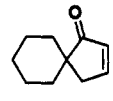
Scheme I



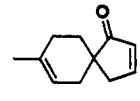
respectively (Table I, run 2). However, a fair amount of dehalogenation product (14%) was obtained because it is difficult to remove trace water from Bu_4NF. Thus, we chose $(Et_2N)_3S^+TMSF_2^-$ (TASF)[5] as the fluoride source. When 1 (2 equiv) was added to a DMF soltuion of **2a** (1 equiv) in the presence of TASF (2 equiv) at −50 °C and the solution was stirred at the same temperature for 1 h, the desired products, **3a**, **4a**, and **5a**, were obtained in 84% yield (run 3). The formation of the silylated compound **4a** suggests that the carbonyl group of **2a** coordinates to the hypervalent silicate formed from 1 and TASF.

Subsequently, vinyl iodide **2b**, was treated with 1 in the presence of TASF in DMF at −50 °C (Table II, run 1). In this reaction, the desired product **3b** was obtained in 46% yield along with the dehalogenation product **6b** (42% yield). In order to improve the yield of the desired product **3b**, a variety of conditions were examined. For the solvent, THF and NMP (1-methyl-2-pyrrolidinone) can be used, but the use of CH_2Cl_2 and CH_3CN afforded the dehalogenation product **6b** (85–90% yield). When the reaction was carried out at a higher temperature, CsF was suitable (Table II, runs 7 and 8).

Using this procedure, the reaction of various vinyl iodides **2c–g** with 1 in the presence of CsF was examined. The vinyl iodides, **2c** and **2d**, were prepared by palladium-catalyzed coupling of (*E*)-3-(trimethylsilyl)-2-propenyl acetate[6] with 1,3-diketones **7**. The other vinyl iodides **2e**, **2f**, and **2g**, were prepared by alkylation of compounds **9e**, **9f**, and **9g** with (*Z*)-iodo-3-(mesyloxy)-1-propene.[7] The results for the cyclization of vinyl iodides **2c–g** are shown in Table III. The cyclized compounds **3c–g** were obtained in good to excellent yields. In the reaction of **2e** or **2f** with 1, the initial products, **10e** or **10f**, further reacted with the



10e



10f

† Hokkaido University.
‡ University of Tokyo.

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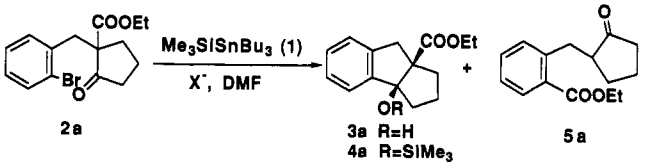
Table I. Effect of Halide Anion on the Reaction of 2a and 1

run	X^-	temp (°C)	yield (%) 3a	4a	5a
1	Bu_4NF	60	32	–	–
2	Bu_4NF	−50	55	–	15
3	TASF[a]	−50	41	25	18

[a] TASF = $(Et_2N)_3S^+TMSF_2^-$.

Scheme II



Scheme III

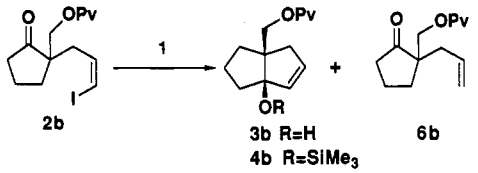
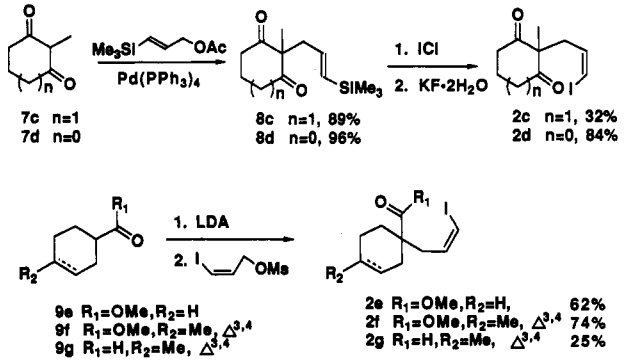


Table II. Reaction of 2b with 1

run	F^-	solvent	reaction conditions temp (°C)	time (h)	yield (%) 3b	4b	6b
1	TASF	DMF	−50	1	46	–	42
2	TASF	DMF	−30	1	52	–	37
3	TASF	CH_2Cl_2	−30	1	3	–	89
4	TASF	CH_3CN	−30	1	–	–	84
5	TASF	THF	−30	1	10	30	33
6	TASF	NMP	−20	1	33	–	28
7	CsF	DMF	rt	20 min	55	–	42
8	CsF	DMF	60	20 min	58	–	36

Scheme IV



stannyl anion to provide the stannylated product **3e** or **3f**. The reaction of the aryl halides **2h–j** with 1 and TASF were reexamined.[3b] The results are shown in Table III. All yields of these reactions were better than those obtained with R_4NCl.

Syntheses of Bicyclo[3.3.0] and Bicyclo[4.3.0] Analogues of the Wieland–Miescher Ketone. The bicyclo[3.3.0] and bicyclo[4.3.0] analogues[8] **11** and **12** of the Wieland–Miescher ketone, are useful building blocks for fused cyclopentanoid natural products. However, ring construction of the fused cyclopentenones **11** and **12** from 2-methyl-1,3-cyclopentanedione or 2-methyl-1,3-cyclohexanedione derivatives using the standard aldol conditions is quite difficult. It was expected that the allyl alcohols **3c** and **3d** should be converted to the fused cyclopentenone derivatives **11** and **12**. As expected, oxidation of compound **3c** with PCC gave an unsaturated ketone **11** in 87% yield. However, the desired five-membered ketone **12** was not obtained by similar treatment of compound **3d**. Various attempts to convert **3d** into the ketone **12** by oxidation were unsuccessful. Thus, when compound **3d** was treated with $SOCl_2$ in pyridine, we could obtain the allyl chloride **13** (74% yield) in addition to the allyl alcohol **14** (24% yield).[9] The former product was treated with Ag_2CO_3 in the presence of $AgNO_3$ (10 mol %) in aqueous acetone[10] to give the allyl alcohol **14** (52% yield) along with **3d** (18% yield). Compound **14** was oxidized with PCC to afford the Wieland–Miescher ketone analogue **12** in 68% yield. In practice, a mixture of the crude products **13** and **14** obtained by treatment of **3d** with $SOCl_2$–pyridine, was treated with Ag_2CO_3 in the presence of $AgNO_3$ to give **14** in 58% yield along with compound **3d** (18% yield).

Formal Total Synthesis of Acorone. The spiro compounds **3e–g** appeared to be potentially versatile intermediates for the synthesis of biologically active spiro sesquiterpenes. The spirocyclopentenone **3f** or **3g** is a very attractive intermediate for the synthesis of acorone (**15**).[11] Thus, we tried to prepare the natural product acorone (**15**) from **3f**. Our plan is shown in Scheme VI. Reduction of **3f** with $NaBH_4$ followed by treatment with MsCl in the presence of Et_3N afforded four inseparable isomers of the mesylate.[12] When $LiAl[OC(CH_3)_3]_3H$ was used as the reducing reagents, the alcohol *cis*-**17** was obtained in 89% yield along with the *trans* isomer (11% yield). Treatment of *cis*-**17** with MsCl followed by treatment with DBU smoothly proceeded to afford the allyl stannane **18** in 78% yield along with the mesylate of *cis*-**17** (17% yield). Compound **18** was easily converted to the α,β-unsaturated ketone **16** by Collins oxidation[2b] in 76% yield. Thus, the formal total synthesis of acorone (**15**) was realized.

In conclusion, the stannyl anion can be easily generated from $Me_3SiSnBu_3$ in the presence of TASF or CsF in DMF under mild conditions. Using this stannyl anion, an aryl or vinyl anion can be formed from an aryl or vinyl halide via a halogen–metal exchange process. The important characteristics of this procedure are that $Me_3SiSnBu_3$ is

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(9) The reason why the latter alcohol **14** was obtained is not clear. The intramolecular allylic rerrangement of the chlorosulfonyl group of the intermediate would afford the allyl alcohol **14**.

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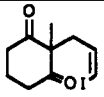
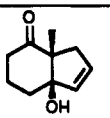
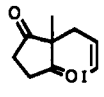
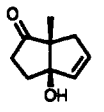
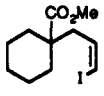
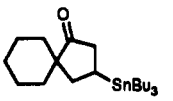
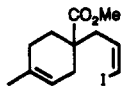
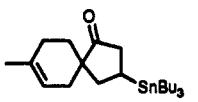
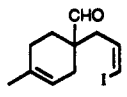
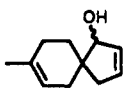
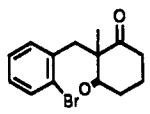
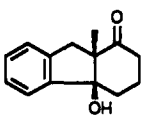
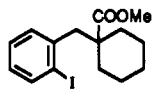
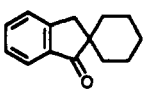
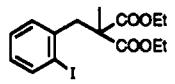
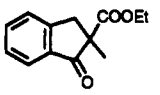
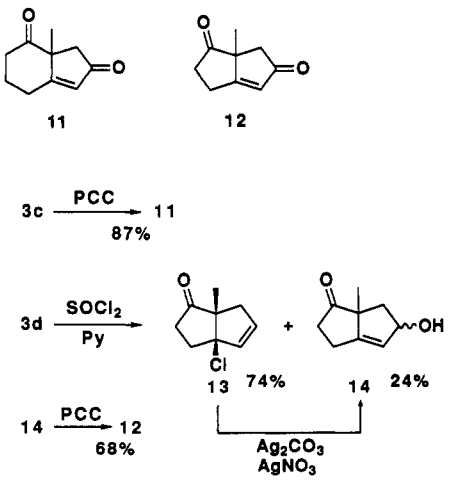
(12) An inseparable mixture of the mesylate of **17** was treated with DBU to produce the desired product **18** in 42% yield along with the mesylate **17** (32% yield). The NMR spectrum of the starting mesylate showed the presence of four isomers and that of the recovered mesylate indicated that two isomers remained unchanged. Presumably, the neighboring bulky stannyl group would prevent access of DBU to the anti β-hydrogen. Thus, the stereochemistry of the mesyloxy group and the stannyl group of the recovered mesylate should be *trans*. In order to obtain *cis*-**17**, $LiAl[OC(CH_3)_3]_3H$ was used as the reducing reagents.

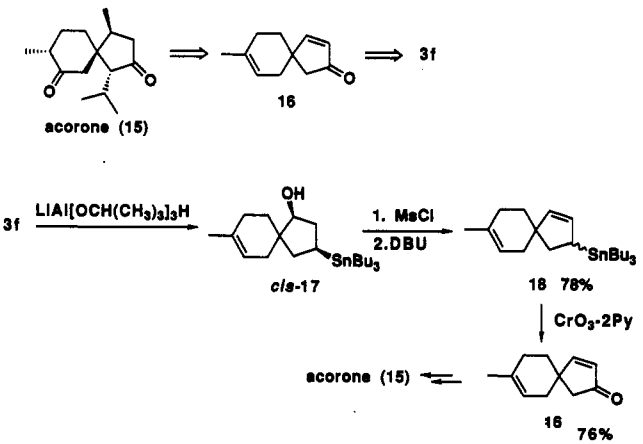
Table III. Cyclization by Use of $Me_3SiSnBu_3$ and F^-

run	substrate	reagent	temp (°C)	time (h)	product	yield (%)
1	 2c	CsF	rt	1	 3c	86
2	 2d	CsF	rt	1	 3d	81
3	 2e	CsF	60	1	 3e	60
4	 2f	CsF	60	1	 3f	58
5	 2g	CsF	60	1	 3g	75
6	 2h	TASF	−30	1	 3h	93
7	 2i	TASF	−30	1	 3i	73
8	 2j	TASF	−50	2	 3j	90

Scheme V



Scheme VI



stable and commercially available and generation of the stannyl anion is easy. Especially, Bu_3SnBr or Bu_3SnI produced by the halogen–metal exchange process is easily removed from the reaction mixture, because they are converted to insoluble Bu_3SnF under the reaction conditions.

Experimental Section

Solvents were distilled under an argon atmosphere from sodium benzophenone (THF), CaH_2 (DMF, Et_3N), or P_2O_5 (CH_2Cl_2). All other reagents and solvents were purified when necessary by standard procedures. $Me_3SiSnBu_3$[4] and TASF[5c] were prepared by the literature method. The solvent (THF) of TASF (1 M THF solution) was replaced with DMF before the reaction was

carried out. NMR spectra were recorded at 100 MHz and 270 MHz. Melting points are uncorrected.

(*Z*)-2-(3-Iodo-2-propenyl)-2-methyl-1,3-cyclohexanedione (2c). A solution of 2-methyl-1,3-cyclohexanedione (**7c**) (518 mg, 4.10 mmol), (*E*)-3-(trimethylsilyl)-2-propenyl acetate[6] (1.07 g, 6.23 mmol), $Pd(PPh_3)_4$ (243 mg, 0.21 mmol), and DBU (0.74 mL, 4.95 mmol) in THF (5 mL) was degassed through a freeze-pump-thaw cycle and was stirred at room temperature for 31 h. Water was added and the solution was extracted with ether. The organic layer was washed with brine dried over Na_2SO_4 and concentrated. The residue was purified by chromatography on silica gel [hexane–ethyl acetate (10:1 and then 5:1)] to give a colorless oil of **8c** (873 mg, 89%): IR (neat) 1725, 1695, 1615 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 0.01 (s, 9 H), 1.21 (s, 3 H), 1.7–2.1 (m, 2 H), 2.3–2.5 (m, 6 H), 6.6–6.8 (m, 2 H); MS *m/z* 238 (M^+), 223, 210, 165, 75; HRMS *m/z* calcd for $C_{13}H_{22}O_2Si$ 238.1389, found 238.1417. To a solution of **8c** (438 mg, 1.84 mmol) in CCl_4 (2.0 mL) was added a solution of ICl (363 mg, 2.23 mmol) in CCl_4 (3.1 mL) at 0 °C[13] and the solution was stirred at the same temperature for 15 min. To the reaction mixture was added 10% $Na_2S_2O_3$ solution and the aqueous layer was extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. To the residue in DMSO (5.0 mL) was added $KF{\cdot}2H_2O$ (264 mg, 2.80 mmol) at 0 °C and the solution was stirred at room temperature for 1.5 h. Water was added, the aqueous layer was extracted with ether, and the organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel [hexane–ethyl acetate (3:1)] to give a colorless oil of **2c** (171 mg, 32%). **2c**: IR (neat) 1726, 1695, 1610 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.32 (s, 3 H), 1.8–2.2 (m, 2 H), 2.63 (dd, J = 6.6, 1.5 Hz, 2 H), 2.4–2.8 (m, 4 H), 5.99 (dt, J = 7.8, 6.6 Hz, 1 H), 6.37 (dt, J = 7.8, 1.5 Hz, 1 H); MS *m/z* 293 ($M^+ + 1$), 165, 137; HRMS *m/z* calcd for $C_{10}H_{14}IO_2$ 293.0039, found 293.0058. Anal. Calcd for $C_{10}H_{13}IO_2$: C, 41.12; H, 4.49; I, 43.44. Found: C, 41.22; H, 4.54; I, 43.33.

(*Z*)-2-(3-Iodo-2-propenyl)-2-methyl-1,3-cyclopentanedione (2d). A solution of 2-methyl-1,3-cyclopentanedione (**7d**) (394 mg, 3.52 mmol), (*E*)-3-(trimethylsilyl)-2-propenyl acetate[6] (759 mg, 4.41 mmol), $Pd(PPh_3)_4$ (135 mg, 0.12 mmol), and DBU (0.63 mL, 4.21 mmol) in THF (10 mL) was degassed through a freeze-pump-thaw cycle and was stirred at room temperature for 34 h. Water was added and the solution was extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel [hexane–ethyl acetate (5:1)] to give a colorless oil of **8d** (754 mg, 96%): IR (neat) 1725, 1615, 1249 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 0.02 (s, 9 H), 1.10 (s, 3 H), 2.39 (d, J = 5.9 Hz, 2 H), 2.55–2.80 (m, 4 H), 5.70 (d, J = 18.3 Hz, 1 H), 5.79 (dd, J = 18.3, 5.9 Hz, 1 H); MS *m/z* 224 (M^+), 209, 151; HRMS *m/z* calcd for $C_{12}H_{20}O_2Si$ 224.1260, found 224.1246. To a solution of **8d** (445 mg, 1.98 mmol) in CCl_4 (4.0 mL) was added a solution of ICl (376 mg, 2.32 mmol) in CCl_4 (1.2 mL) at 0 °C[13] and the solution was stirred at the same temperature for 15 min. To the reaction mixture was added 10% $Na_2S_2O_3$ solution and the aqueous layer was extracted with ether. The organic layer was washed with brine dried over Na_2SO_4 and concentrated. To the residue in DMSO (5.0 mL) was added $KF{\cdot}2H_2O$ (323 mg, 4.34 mmol) at 0 °C and the solution was stirred at room temperature for 1 h. Water was added, the aqueous layer was extracted with ether, and the organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel [hexane–ethyl acetate (3:1)] to give a colorless oil of **2d** (461 mg, 84%). **2d**: IR (neat) 1724, 1610 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.17 (s, 3 H), 2.46 (dd, J = 7.0, 1.1 Hz, 2 H), 2.80 (s, 4 H), 6.10 (dt, J = 7.7, 7.0 Hz, 1 H), 6.44 (dt, J = 7.7, 1.1 Hz, 1 H); MS *m/z* 279 ($M^+ + 1$), 151, 123, 109; HRMS *m/z* calcd for $C_9H_{11}IO_2$ 277.9804, found 277.9824. Anal. Calcd for $C_9H_{11}IO_2$: C, 38.73; H, 3.97; I, 45.63. Found: C, 39.03; H, 4.05; I, 45.41.

(*Z*)-Methyl 1-(3-Iodo-2-propenyl)cyclohexane-1-carboxylate (2e). To a solution of LDA prepared from BuLi (1.42 N hexane solution, 0.4 mL, 0.57 mmol) and diisopropylamine (63 mg, 0.62 mmol) in THF (4.0 mL) was added methyl cyclohexanecarboxylate **9e** (74 mg, 0.52 mmol) at −78 °C and the solution was stirred at 0 °C for 0.5 h. To the solution was added a solution of (*Z*)-iodo-3-(mesyloxy)-1-propene[7] (136 mg, 0.52 mmol) in THF (1 mL) at −78 °C. After the solution was stirred at 0 °C for 2.5 h, saturated NH_4Cl solution was added and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel [hexane–ethyl acetate (20:1)] to give a colorless oil of **2e** (99 mg, 62%). **2e**: IR (neat) 1730, 1610, 1216 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 1.0–1.8 (m, 8 H), 1.9–2.2 (m, 2 H), 2.34 (dd, J = 6.8, 1.2 Hz, 2 H), 3.69 (s, 3 H), 6.08 (dt, J = 7.3, 6.8 Hz, 1 H), 6.31 (dt, J = 7.3, 1.2 Hz, 1 H); MS *m/z* 308 (M^+), 249, 181, 121; HRMS *m/z* calcd for $C_{11}H_{17}IO_2$ 308.0273, found 308.0251.

(*Z*)-Methyl 1-(3-Iodo-2-propenyl)-4-methylcyclohex-3-ene-1-carboxylate (2f). To a solution of LDA prepared from BuLi (1.65 N hexane solution, 2.2 mL, 3.63 mmol) and diisopropylamine (397 mg, 3.92 mmol) in THF (20 mL) was added a solution of methyl 4-methylcyclohex-3-ene-1-carboxylate[14] (**9f**) (496 mg, 3.22 mmol) in THF (5 mL) at −78 °C and the solution was stirred at −78 °C for 1 h. To the solution was added a solution of (*Z*)-iodo-3-(mesyloxy)-1-propene[7] (1.09 g, 4.14 mmol) in THF (5 mL) at −78 °C. After the solution was stirred at 0 °C for 5 h, saturated NH_4Cl solution was added and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel [hexane–ethyl acetate (20:1)] to give a colorless oil of **2f** (761 mg, 74%). **2f**: IR (neat) 1733, 1609, 1213 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 1.64 (s, 3 H), 1.8–2.7 (m, 6 H), 2.42 (dd, J = 6.6, 1.2 Hz, 2 H), 3.68 (s, 3 H), 5.28 (brs, 1 H), 6.10 (dt, J = 7.5, 6.6 Hz, 1 H), 6.32 (dt, J = 7.5, 1.2 Hz, 1 H); MS *m/z* 320 (M^+), 261, 193, 133; HRMS *m/z* calcd for $C_{12}H_{17}IO_2$ 320.0273, found 320.0260. Anal. Calcd for $C_{12}H_{17}IO_2$: C, 45.02; H, 5.35; I, 39.64. Found: C, 44.99; H, 5.36; I, 39.48.

(*Z*)-1-(3-Iodo-2-propenyl)-4-methylcyclohex-3-ene-1-carbaldehyde (2g). From 4-methylcyclohex-3-ene-1-carbaldehyde (**9g**),[14] compound **2g** was prepared in a similar procedure to that of the preparation of **2e**. A crude product was purified by chromatography on silica gel [hexane–ethyl acetate (50:1–5:1)] to give a colorless oil of **2g** (25%). **2g**: IR (neat) 1725, 1609 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 1.5–1.8 (m, 1 H), 1.64 (s, 3 H), 1.9–2.2 (m, 4 H), 2.3–2.5 (m, 1 H), 2.37 (dd, J = 7.0, 1.5 Hz, 2 H), 5.38 (brs, 1 H), 6.08 (dt, J = 7.3, 7.0 Hz, 1 H), 6.35 (dt, J = 7.3, 1.5 Hz, 1 H), 9.50 (s, 1 H); MS *m/z* 290 (M^+), 261, 163; HRMS *m/z* calcd for $C_{11}H_{15}IO$ 290.0168, found 290.0149.

General Procedure for the Cyclization Using Stannyl Anion Generated from $Me_3SiSnBu_3$ and F^-. To a solution of TASF or CsF (2 equiv) and the substrate (1 equiv) in DMF (0.15 M solution) was added $Me_3SiSnBu_3$ (2 equiv) at the appropriate temperature and the solution was stirred at the same temperature. After the spot of the starting material had disappeared on TLC, 10% NH_4OH was added and the aqueous layer was extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel.

Cyclization of 2b. A crude product which was prepared from **2b** (37 mg, 0.10 mmol), $Me_3SiSnBu_3$ (73 mg, 0.20 mmol), and CsF (35 mg, 0.23 mmol) in DMF (0.7 mL) was purified by chromatography on silica gel [hexane–ethyl acetate (10:1–5:1)] to give a colorless oil of **3b** (14 mg, 58%) and **6b** (9 mg, 36%). **3b**: IR (neat) 3454, 1729, 1288 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 1.19 (s, 9 H), 1.4–1.9 (m, 6 H), 1.93 (brs, 1 H), 2.15 (ddd, J = 17.8, 2.2, 2.2 Hz, 1 H), 2.55 (ddd, J = 17.8, 2.2, 2.2 Hz, 1 H), 4.04 and 4.22 (ABq, J = 11.0 Hz, 2 H), 5.56 (ddd, J = 5.6, 2.2, 2.2 Hz, 1 H), 5.81 (ddd, J = 5.6, 2.2, 2.2 Hz, 1 H); MS *m/z* 238 (M^+), 221, 154, 136; HRMS *m/z* calcd for $C_{14}H_{22}O_3$ 238.1569, found 238.1558. Anal. Calcd for $C_{14}H_{22}O_3$: C, 70.56; H, 9.30. Found: C, 70.49; H, 9.48. When THF was used as solvent, **4b** was obtained along with **3b** and **6b** (Table II, run 5). **4b**: IR (neat) 1729, 1627, 1286 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.08 (s, 9 H), 1.20 (s, 9 H), 1.1–1.4 (m, 2 H), 1.5–1.7 (m, 2 H), 1.7–1.9 (m, 2 H), 2.13 (ddd, J = 17.2, 2.2, 2.2 Hz, 1 H), 2.51 (ddd, J = 17.2, 2.2, 2.2 Hz, 1 H), 3.99 and 4.08 (ABq, J = 11.0 Hz, 2 H), 5.57 (ddd, J = 5.5, 2.2, 2.2 Hz, 1

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H), 5.77 (ddd, J = 5.5, 2.2, 2.2 Hz, 1 H); MS m/z 310 (M^+), 221, 208; HRMS m/z calcd for $C_{17}H_{30}O_3Si$ 310.1964, found 310.1958.

3a-Hydroxy-7a-methyl-3a,4,5,6,7,7a-hexahydro-7-indenone (3c). A crude product which was prepared from **2c** (44 mg, 0.15 mmol), $Me_3SiSnBu_3$ (109 mg, 0.30 mmol), and CsF (48 mg, 0.32 mmol) in DMF (1 mL) was purified by chromatography on silica gel [hexane–ethyl acetate (3:1–2:1)] to give a colorless oil of **3c** (21 mg, 86%). **3c**: IR (neat) 3441, 1698, 1610 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.24 (s, 3 H), 1.49 (brs, 1 H), 1.8–2.1 (m, 4 H), 2.16 (ddd, J = 16.9, 2.6, 2.2 Hz, 1 H), 2.3–2.5 (m, 2 H), 3.13 (ddd, J = 16.9, 2.6, 1.5, 1 H), 5.68 (ddd, J = 5.9, 2.6, 1.5 Hz, 1 H), 6.01 (ddd, J = 5.9, 2.6, 1.5 Hz, 1 H); MS m/z 166 (M^+), 148, 120; HRMS m/z calcd for $C_{10}H_{14}O_2$ 166.0993, found 166.0966.

3a-Hydroxy-6a-methyl-1,2,3,3a,6,6a-hexahydro-1-pentalenone (3d). A crude product which was prepared from **2d** (323 mg, 1.16 mmol), $Me_3SiSnBu_3$ (842 mg, 2.32 mmol), and CsF (353 mg, 2.32 mmol) in DMF (8 mL) was purified by chromatography on silica gel [hexane–ethyl acetate (4:1–2:1)] to give a colorless oil of **3d** (143 mg, 81%). **3d**: IR (neat) 3486, 1736, 1611 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.10 (s, 3 H), 1.66 (brs, 1 H), 2.0–2.2 (m, 2 H), 2.3–2.5 (m, 2 H), 2.32 (ddd, J = 17.6, 2.2, 2.2 Hz, 1 H), 2.65 (ddd, J = 17.6, 2.2, 2.2 Hz, 1 H), 5.72 (ddd, J = 5.5, 2.2, 2.2 Hz, 1 H), 5.94 (ddd, J = 5.5, 2.2, 2.2 Hz, 1 H); MS m/z 152 (M^+), 134, 124; HRMS m/z calcd for $C_9H_{12}O_2$ 152.0837, found 152.0826. Anal. Calcd for $C_{11}H_{14}O_3$ (acetate of **3d**): C, 68.02; H, 7.27. Found: C, 67.73; H, 7.32.

3-(Tributylstannyl)spiro[4.5]decanone (3e). A crude product which was prepared from **2e** (33 mg, 0.105 mmol), $Me_3SiSnBu_3$ (114 mg, 0.32 mmol), and CsF (52 mg, 0.34 mmol) in DMF (0.8 mL) was purified by chromatography on silica gel [hexane–ethyl acetate (30:1–10:1)] to give a colorless oil of **3e** (28 mg, 60%). **3e**: IR (neat) 1725 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.7–1.1 (m, 16 H), 1.1–1.9 (m, 24 H), 1.9–2.7 (m, 2 H); MS m/z 442 (M^+), 415, 385, 329; HRMS m/z calcd for $C_{22}H_{42}O^{120}Sn$ 442.2258, found 442.2256.

8-Methyl-3-(tributylstannyl)spiro[4.5]dec-7-en-1-one (3f). A crude product which was prepared from **2f** (47 mg, 0.15 mmol), $Me_3SiSnBu_3$ (166 mg, 0.46 mmol), and CsF (70 mg, 0.46 mmol) in DMF (1 mL) was purified by chromatography on silica gel [hexane–ethyl acetate (50:1–10:1)] to give a colorless oil of **3f** (39 mg, 58%). **3f**: IR (neat) 1734 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.7–1.0 (m, 16 H), 1.1–1.8 (m, 16 H), 1.66 (s, 3 H), 1.8–2.7 (m, 6 H), 5.36 (brs, 1 H); MS m/z 454 (M^+), 397, 341; HRMS m/z calcd for $C_{23}H_{42}O^{120}Sn$ 454.2258, found 454.2270. Anal. Calcd for $C_{23}H_{42}OSn$: C, 60.94; H, 9.34. Found: C, 61.13; H, 9.45.

8-Methylspiro[4.4]deca-2,7-dien-1-ol (3g). A crude product which was prepared from **2g** (32 mg, 0.11 mmol), CsF (35 mg, 0.23 mmol), and $Me_3SiSnBu_3$ (83 mg, 0.23 mmol) in DMF (0.8 mL) was purified by chromatography on silica gel [hexane–ethyl acetate (20:1–5:1)] to give a colorless oil of **3g** (14 mg, 75%). **3g**: IR (neat) 3345, 1617 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.66 (s, 3 H), 1.5–1.7 (m, 2 H), 1.8–2.4 (m, 7 H), 4.22 and 4.33 (brs and brs, 1 H), 5.26–5.34 and 5.42–5.49 (m and m, 1 H), 5.76 and 5.83 (ddd and ddd, J = 5.9, 4.4, 2.2 Hz, 1 H), 5.91 and 5.96 (ddd and ddd, J = 5.9, 2.6, 2.2 Hz, 1 H); MS m/z 164 (M^+), 146, 131; HRMS m/z calcd for $C_{11}H_{16}O$ 164.1202, found 164.1176. Anal. Calcd for $C_{13}H_{18}O_2$ (acetate of **3g**) C, 75.69; H, 8.80. Found: C, 75.54; H, 8.86.

7a-Methyl-2,4,5,6,7,7a-hexahydro-2,7-indenedione (11). To a solution of **3c** (20 mg, 0.12 mmol) and 4A molecular sieves (105 mg) in CH_2Cl_2 (0.7 mL) was added PCC (58 mg, 0.27 mmol) at 0 °C and the solution was stirred at room temperature for 5 h. Ether was added to the solution and the undissolved material was filtered through on the Florisil. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel [hexane–ethyl acetate (1:1)] to give colorless crystals of **11**[8a] (17 mg, 87%). **11**: IR (Nujol) 1713, 1621 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.53 (s, 3 H), 1.6–1.8 (m, 1 H), 2.14 (d, J = 19.1 Hz, 1 H), 2.2–2.5 (m, 2 H), 2.6–2.9 (m, 3 H), 3.21 (d, J = 19.1 Hz, 1 H), 5.82 (s, 1 H); MS m/z 164 (M^+), 136, 108; HRMS m/z calcd for $C_{10}H_{12}O_2$ 164.0838, found 164.0849. Anal. Calcd for $C_{10}H_{12}O_2$: C, 73.15; H, 7.37. Found: C, 73.20; H, 7.47.

5a-Hydroxy-6a-methyl-1,2,3,5,6,6a-hexahydro-1-pentalenone (14). To the solution of **3d** (20 mg, 0.13 mmol) and pyridine (43 μL, 0.53 mmol) in CH_2Cl_2 (0.8 mL) was added a solution of $SOCl_2$ (20 μL 0.27 mmol) in CH_2Cl_2 (0.2 mL) at 0 °C. The solution was stirred for 30 min at the same temperature. Ether was added and the undissolved material was filtered off through the short silica gel column. The solvent was removed under reduced pressure and the residue was dissolved in acetone–H_2O (3:1, 1.0 mL). To the solution was added $AgNO_3$ (4 mg, 0.024 mmol) and Ag_2CO_3 (56 mg, 0.20 mmol) and the solution was stirred for 1 h. Undissolved AgCl was filtered off and the solvent was removed. The residue was purified by chromatography on silica gel [hexane–ethyl acetate (1:1)] to give a colorless oil of **14** (12 mg, 58%) and **3d** (4 mg, 18%). **14**: IR (neat) 3396, 1743, 1666 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.37 (s, 3 H), 1.61 (brs, 1 H), 2.20 (dd, J = 14.3, 6.6 Hz, 1 H), 2.5–2.9 (m, 4 H), 2.71 (dd, J = 14.3, 2.8 Hz, 1 H), 4.91 (dd, J = 6.6, 2.8 Hz, 1 H), 5.67 (brs, 1 H); MS m/z 152 (M^+), 135, 123; HRMS m/z calcd for $C_9H_{12}O_2$ 152.0837, found 152.0809.

2,3,6,6a-Tetrahydro-6a-methyl-1,5-pentalenedione (12). To a solution of **14** (18 mg, 0.12 mmol) and 4A molecular sieves (111 mg) in CH_2Cl_2 (1 mL) was added PCC (40 mg, 0.186 mmol) at 0 °C and the solution was stirred at room temperature for 3 h. Ether was added to the solution and the undissolved material was filtered through on the Florisil. The solvent was removed under reduced pressure and the residue was purified by chromatography on silica gel [hexane–ethyl acetate (1:1)] to give colorless crystals of **12**[8f] (12 mg, 68%). **12**: IR (neat) 1751, 1709, 1634 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 1.36 (s, 3 H), 2.0–2.5 (m, 1 H), 2.31 (d, J = 18.1 Hz, 1 H), 2.64 (d, J = 18.1 Hz, 1 H), 2.8–3.3 (m, 3 H), 6.02 (s, 1 H); MS m/z 150 (M^+), 122, 107, 79; HRMS m/z calcd for $C_9H_{10}O_2$ 150.0681, found 150.0660.

***cis*-8-Methyl-3-(tributylstannyl)spiro[4.5]dec-7-en-1-ol (*cis*-17).** To a solution of **3f** (16 mg, 0.036 mmol) in THF (1.0 mL) was added $LiAl[OC(CH_3)_3]_3H$ (48 mg, 0.197 mmol) at −78 °C and the solution was stirred at 0 °C for 5 h. To the solution was added $Na_2SO_4 \cdot 10H_2O$ and the solution was stirred overnight. Undissolved material was filtered off and the solvent was removed. The residue was purified by preparative thin-layer chromatography on silica gel, [hexane–ethyl acetate (7:1)] to give a colorless oil of *cis*-**17** (14 mg, 89%) and *trans*-**17** (2 mg, 11%). *cis*-**17**: IR (neat) 3370 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 0.7–1.0 (m, 16 H), 1.1–2.5 (m, 26 H), 3.7–3.9 (m, 1 H), 5.44 (brs, 1 H); MS m/z 455 (M^+), 399; HRMS m/z calcd for $C_{23}H_{44}O^{120}Sn$ 456.2414, found 456.2394.

8-Methyl-3-(tributylstannyl)spiro[4.5]deca-1,7-diene (18). To a solution of *cis*-**17** (11 mg, 0.024 mmol) and NEt_3 (25 μL, 0.18 mmol) in CH_2Cl_2 (0.3 mL) was added MsCl (6.0 μL, 0.078 mmol) at −30 °C and the solution was stirred for 1 h. Ether was added and the organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by short column chromatography on silica gel (ethyl acetate). Solvent was removed and the residue was dissolved in DBU (0.5 mL). The solution was warmed at 80 °C for 24 h. Ethyl acetate was added and the organic layer was washed with brine, dried over Na_2SO_4, and concentrated. The residue was purified by chromatography on silica gel [hexane–ethyl acetate (100:1)] to give a colorless oil of **18** (8 mg, 78%) and mesylate of *cis*-**17** (2 mg, 19%). **18**: IR (neat) 1600 cm^{-1}; ^1H NMR (270 MHz) ($CDCl_3$) δ 0.7–1.0 (m, 15 H), 1.2–1.6 (m, 16 H), 1.66 (s, 3 H), 1.7–2.1 (m, 4 H), 2.4–2.5 (m, 1 H), 5.34 (brs, 1 H), 5.38 (dd, J = 5.5, 2.6 Hz, 1 H), 5.72 (dd, J = 5.5, 2.2 Hz, 1 H); MS m/z 437 (M^+), 381; HRMS m/z calcd for $C_{23}H_{42}{}^{120}Sn$ 438.2309, found 438.2292. Anal. Calcd for $C_{23}H_{42}Sn$: C, 63.17; H, 9.68. Found: C, 63.33; H, 9.96.

8-Methylspiro[4.5]deca-1,7-dien-3-one (16). To a solution of **18** (20 mg, 0.046 mmol) and 4A molecular sieves (140 mg) was added $CrO_3 \cdot 2C_5H_5N$ solution[2b] [a solution of CrO_3 (48 mg, 0.48 mmol) and pyridine (85 μL, 1.05 mmol) in 0.5 mL of CH_2Cl_2] and the solution was stirred at room temperature for 5 h. Ether was added and the solution was passed through a short column of Florisil. The solvent was removed and the residue was purified by preparative thin-layer chromatography on silica gel [hexane–ethyl acetate (10:1)] to give a colorless oil of **16**[11a] (6 mg, 76%). **16**: IR (neat) 1714, 1588 cm^{-1}; ^1H NMR (100 MHz) ($CDCl_3$) δ 1.70 (s, 3 H), 1.5–2.3 (m, 6 H), 2.19 (s, 2 H), 5.39 (brs, 1 H), 6.07 (d, J = 5.9 Hz, 1 H), 7.56 (d, J = 5.9 Hz, 1 H); MS m/z 162 (M^+), 133..