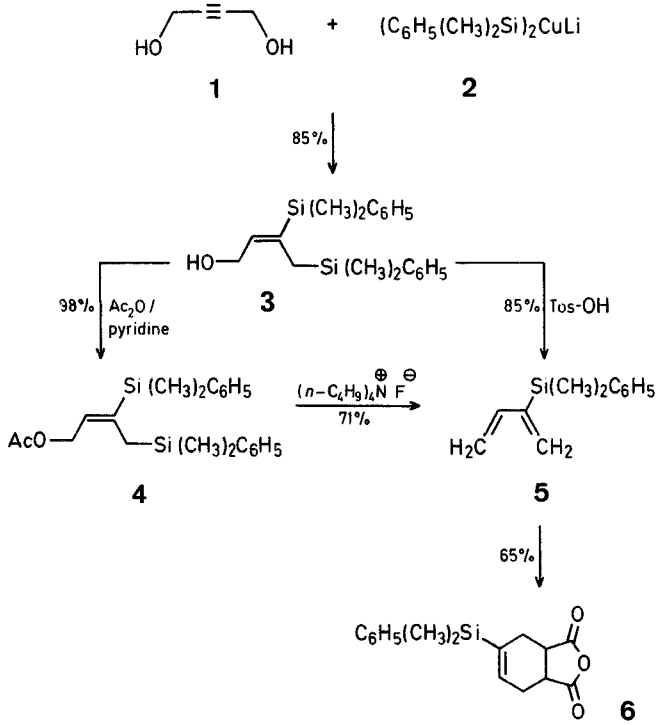
Simple Syntheses of 2-Silyl- and 2-Stannyl-1,3-butadienes

Ian FLEMING*, Maurizio TADDEI

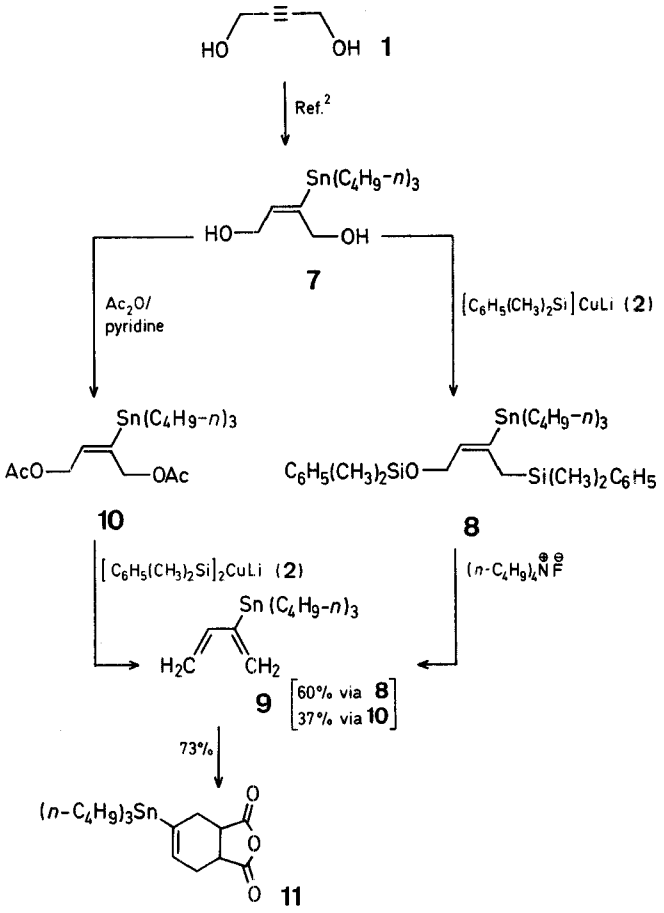
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England

2-Dimethylphenylsilylbutadiene and 2-tributylstannylbutadiene are prepared from 2-butyne-1,4-diol.

In the preceding communication[1], we reported the tin-cupration of 2-butyne-1,4-diol (**1**). When we tried the corresponding silyl-cupration, we observed instead an unexpected reaction: in addition to the silyl-cupration of the acetylene group, the hydroxy group adjacent to the silyl group was displaced to give the disilylated butenol **3**. The silyl-cupration of the triple bond was well precedented in our own work[2], but the displacement of the hydroxy group was not. We have observed the formation of allylsilanes from tertiary allylic acetates[3], but not from allylic alcohols, let alone primary allylic alcohols. The alcohol **3** is a convenient precursor of 2-[dimethyl-(phenyl)-silyl]-butadiene (**5**), which can be prepared either by direct treatment with acid (85%), or by acetylation (**3** → **4**), followed by fluoride ion-catalysed displacement of the silyl and acetate groups (71%). The latter method makes it possible to isolate the chromatographically pure diene, whereas the former gives an inseparable mixture of the diene and siloxane by-products. However, if the diene is to be used in Diels-Alder reactions (e.g. **5** → **6**), these by-products can easily be removed after adduct formation, and the former method is then the more simple and higher-yielding route. These routes to the 2-silylbutadiene are easier than existing routes[4], and are almost certainly adaptable to using other silyl groups, since we have already shown[5] that the silyl-cupration reaction of alkynes works with the trimethylsilyl-cuprate reagent as well as with the more accessible dimethyl-(phenyl)-silyl-cuprate.



The unexpected displacement of the primary alcohol group also took place with the (*E*)-stannylbutenediol **7**. The product (**8**) was a silyl ether, which could be converted directly into the 2-stannylbutadiene **9**. Alternatively, the diacetate (**10**) of the diol reacted with the silyl-cuprate reagent to give a regioisomeric mixture of allylsilanes, which gave the same diene (**9**) on treatment with fluoride ion. Curiously, the (*Z*)-isomer of **7** did not react with the silyl-cuprate reagent. 2-Stannyldienes undergo Diels-Alder reactions (e.g. **9** → **11**) and are also useful for the synthesis of 2-lithiobutadiene[6].



3,4-Bis[dimethylphenylsilyl]-2-butenol (3):
1,4-Butynediol (**1**; 1 g, 11 mmol) is added dropwise, with stirring at 0°C, to the silyl-cuprate reagent **2**[2] [prepared from dimethylphenylsilyl-lithium (23.2 mmol) and copper(I) cyanide (1.04 g, 11.6 mmol) in tetrahydrofuran (15 ml)]. After 1.5 h, the mixture is allowed to warm to room temperature, and ammonium chloride solution (20 ml) and ether (100 ml) are added. The organic layers are washed with ammonium chloride solution (3 × 20 ml), dried with magnesium sulphate, and evaporated. The residue is flash-chromatographed on silica gel, eluting with ether/light petroleum (b.p. 30–50°C) (2/5) to give the alcohol **3** as an oil; yield: 3.2 g (85%).

$C_{20}H_{28}OSi_2$	calc.	C 70.58	H 8.28
(340.6)	found	69.96	8.32

I.R. (liquid film): ν = 3300, 1250, 1010 cm^{-1}.

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 0.18 [s, 6H, $Si(CH_3)_2$]; 0.22 [s, 6H, $Si(CH_3)_2$]; 1.5 (br.s, 1H, OH); 1.98 (s, 2H, CH_2—Si); 3.95 (d, 2H, J = 6 Hz, OCH_2); 5.90 (t, 1H, J = 6 Hz, =CH); 7.4 ppm (m, 10 H_{arom}).

3,4-Bis[dimethylphenylsilyl]-2-butenyl Acetate (4):
The alcohol **3** (1 g, 2.9 mmol) and acetic anhydride (3 ml) are kept in pyridine (5 ml) at 80°C for 4 h. Ether (50 ml) is added at room temperature, the solution is washed with 1 normal hydrochloric acid (20 ml) and brine and dried with magnesium sulphate. Flash chromatography on silica gel eluting with ether/light petroleum (b.p. 30–50°C) (1/5) gives the acetate **4** as an oil; yield: 1.1 g (98%).

$C_{22}H_{30}O_2Si_2$	calc.	C 69.07	H 7.85
(382.7)	found	68.96	7.87

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 0.12 [s, 6H, $Si(CH_3)_2$]; 0.22 [s, 6H, $Si(CH_3)_2$]; 2.0 (s, 5H, H_3C—CO and CH_2—Si); 4.38 (d, 2H, J = 6 Hz, CH_2—O); 5.75 (t, 2H, J = 6 Hz, CH=); 7.3 ppm (m, 10 H_{arom}).

2-Dimethylphenylsilyl)-1,3-butadiene (5):

Method A: The acetate **4** (1 g, 2.8 mmol) is added to tetrabutylammonium fluoride in tetrahydrofuran (14 ml of a 1 molar solution) at 0 °C. The mixture is stirred at room temperature for 3 h and then extracted with light petroleum (150 ml, b.p. 30–50 °C), the organic layer dried with magnesium sulphate, and chromatographed on silica gel eluting with pentane to give the diene **5** as an oil; yield: 375 mg (71%).

$C_{12}H_{16}Si$	calc.	C 76.59	H 8.81
(188.3)	found	76.80	8.49

I.R. (liquid film): ν = 2960, 1650, 1280, 840 cm^{-1}.

^{1}H-N.M.R. (CCl_4/TMS_{int}): δ = 0.45 [s, 6H, $Si(CH_3)_2$]; 4.9–5.3 (m, 2H, H_2C=CH); 5.5–6.0 (m, 2H, Si—C=CH_2); 6.5 (m, 1H, CH=); 7.3 ppm (m, 5 H_{arom}).

Method B: The alcohol **3** (3 g, 8.8 mmol) and toluene-*p*-sulphonic acid (1.7 g, 8.8 mmol) are refluxed in ether (50 ml) overnight. The mixture is then diluted with light petroleum (b.p. 40–60 °C), washed with 10% sodium carbonate solution and brine, and dried with magnesium sulphate; the solvent is evaporated and the residue subjected to Kugelrohr distillation to give a mixture of diene **5** and siloxane by-products (ratio 8/1, as determined by ^{1}H-N.M.R.); yield 1.8 g (85%); b.p. 100 °C/1 torr.

4-Dimethylphenylsilyl-1,2,3,6-tetrahydrophthalic Anhydride (6):

Equimolecular amounts of diene **5** and maleic anhydride are heated at 60 °C for 2 h. The product is crystallised from methanol; yield: 65–70%; m.p. 62–63 °C.

$C_{16}H_{18}O_3Si$	calc.	C 67.11	H 6.29
(286.4)	found	67.31	6.30

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 0.31 [s, 6H, $Si(CH_3)_2$]; 2.0–2.8 (m, 4H, 2 CH_2); 3.2 (m, 2H, 2 CH—CO); 6.3 (m, 1H, Si—C=CH); 7.4 ppm (m, 5 H_{arom}).

2-Tributylstannyl-1,3-butadiene (9):

Method A:

2-Tributylstannyl-4-dimethylphenylsiloxy-1-dimethylphenylsilyl-2-butene (**8**): 2-Tributylstannyl-2-butene-1,4-diol (**7**; 4.0 g, 10.61 mmol) is added with stirring at 0 °C to the silyl-cuprate reagent **2**[2] [prepared from dimethylphenylsilyl-lithium (33.3 mmol) and copper(I) cyanide (1.46 g, 16.3 mmol) in tetrahydrofuran (80 ml)]. Stirring at 0 °C is continued for 4 h and the mixture then allowed to come to room temperature. Basic ammonium chloride solution (2 ml) is added and the mixture stirred overnight. Ether (300 ml) is added and the mixture filtered through silica gel and dried with magnesium sulfate; the solvents evaporated off. The residue is chromatographed on silica gel eluting with ether/light petroleum (b.p. 30–50 °C) (1/4) to give the silyl ether **8**; yield: 3.6 g (54%). The product is used directly in the next step.

I.R. (liquid film): ν = 2980, 1620, 1250 cm^{-1}.

^{1}H-N.M.R. (CCl_4/TMS_{int}): δ = 0.25 [s, 6H, $Si(CH_3)_2$]; 0.29 [s, 6H, $Si(CH_3)_2$]; 0.7–1.7 [m, 27H, (n-$C_4H_9)_3$Sn]; 2.0 (s, 2H, Si—CH_2); 3.82 (d, 2H, J = 6 Hz, OCH_2); 5.50 (t, 1H, J = 6 Hz, CH=); 7.2–7.7 ppm (m, 10 H_{arom}).

2-Tributylstannyl-1,3-butadiene (**9**): The silyl ether **8** (3.6 g) is stirred with tetrabutylammonium fluoride in tetrahydrofuran (15 ml of a 1 molar solution) at room temperature overnight. Pentane (50 ml) is then added, the pentane layer dried with magnesium sulphate, the solvent evaporated, and the residue chromatographed on silica gel eluting with light petroleum (b.p. 40–60 °C) to give the diene **9**[7] as an oil; yield: 1.2 g (60%).

$C_{16}H_{32}Sn$	calc.	C 56.00	H 9.34
(343.1)	found	56.10	9.39

I.R. (liquid film): ν = 2960, 1640 cm^{-1}.

^{1}H-N.M.R. (CCl_4/TMS_{int}): δ = 0.9–1.7 [m, 27H, (n-$C_4H_9)_3$Sn]; 5.1–6.0 (m, 4H, 2 = CH_2); 6.7 ppm (m, 1H, =CH).

Method B:

1,4-Diacetoxy-2-tributylstannyl-2-butene (**10**): 2-Tributylstannyl-2-butene-1,4-diol (**7**; 2 g, 5.3 mmol) is kept with acetic anhydride (1.7 g, 17 mmol) in pyridine (30 ml) at 85 °C for 4 h. The mixture is cooled, ether (50 ml) is added, and the solution is washed with 1 normal hydrochloric acid (20 ml) and brine, and dried with magnesium sulphate. Evaporation of the solvent gives product **10**; yield: 1.67 g (68%). The product is used directly in the next step.

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 0.7–1.8 [m, 27H, (n-$C_4H_9)_3$Sn]; 2.05 (s, 6H, 2 O—CO—CH_3); 4.56 (d, 2H, J = 6 Hz, AcO—CH_2—CH); 4.71 (s, 2H, Sn—C—CH_2—OAc); 6.45 ppm (t, 1H, J = 6 Hz, AcO—CH_2—CH).

2-Tributylstannyl-1,3-butadiene (**9**): A solution of the diacetate **10** (1.67 g, 3.6 mmol) is added with stirring at −78 °C to the silyl-cuprate reagent **2**[2] [prepared from dimethylphenylsilyl-lithium (3.1 mmol) and copper(I) cyanide (146 mg, 1.6 mmol) in tetrahydrofuran (5 ml)], and the mixture is allowed to come to room temperature. Basic ammonium chloride solution (3 ml) is added, followed by ether (25 ml). The organic layer is washed with brine, dried with magnesium sulphate, and evaporated to give a mixture of products which is stirred with tetrabutylammonium fluoride in tetrahydrofuran (20 ml of a 1 molar solution) at room temperature overnight. Pentane (50 ml) is added, the organic layer is dried with magnesium sulphate and evaporated. The residue is column-chromatographed on silica gel using pentane as eluent to give the diene **9** as an oil; yield: 678 mg (37%).

4-Tributylstannyl-1,2,3,6-tetrahydrophthalic Anhydride (11):

A mixture of diene **9** (0.5 g, 1.4 mmol; obtained by Method A) and maleic anhydride (137 mg, 1.4 mmol) is heated in a sealed tube at 100 °C for 4 h. Column chromatography of the resultant product on silica gel using ether as eluent and crystallisation from ether/light petroleum (b.p. 40–60 °C) (2/3) affords the Diels-Alder adduct **11**, yield: 0.46 g (73%); m.p. 39–41 °C.

$C_{20}H_{34}O_3Sn$	calc.	C 54.46	H 7.71
(441.2)	found	54.39	7.69

^{1}H-N.M.R. ($CDCl_3$/TMS_{int}): δ = 0.8–1.8 [m, 27H, (n—$C_4H_9)_3$Sn]; 1.9–2.5 (m, 4H, 2 CH_2); 3.1 (m, 2H, 2 CH—CO); 6.1 ppm (m, 1H, C=CH).

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