# Convenient synthesis of silyl substituted butadienes; a new route to silicon tethered intramolecular Diels–Alder reaction precursors

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The preparation of a series of silyl substituted butadienes is reported together with their application in the silicon-tethered intramolecular Diels–Alder reaction (IMDA).

Silyl substituted butadienes are intermediates of considerable potential as substrates for the Diels–Alder reaction.[1] We were particularly interested in investigating and developing their use in an intramolecular variant of this reaction, our goal being the preparation of a range of substrates with the generalised structure **1** which we hoped would allow us to access a range of bicyclic compounds **2** (Scheme 1).
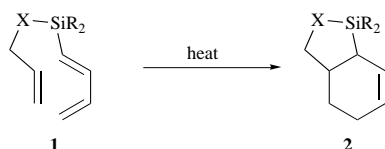
Scheme 1 R = Alkyl, aryl; X = O, (CH₂)ₙ

This approach, in which the silicon is attached directly to the diene unit, has been the subject of only two previous reports,[2] despite considerable interest in the area of silicon-tethered reactions.[3]

We thus required a convenient and flexible synthesis of a range of silylated butadienes **5** and **6** and hoped to access them *via* the silylated allylic alcohols **4** which are conveniently prepared by hydrosilylation of the prop-2-ynyl alcohols **3**.[4] These alcohols would then allow easy access to the required substrates *via* a variety of methods, for example *via* dehydration (**5**) or a Wittig reaction (**6**) (Scheme 2).

As a preliminary investigation we took a range of substrate alcohols **3a–e** and effected hydrosilylation using conditions previously described by Murphy *et al.*[4] utilising the readily prepared catalyst **7**.[5] As can be seen (Table 1) the reaction
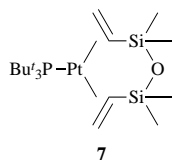
proceeded, to give the alcohols **4a–g**, with excellent regioselectivity and in good yield in most cases.

Treatment of these alcohols with camphorsulfonic acid (CSA) under azeotropic conditions in either benzene, toluene or xylene, led to the formation of the corresponding diene **5a–g** in acceptable yields (Table 1).

As is apparent, the best yields for the elimination step are found, unsurprisingly, with the tertiary alcoholic substrates (**4a,b,e** and **f**) and the elimination is effective for alkyl as well as aryl substituted silanes. The yield for the secondary alcohol (**4c**) is somewhat lower (49%) but still acceptable. However, when we
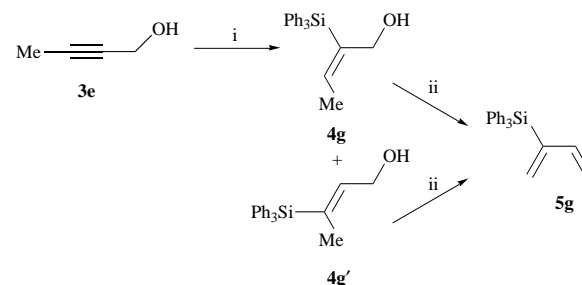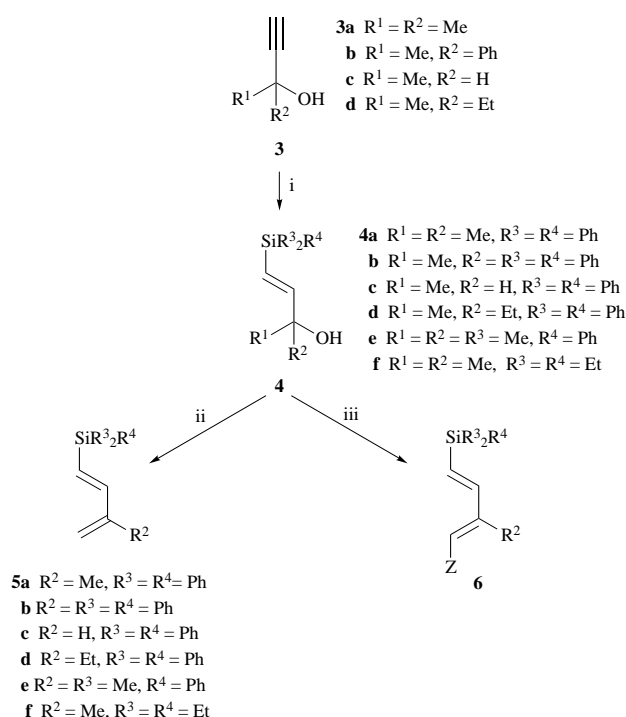
Scheme 2 i, HSiR³₂R⁴, [Pt]⁰; ii, heat, H⁺/−H₂O; iii, R¹ = H; (a) PCC, (b) ZCHPPh₃; Z = H, R, Ar, CN, COR, COOR

consider the eliminations from the primary alcohols (**4g** and **g′**) the yields are now somewhat diminished, but despite this the reaction is readily amenable to scaling up and is thus still of synthetic use; indeed yields are generally better when the reactions are performed on a medium scale (3–5 g). A final example, using the unsymmetrical alcohol **3d**, helps highlight the limitations of this method.

With this preliminary work in hand we hoped to assess the potential use of this methodology in the preparation of precursors for the silicon-tethered IMDA. Thus we prepared diphenyl(but-3-enyl)silane **8** from commercially available chlorodiphenylsilane by treatment with the Grignard of 4-bromobut-1-ene; this was then reacted under our standard conditions with **3a** to give the diene precursor **9** in 68% yield for the two steps. On heating **9** in toluene containing catalytic CSA the diene **10** was produced in 78% yield, which on further heating

Table 1

Alcohol 3	t/h^a	Product 4 (% yield)	Conditions^b	Product 5 (% yield)
3a	21	4a (80)	PhMe, 3 h, 2% CSA	5a (84)
3b	6.5	4b (83)	PhH, 4 h, 5% CSA	5b (52)
3c	4	4c (88)	$C_6H_4Me_2$, 2 h, 5% CSA	5c (49)
3d	24	4d (67)	PhMe, 2 h, 11% CSA	5d + 5d' (1:2.4)^c (total 69)
3a	3	4e (85)	PhMe, 2 h, 5% CSA	5e (66)
3a	4	4f (69)	PhMe, 1.5 h, 5% CSA	5f (54)
3e	5.5	4g (44)	$C_6H_4Me_2$, 1.5 h, 19% CSA	5g (39)
		+ 4g' (50)	$C_6H_4Me_2$, 3 h, 17% CSA	5g' (29)

^{a} Silane (1 equiv.) and alcohol (1.4 equiv.) were heated under reflux in the presence of catalyst 7 for the stated times. ^{b} Alcohol 4 and camphorsulfonic acid (CSA) were heated in the solvent given with azeotropic removal of water, until TLC indicated the complete consumption of starting material. ^{c}

$$5d' = \quad Ph_3Si \diagdown \diagup \diagup Me$$

E:Z 2.3:1
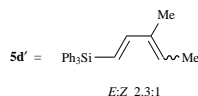
(xylene, sealed tube, 180–200 °C) for 40 h gave the cyclised products 11a and b as an inseparable 5:2 mixture of isomers (90% conversion) (Scheme 3).
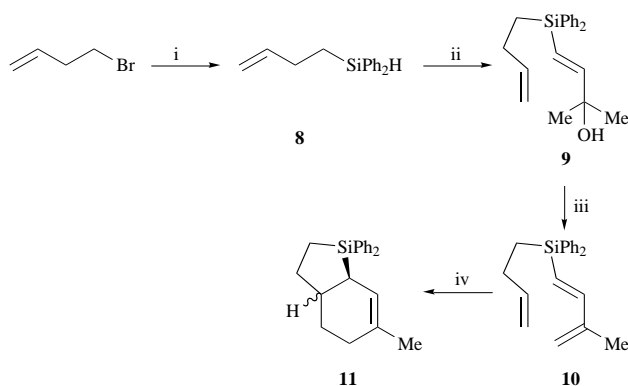

Scheme 3 i, Mg–Et$_2$O then ClHSiPh$_2$; ii, 3a, catalytic 7, THF reflux 3 h (68% for 2 steps); iii, heat, toluene, CSA (10% w/w) 2 h, 78%; iv, xylene 180–200 °C, sealed tube for 40 h (quantitative recovery, 90% conversion)

Similarly hydrosilylation of prop-2-ynyl alcohol using diphenyl(but-3-enyl)silane 8 gave the alcohol 12 in 77% yield. Oxidation of this intermediate and immediate reaction of the resultant aldehyde with ethoxycarbonylmethylenetriphenylphosphorane led to the formation of 13 in excellent overall yield. Heating of 13 in a sealed tube for 16 h (180–200 °C) led to the formation of a separable 1:1 mixture of the cyclised products 14a and b (quantitative conversion, 53% isolated yield) (Scheme 4).

In conclusion, we have demonstrated a convenient and rapid method for the preparation of a range of potentially useful silylated dienes and have applied the method to an initial study of the intramolecular Diels–Alder reaction of such substrates. We are currently investigating the factors that affect the stereoselectivity of this IMDA reaction and its potential applications in synthesis.

Experimental

Column chromatography was carried out on Kieselgel (230–400 mesh) with the eluent specified in each case; all substances are
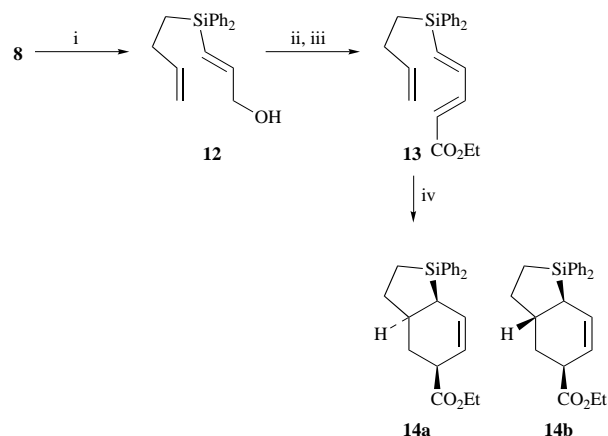
Scheme 4 i, Prop-2-ynyl alcohol, catalytic 7, THF reflux 3 h (77%); ii, 2 equiv. PCC, DCM, RT, 3 h; iii, EtO$_2$CCHPPh$_3$, DCM, reflux (68% for 2 steps); iv, xylene 180–200 °C, sealed tube, 16 h (14a:14b 1:1, 53%)

oils unless otherwise stated. TLC was conducted on precoated Kieselgel 60 F$_{254}$ (Art. 5554; Merck) glass plates. All reactions were conducted in oven-dried apparatus under a static atmosphere of argon. Light petroleum refers to the fraction boiling in the range 35–60 °C. Diethyl ether and THF were dried and distilled using standard methods; all other reagents are used as supplied. Chemical shifts are reported as δ values relative to tetramethylsilane as an internal standard; J values are given in Hz. ^{1}H and ^{13}C NMR spectra were recorded in deuteriochloroform on a Bruker AC250 spectrometer. IR Spectra were recorded as thin films (oils) or in KBr on a Perkin-Elmer 1600 series instrument. Mass spectra were recorded on a VG Masslab Model 12/253 spectrometer using CI (with ammonia as the reagent gas) or EI.

General procedure for hydrosilylation

The silane (1 equiv.) and the acetylenic alcohol 3 (1.4 equiv.) were dissolved in THF (5 ml per g of silane) and the catalyst 7 (5–10 mg per g of silane) added; the reaction mixture was then refluxed for the stated period (Table 1). The reaction was then cooled, evaporated and the crude product purified by flash chromatography (10–20% diethyl ether in light petroleum).

Spectral data for the alcohols 4a–g

3-Hydroxy-3-methyl-1-triphenylsilylbut-1-ene 4a. Mp 98–99 °C; δ_H 7.54–7.25 (15 H, m, ArH), 6.39 (1 H, d, J 18.7), 6.29 (1 H, d, J 18.7), 1.60 (1 H, br s, OH), 1.33 (6 H, s, 2 × CH$_3$); δ_C 159.09, 135.84, 129.59, 128.09, 127.91, 118.62, 72.47, 29.42; v_{max}/cm^{-1} 3400 (OH), 3064, 2975 (CH), 1626 (C=C); m/z (CI) 344 [(M + NH$_4$ − H$_2$O)$^+$, 25%], 362 [(M + NH$_4$)$^+$, 2] {Found: 362.1940 [(M + NH$_4$)$^+$]. Calc. for C$_{25}$H$_{28}$NOSi: 362.1940}.

3-Hydroxy-3-phenyl-1-triphenylsilylbut-1-ene 4b. Oil; δ_H 7.6–7.23 (20 H, m, ArH), 6.59 (1 H, d, J 19.0), 6.52 (1 H, d, J 19.0), 2.10 (1 H, s, OH), 1.72 (3 H, s, CH$_3$); δ_C 157.39, 146.15, 136.04, 134.44, 129.69, 128.38, 128.00, 127.16, 125.37, 120.21, 75.98, 29.33; v_{max}/cm^{-1} 3438 (OH), 3066, 2977 (CH), 1621 (C=C); m/z 406 (M$^+$, 5%), 424 [(M + NH$_4$)$^+$, 2] {Found: 424.2097 [(M + NH$_4$)$^+$]. Calc. for C$_{28}$H$_{30}$NOSi: 424.2097}.

3-Hydroxy-1-triphenylsilylbut-1-ene 4c. Mp 128–129 °C; δ_H 7.58–7.37 (15 H, m, ArH), 6.45 (1 H, dd, J 18.6, 1.1), 6.28 (1 H, dd, J 18.6, 4.4), 4.45 (1 H, m), 1.70 (1 H, br s, OH), 1.33 (1 H, d, J 6.5, Me); δ_C 155.34, 135.88, 134.27, 129.52, 127.83, 121.54, 70.30, 22.92; v_{max}/cm^{-1} 3446 (OH), 3065, 2994 (CH), 1624 (C=C); m/z 330 (M$^+$, 10%), 348 [(M + NH$_4$)$^+$, 20] {Found: 348.1784 [(M + NH$_4$)$^+$]. Calc. for C$_{22}$H$_{26}$NOSi: 348.1784}.

3-Hydroxy-3-methyl-1-triphenylsilylpent-1-ene 4d. Oil; δ_H 7.56–7.29 (15 H, m, ArH), 6.40 (1 H, d, J 18.7), 6.18 (1 H, d, J 18.7), 1.58 (3 H, m, CH$_2$, OH), 1.28 (3 H, s), 0.87 (3 H, t, J 7.7); δ_C 158.19, 135.92, 134.57, 129.52, 127.86, 119.73, 74.80, 34.68, 27.40, 8.26; v_{max}/cm^{-1} 3433 (OH), 3067, 2968 (CH), 1618 (C=C);

m/z (CI) 358 [(M − H$_2$O + NH$_4$)$^+$, 20%], 376 [(M + NH$_4$)$^+$, 3] {Found: 376.2097 [(M + NH$_4$)$^+$]. Calc. for C$_{20}$H$_{30}$NOSi: 376.2097}.

3-Hydroxy-3-methyl-1-phenyldimethylsilylbut-1-ene 4e. Oil; δ_H 7.54–7.23 (5 H, m, ArH), 6.23 (1 H, d, *J* 18.7), 5.93 (1 H, d, *J* 18.7), 1.52 (1 H, br s, OH), 1.27 (6 H, s, 2 × CH$_3$), 0.32 (6 H, s, 2 × CH$_3$); δ_C 155.06, 138.66, 137.77, 128.93, 127.74, 122.44, 72.05, 29.30, −2.57; v_{max}/cm^{-1} 3342 (OH), 3068, 2972 (CH), 1616 (C=C); *m/z* 203 [(M + H − H$_2$O)$^+$, 45%], 220 [(M − H$_2$O + NH$_4$)$^+$, 100], 221 [(M + H)$^+$, 20], 238 [(M + NH$_4$)$^+$, 12] {Found: 238.1627 [(M + NH$_4$)$^+$]. Calc. for C$_{13}$H$_{24}$NOSi: 238.1627}.

3-Hydroxy-3-methyl-1-triethylsilylbut-1-ene 4f. Oil; δ_H 6.16 (1 H, d, *J* 18.7), 5.72 (1 H, d, *J* 18.7), 1.53 (1 H, br s, OH), 1.33 (6 H, s, 2 × CH$_3$), 0.93 (9 H, t, *J* 7.7, 3 × C*H*$_3$CH$_2$Si), 0.57 (6 H, q, *J* 7.7, 3 × CH$_3$C*H*$_2$Si); δ_C 154.76, 120.33, 72.07, 29.4, 7.27, 3.38; v_{max}/cm^{-1} 3383 (OH), 2954 (CH), 1620 (C=C); *m/z* 183 [(M + H − H$_2$O)$^+$, 35%], 200 [(M − H$_2$O + NH$_4$)$^+$, 50] {Found: 200.1835 [(M − H$_2$O + NH$_4$)$^+$]. Calc. for C$_{11}$H$_{26}$NSi: 200.1835}.

1-Hydroxy-2-triphenylsilylbut-2-ene 4g. Mp 131–132 °C; δ_H 7.57–7.17 (15 H, m, ArH), 6.12 (1 H, q, *J* 7.0), 4.43 (2 H, s), 1.85 (3 H, d, *J* 7.0), 1.07 (1 H, br s, OH); δ_C 144.46, 136.78, 126.22, 134.55, 129.52, 127.93, 60.79, 15.30; v_{max}/cm^{-1} 3054 (OH), 3049 (CH), 1608 (C=C); *m/z* 348 [(M + NH$_4$)$^+$, 20%] {Found: 348.1784 [(M + NH$_4$)$^+$]. Calc. for C$_{22}$H$_{26}$NOSi: 348.1784}.

1-Hydroxy-3-triphenylsilylbut-2-ene 4g′. Mp 135–136 °C; δ_H 7.57–7.12 (15 H, m, ArH), 6.01 (1 H, tq, *J* 1.0, 5.4), 4.33 (2 H, *J* 5.4), 1.84 (3 H, d, *J* 1.0), 1.33 (1 H, br s, OH); δ_C 145.02, 136.24, 133.71, 133.50, 129.55, 127.88, 60.14, 16.50; v_{max}/cm^{-1} 3278 (OH), 3064 (CH), 1618 (C=C); *m/z* 330 (M$^+$, 8), 348 [(M + NH$_4$)$^+$, 15] {Found: 348.1784 [(M + NH$_4$)$^+$]. Calc. for C$_{22}$H$_{26}$NOSi: 348.1784}.

General procedure for dehydration

The alcohol **4** was dissolved in the required solvent (Table 1; 20 ml per gram of substrate) and CSA (50–200 mg per gram of substrate) was added. The reaction was then equipped with a Dean–Stark apparatus and heated under reflux (with gradual concentration of the reaction by removal of toluene) until TLC indicated complete consumption of starting material. After cooling to room temperature the reaction mixture was diluted with diethyl ether (*ca.* 30–50 ml), washed with saturated aqueous sodium hydrogen carbonate (2 × 30 ml), dried and evaporated. Column chromatography (0–2% diethyl ether in light petroleum) gave the dienes **5**.

Spectral data for the butadienes 5a–c and 5e–g

3-Methyl-1-triphenylsilylbuta-1,3-diene 5a. Mp 112–115 °C; δ_H 7.68–7.23 (15 H, m, ArH), 6.76 (1 H, d, *J* 18.8), 6.35 (1 H, d, *J* 18.8), 5.51 (1 H, br s), 5.16 (1 H, br s), 1.98 (3 H, s, CH$_3$); δ_C 151.58, 143.21, 135.90, 134.30, 129.45, 127.79, 122.56, 118.70, 17.98; v_{max}/cm^{-1} 3065, 3000 (CH), 1603 (C=C); *m/z* 334 [(M + NH$_4$)$^+$, 20%], 327 [(M + H)$^+$, 15] {Found: 327.1569 [(M + H)$^+$]; C, 84.42; H, 6.93%. Calc. for C$_{23}$H$_{23}$Si: 327.1569; C, 84.61; H, 6.79%}.

3-Phenyl-1-triphenylsilylbuta-1,3-diene 5b. Mp (glass) 80–90 °C; δ_H 7.54–7.14 (20 H, m, ArH), 6.84 (1 H, d, *J* 18.7), 6.35 (1 H, d, *J* 18.7), 5.27 (2 H, br s, 2 × CH); δ_C 145.48, 141.95, 136.07, 135.98, 134.93, 134.60, 129.21, 128.81, 127.90, 127.45, 124.81, 120.13; v_{max}/cm^{-1} 3018 (CH), 1598 (C=C); *m/z* 406 [(M + NH$_4$)$^+$, 32%], 389 [(M + H)$^+$, 30] {Found: 389.1726 [(M + H)$^+$]. Calc. for C$_{28}$H$_{25}$Si: 389.1726}.

1-Triphenylsilylbuta-1,3-diene 5c. Mp 107–109 °C; δ_H 7.56–7.25 (15 H, m, ArH), 6.67–6.29 (3 H, m), 5.19 (2 H, m); δ_C 149.64, 139.56, 135.98, 135.80, 134.43, 129.59, 127.91, 119.34; v_{max}/cm^{-1} 3013 (CH), 1583, 1565 (C=C); *m/z* 330 [(M + NH$_4$)$^+$, 5%], 276 [(M + NH$_4$ − C$_4$H$_6$)$^+$, 80] {Found: 330.1678 [(M + NH$_4$)$^+$]. Calc. for C$_{22}$H$_{24}$NSi: 330.1678}.

3-Methyl-1-dimethylphenylsilylbuta-1,3-diene 5e. Oil; δ_H 7.51–7.29 (5 H, m, ArH), 6.64 (1 H, d, *J* 18.7), 5.91 (1 H, d, *J* 18.7), 5.07 (1 H, br s), 5.01 (1 H, br s), 1.84 (3 H, s, CH$_3$), 0.36 (6 H, s, 2 × SiCH$_3$); δ_C 2.48, 18.00, 117.75, 126.97, 127.82, 129.01, 133.92, 138.81, 143.44, 148.20; v_{max}/cm^{-1} 3068, 2957 (CH), 1577 (C=C); *m/z* 202 (M$^+$, 20%); 187 [(M − CH$_3$)$^+$, 90] {Found: 202.1178 (M$^+$). Calc. for C$_{13}$H$_{18}$Si: 202.1178}.

3-Methyl-1-triethylsilylbuta-1,3-diene 5f. Oil; δ_H 6.61 (1 H, d, *J* 19.0), 5.76 (1 H, d, *J* 19.0), 5.04 (1 H, br s), 4.91 (1 H, br s), 1.85 (3 H, s, CH$_3$), 0.96 (9 H, t, *J* 7.9, SiCH$_2$C*H*$_3$), 0.60 (6 H, q, *J* 7.9, SiC*H*$_2$CH$_3$); δ_C 147.70, 143.60, 125.62, 116.80, 17.87, 7.35, 3.48; v_{max}/cm^{-1} 2953 (CH), 1572 (C=C); *m/z* 200 [(M + NH$_4$)$^+$, 70%], 183 [(M + H)$^+$, 90] {Found: 183.1569 [(M + H)$^+$]. Calc. for C$_{12}$H$_{23}$Si, 183.1569}.

2-Triphenylsilylbuta-1,3-diene 5g. Mp 70–77 °C; δ_H 7.60–7.26 (15 H, m, ArH), 6.67 (1 H, dd, *J* 18.0, 10.8), 6.15 (1 H, d, *J* 2.5), 5.47 (1 H, d, *J* 2.5), 5.06 (1 H, d, *J* 18.0), 5.02 (1 H, d, *J* 10.8); δ_C 144.42, 141.27, 136.26, 135.11, 134.10, 129.53, 127.85, 118.52; v_{max}/cm^{-1} 3066 (CH), 1614 (C=C); *m/z* 330 [(M + NH$_4$)$^+$, 80%], 276 [(M + NH$_4$ − C$_4$H$_6$)$^+$, 100] {Found: 330.1678 [(M + NH$_4$)$^+$]. Calc. for C$_{22}$H$_{24}$NOSi: 330.1678}.

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