

Synthesis of Alkyl and Aryl Substituted Buta-1,2,3-trienes

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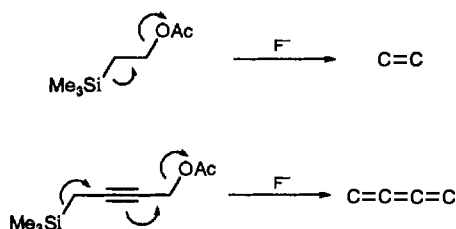
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Reaction of the lithium or cerium(III) anion of 3-alkyl or 3-aryl substituted 3-trimethylsilylprop-1-yne **1** with aldehydes or ketones afforded 1-hydroxy-4-trimethylsilylbut-2-yne **2** in good yields. Conversion of the silyl prop-2-ynylic alcohols **2** into the corresponding acetates **3** followed by tetrabutylammonium fluoride-induced, 1,4-elimination gave alkyl and aryl substituted buta-1,2,3-trienes **4** in good yields.

Butatrienes are an interesting class of compounds which have recently been shown to possess interesting non-linear optical¹ and amphoteric multistage redox properties.² They have also been used as intermediates for the preparation of biologically active enediynes³ and have potential as ferromagnetic materials and as intermediates for two-dimensional carbon networks such as radialenes.⁴ Although there are several synthetic methods for the preparation of buta-1,2,3-trienes,⁵ there are only a handful of procedures for the preparation of alkyl substituted buta-1,2,3-trienes.⁶ Most of the known butatrienes are aryl or *tert*-butyl substituted because of their greater stability towards oxygen and acids. In a preliminary communication,⁵ we disclosed a facile synthetic method for the preparation of 1-alkyl-4-aryl- and 1,1-dialkyl-4-arylbuta-1,2,3-trienes. In this report, we extend this methodology to include the synthesis of 1,4-dialkyl- and 1,1,4-trialkylbuta-1,2,3-trienes as well as the full details of their preparations.⁷

Results and Discussion

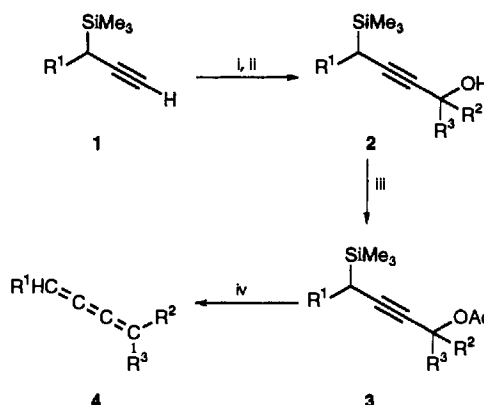
Synthesis.—Our methodology is based on the well documented⁸ synthesis of alkenes by 1,2-elimination reactions of β -acetoxy organosilanes (Scheme 1). We envisaged that by



Scheme 1 1,2- (top) and 1,4-eliminations (bottom)

insertion of an acetylenic functionality between the acetoxy and the trimethylsilyl groups, the analogous 1,4-elimination should become plausible with the formation of the highly reactive buta-1,2,3-triene. In fact, the base-catalysed elimination of 1-hydroxy-4-trimethylsilylbut-2-ynes to give buta-1,3-dienes and the reaction stereochemistry had previously been disclosed in the literature.⁹

3-Phenyl-3-trimethylsilylprop-1-yne **1a** (R = Ph) or 3-trimethylsilylhex-1-yne **1b** (R = Pr), readily available¹⁰ in 100 g quantities, can be converted into the corresponding lithium acetylides on treatment with butyllithium (1 equiv.) at 0 °C (Scheme 2). The resulting anion can be trapped with aldehydes or ketones to give a diastereoisomeric mixture of silyl propynylic alcohol **2** in good yields (Table 1). There is little 1,4-asymmetric induction for the addition of the acetylde anion to the carbonyl compounds. Typical diastereoisomeric ratios of the alcohols are between 1 : 1 and 2 : 1. The ratio is higher for



Scheme 2 Reagents: i, BuLi, THF or BuLi, CeCl₃, THF; ii, R²R³C=O; iii, DMAP, Ac₂O, NEt₃, ether; iv, TBAF, ether

Table 1 Yields of reactions i–iv (%)

Entry	R ¹	R ²	R ³	2	3	4
a	Ph	H	Ph	75	84	83
b	Ph	H	C ₆ H ₁₃	90*	91	70
c	Ph	H	Pr ⁱ	78*	78	89
d	Ph	H	Bu ^t	80	90	93
e	Ph	Me	Me	83*	79	71
f	Pr	H	Ph	72	74	89
g	Pr	H	C ₆ H ₁₃	84*	83	92
h	Pr	H	Bu ^t	89	78	91
i	Pr	Me	Me	90*	92	83

* Addition of CeCl₃.

sterically hindered aldehydes such as pivalaldehyde. For easily enolizable aldehydes such as heptanal (entries **b** and **g**), the yield of the prop-2-ynylic alcohol **2** from the reaction is poor. However, conversion of the organolithium into organocerium¹¹ by the addition of CeCl₃ results in a very clean transformation. The alcohol **2** is then converted into the corresponding acetate **3** (dimethylaminopyridine, triethylamine, acetic anhydride), subsequent treatment of which with tetrabutylammonium fluoride results in a facile 1,4-elimination to give the substituted butatriene **4**. Upon quenching with aqueous sodium carbonate, extractive work up with hexane (degassed) under nitrogen and then flash chromatography on Florisil, the butatriene **4** can be isolated as a mixture of (*E*)- and (*Z*)-isomers with >90% purity. On contact with alumina or silica gel, the butatriene polymerizes rapidly to form a solid precipitate.

Both the prop-2-ynylic alcohols **2** and the acetates **3** are pale yellow, light- and heat-sensitive oils. The stability of the buta-

1,2,3-trienes depends heavily on the nature of the substituent. Phenyl or *tert*-butyl substituted butatrienes are more stable and can be stored at $-30\text{ }^{\circ}\text{C}$ for days in hexane solutions. The alkyl analogues are less stable and tend to polymerize upon concentration from hexane solutions. For example, 4-methyl-1-phenylpenta-1,2,3-triene **4e** polymerizes at $25\text{ }^{\circ}\text{C}$ during ^{13}C NMR data acquisition. When subjected to mass spectrometric analysis, the butatrienes **4e** and **4i** produced many higher molecular weight peaks in addition to the parent ion signal, suggesting that the polymerization process may take place during sample injection.

These butatrienes **4** exhibit interesting spectroscopic properties. Thus, for 1,4-disubstituted butatrienes, the two protons (δ 6.22–6.5) couple to each other with a long-range coupling constant of $^5J_{\text{HH}}$ 7 Hz. There is little difference (<0.5 Hz) between the *cis*- and *trans*-coupling constants of the butatrienes and, therefore, it is difficult to assign the geometry of the triene system. The presence of the butatriene skeleton was also confirmed by the characteristic CH coupling constants ($^1J_{\text{CH}}$ 158–165 Hz) of the terminal olefinic carbons in their ^{13}C NMR spectra.

In summary, we have developed a facile method for the synthesis of both the alkyl- and aryl-substituted buta-1,2,3-trienes. Our method also allows us to prepare 1,4-unsymmetrically substituted butatrienes. The yields of the reactions are high and the butatrienes can be prepared in gram quantities.

Experimental

General.—IR spectra were recorded on a Nicolet (205) FT-IR spectrophotometer for samples as neat films on KBr disks and reported in wavenumbers (cm^{-1}). ^1H NMR spectra were recorded on a Bruker Cryospec WM 250 (250 MHz) spectrometer for samples in CDCl_3 solution with dichloromethane (δ 5.32) or residual CHCl_3 (δ 7.24) as internal standards. Coupling constants (J) are reported in Hz. ^{13}C NMR spectra were obtained for samples in CDCl_3 on a Bruker WM 250 spectrometer at 62.9 MHz. Mass spectra were obtained on a Finnegan MAT 95 instrument. Elemental analyses were carried out by Medac Ltd., Uxbridge, U.K. Deuteriated chloroform (CDCl_3) was freshly distilled over sodium hydrogen carbonate before use.

General Procedure for the Synthesis of Silyl Prop-2-ynylic Alcohols 2.—**Method A.** To a stirred solution of the acetylene **1**¹⁰ (6.4 mmol) in dry THF (20 cm^3) was added butyllithium (1.6 mol dm^{-3} in hexane; 4.0 cm^3 , 6.4 mmol) dropwise at $0\text{ }^{\circ}\text{C}$ under nitrogen. The resulting solution was stirred at $20\text{ }^{\circ}\text{C}$ for 30 min and then cooled to $-78\text{ }^{\circ}\text{C}$. A solution of the aldehyde or ketone (6.4 mmol) in dry THF (15 cm^3) was then added to the mixture which was then stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h and then gradually warmed up to $20\text{ }^{\circ}\text{C}$ over a period of 2 h. The reaction mixture was then poured into ice-water and the aqueous phase extracted with ethyl acetate (2 \times 50 cm^3). The combined organic solvents were dried (MgSO_4), filtered and evaporated under reduced pressure, and the residue purified by flash chromatography on silica gel with hexane-ethyl acetate (10:1) as eluent to give the silyl prop-2-ynylic alcohol **2** as an oil.

Method B. To a stirred solution of the acetylene **1**¹⁰ (6.4 mmol) in dry THF (20 cm^3) was added butyllithium (1.6 mol dm^{-3} in hexane; 4.0 cm^3 , 6.4 mmol) dropwise at $0\text{ }^{\circ}\text{C}$ under nitrogen. The resulting solution was stirred at $0\text{ }^{\circ}\text{C}$ for 30 min and then transferred *via* a syringe to a stirred suspension of anhydrous cerium(III) chloride (6.4 mmol) in dry THF (20 cm^3) at $-78\text{ }^{\circ}\text{C}$. This was kept for 30 min at $-78\text{ }^{\circ}\text{C}$, after which the aldehyde or ketone (6.4 mmol) in THF (10 cm^3) was added to it and the whole stirred at this temperature for 1 h; it was then

gradually warmed to $20\text{ }^{\circ}\text{C}$ over a period of 2 h. The mixture was worked up following the same procedure as that described in Method A.

The following silyl prop-2-ynylic alcohols were prepared.

1,4-Diphenyl-4-trimethylsilylbut-2-yn-1-ol **2a** (Method A, 75%): $\nu_{\text{max}}/\text{cm}^{-1}$ 3422 (OH); δ_{H} 0.09 + 0.10 (total 9 H, 2 s, SiMe_3), 2.36–2.40 (1 H, br s, OH), 3.28 (1 H, d, J 2.2, 4-H), 5.62 (1 H, br s, 1-H) and 7.19–7.70 (10 H, m, ArH); δ_{C} -3.2, 29.5, 65.0, 82.8, 87.5, 125.1, 126.5, 127.0, 128.0, 128.1, 128.4, 139.0 and 141.6 [Found (HRMS): 294.1428. Calc. for $\text{C}_{19}\text{H}_{22}\text{OSi}$: 294.1439].

1-Phenyl-1-trimethylsilyldec-2-yn-4-ol **2b** (Method B, 90%): $\nu_{\text{max}}/\text{cm}^{-1}$ 3416 (OH); δ_{H} 0.10 (9 H, s, SiMe_3), 0.94 (3 H, t, J 6.9, 10-H), 1.30–1.50 (6 H, m), 1.51–1.57 (2 H, m), 1.73–1.80 (2 H, m), 2.25–2.45 (1 H, br s, OH), 3.20 (1 H, d, J 2.0, 1-H), 4.47–4.53 (1 H, m, 4-H) and 7.14–7.34 (5 H, m, ArH); δ_{C} -3.3, 14.0, 22.5, 25.3, 28.9, 29.3, 31.8, 38.4, 63.0, 84.1, 85.2, 125.1, 126.9, 128.1 and 139.2 [Found (HRMS): 302.2058. Calc. for $\text{C}_{19}\text{H}_{30}\text{OSi}$: 302.2066].

2-Methyl-6-phenyl-6-trimethylsilylhex-4-yn-3-ol **2c** (Method B, 78%): $\nu_{\text{max}}/\text{cm}^{-1}$ 3416 (OH); δ_{H} 0.07 (9 H, s, SiMe_3), 1.02 (3 H, d, J 6.9, Me), 1.05 (3 H, d, J 6.9, Me), 1.63–1.77 (1 H, br s, OH), 1.85 (1 H, octet, J 6.9, 2-H), 3.19 (1 H, d, J 1.9, 6-H), 4.28–4.34 (1 H, m, 3-H) and 7.13–7.36 (5 H, m, ArH); δ_{C} -3.2, 17.5, 18.3, 29.5, 34.8, 68.4, 82.5, 86.2, 125.2, 127.0, 128.2 and 139.3 [Found (HRMS): 260.1593. Calc. for $\text{C}_{16}\text{H}_{24}\text{OSi}$: 260.1596].

2,2-Dimethyl-6-phenyl-6-trimethylsilylhex-4-yn-3-ol **2d** (Method A, 80%): $\nu_{\text{max}}/\text{cm}^{-1}$ 3466 (OH); δ_{H} 0.10 (9 H, s, SiMe_3), 1.07 (9 H, s, Bu^t), 2.55–2.70 (1 H, br s, OH), 3.21 (1 H, d, J 2, 6-H), 4.13 + 4.15 (total 1 H, 2 d, J 2, 3-H) and 7.10–7.33 (5 H, m, ArH); δ_{C} -3.2, 25.5, 29.5, 35.9, 71.8, 82.5, 86.0, 125.1, 127.0, 128.1 and 139.3 [Found (HRMS): 274.1746. Calc. for $\text{C}_{17}\text{H}_{26}\text{OSi}$: 274.1753].

2-Methyl-5-phenyl-5-trimethylsilylpent-3-yn-2-ol **2e** (Method B, 83%): $\nu_{\text{max}}/\text{cm}^{-1}$ 3395 (OH); δ_{H} 0.10 (9 H, s, SiMe_3), 1.62 (3 H, s, Me), 1.63 (3 H, s, Me), 3.18 (1 H, s, 5-H), 3.30–3.60 (1 H, br s, OH) and 7.12–7.37 (5 H, m, ArH); δ_{C} -3.3, 28.8, 31.8, 31.9, 65.6, 82.5, 88.0, 125.1, 126.9, 127.8 and 139.2 [Found (HRMS): 246.1438. Calc. for $\text{C}_{15}\text{H}_{22}\text{OSi}$: 246.1440].

1-Phenyl-4-trimethylsilylhept-2-yn-1-ol **2f** (Method A, 72%): $\nu_{\text{max}}/\text{cm}^{-1}$ 3437 (OH); δ_{H} 0.09 + 0.10 (total 9 H, 2 s, SiMe_3), 0.95 (3 H, t, J 6.8, 7-H), 1.36–1.50 (3 H, m), 1.53–1.70 (2 H, m), 2.37–2.47 (1 H, br s, OH), 5.47 (1 H, br s, 1-H) and 7.28–7.60 (5 H, m, ArH); δ_{C} -3.2, 13.7, 19.8, 22.8, 31.3, 65.0, 80.8, 89.8, 126.6, 127.9, 128.3 and 141.9 [Found (HRMS): 260.1602. Calc. for $\text{C}_{16}\text{H}_{24}\text{OSi}$: 260.1596].

4-Trimethylsilyltridec-5-yn-7-ol **2g** (Method B, 84%): $\nu_{\text{max}}/\text{cm}^{-1}$ 3460 (OH); δ_{H} 0.09 (9 H, s, SiMe_3), 0.80–0.97 (6 H, m, 1-H and 13-H), 1.22–1.71 (16 H, m) and 4.31–4.44 (1 H, m, 7-H); δ_{C} -3.2, 13.7, 14.0, 19.6, 22.5, 22.7, 25.2, 29.0, 31.3, 31.8, 38.6, 63.1, 82.0 and 87.5 [Found (HRMS): 268.2216. Calc. for $\text{C}_{16}\text{H}_{32}\text{OSi}$: 268.2222].

2,2-Dimethyl-6-trimethylsilylnon-4-yn-3-ol **2h** (Method A, 89%): $\nu_{\text{max}}/\text{cm}^{-1}$ 3459 (OH); δ_{H} 0.06 (9 H, s, SiMe_3), 0.88 (3 H, t, J 6.4, 9-H), 0.93 (9 H, s, Bu^t), 1.32–1.36 (3 H, m), 1.60–1.68 (2 H, m), 1.71–1.78 (1 H, br s, OH) and 3.99 (1 H, d, J 2.1, 3-H); δ_{C} -3.1, 13.7, 19.6, 22.8, 25.4, 31.5, 35.9, 71.9, 80.5 and 88.2 [Found (HRMS): 240.1905. Calc. for $\text{C}_{14}\text{H}_{28}\text{OSi}$: 240.1909].

2-Methyl-5-trimethylsilyloct-3-yn-2-ol **2i** (Method B, 90%): $\nu_{\text{max}}/\text{cm}^{-1}$ 3381 (OH); δ_{H} 0.04 (9 H, s, SiMe_3), 0.87 (3 H, t, J 6.9, 8-H), 1.29–1.36 (3 H, m), 1.46 (6 H, s, 2 \times Me), 1.56–1.62 (2 H, m) and 1.85–1.93 (1 H, br s, OH); δ_{C} -3.2, 13.7, 19.4, 22.7, 31.4, 32.0, 65.5, 84.6 and 85.9 [Found (HRMS): 240.1582. Calc. for $\text{C}_{14}\text{H}_{24}\text{OSi}$: 240.1596].

General Procedure for the Synthesis of Silyl Prop-2-ynylic Acetates 3.—A mixture of the prop-2-ynylic alcohol **2** (4.0 mmol), triethylamine (14.0 mmol), acetic anhydride (14.0

mmol) and dimethylaminopyridine (100 mg, 0.08 mmol) in dry ether (30 cm³) was stirred at 0 °C for 16 h and then poured into ice-water and extracted with diethyl ether (2 × 50 cm³). The organic extracts were washed with saturated brine, dried (MgSO₄), filtered and concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel with hexane-ethyl acetate (20:1) as eluent to give the acetate **3** as a pale yellow oil.

The following silyl prop-2-ynyl acetates were prepared.

1,4-Diphenyl-4-trimethylsilylbut-2-ynyl acetate **3a** (84%): $\nu_{\max}/\text{cm}^{-1}$ 1744 (C=O); δ_{H} 0.11 (9 H, s, SiMe₃), 2.16 (3 H, s, CH₃CO), 3.30 + 3.31 (total 1 H, 2 d, *J* 1.7, 4-H), 6.64 + 6.65 (total 1 H, 2 d, *J* 1.8, 1-H) and 7.20–7.70 (10 H, m, ArH); δ_{C} –3.4, 20.8, 29.3, 66.3, 79.5, 88.3, 125.1, 126.8, 127.5, 128.3, 128.5, 128.7, 137.7, 138.5 and 169.8 [Found (HRMS): 336.1546. Calc. for C₂₁H₂₄O₂Si: 336.1546].

1-Phenyl-1-trimethylsilyldec-2-yn-4-yl acetate **3b** (91%): $\nu_{\max}/\text{cm}^{-1}$ 1736 (C=O); δ_{H} 0.08 (9 H, s, SiMe₃), 0.92 (3 H, t, *J* 7, 10-H), 1.23–1.60 (8 H, m), 1.77–1.88 (2 H, m), 2.10 (3 H, s, CH₃CO), 3.18 + 3.19 (total 1 H, 2 d, *J* 2, 1-H), 5.45–5.53 (1 H, m, 4-H) and 7.09–7.33 (5 H, m, ArH); δ_{C} –3.3, 14.0, 21.0, 22.5, 25.1, 28.8, 29.4, 31.7, 35.3, 65.0, 80.8, 86.0, 125.1, 127.0, 128.1, 139.0 and 170.0 [Found (HRMS): 344.2166. Calc. for C₂₁H₃₂O₂Si: 344.2172].

2-Methyl-6-phenyl-6-trimethylsilylhex-4-yn-3-yl acetate **3c** (78%): $\nu_{\max}/\text{cm}^{-1}$ 1741 (C=O); δ_{H} 0.11 (9 H, s, SiMe₃), 1.09 (3 H, d, *J* 7, Me), 1.12 (3 H, d, *J* 7, Me), 2.03–2.23 (1 H, m, 2-H), 2.15 (3 H, s, CH₃CO), 3.24 (1 H, d, *J* 2, 6-H), 5.35–5.41 (1 H, m, 3-H) and 7.16–7.40 (5 H, m, ArH); δ_{C} –3.2, 17.7, 18.4, 21.0, 29.5, 32.6, 69.8, 79.0, 86.6, 125.1, 127.0, 128.2, 139.1 and 170.2 [Found (HRMS): 302.1688. Calc. for C₁₈H₂₆O₂Si: 302.1702].

2,2-Dimethyl-6-phenyl-6-trimethylsilylhex-4-yn-3-yl acetate **3d** (90%): $\nu_{\max}/\text{cm}^{-1}$ 1744 (C=O); δ_{H} 0.08 (9 H, s, SiMe₃), 1.08 (9 H, s, Bu'), 2.12 (3 H, s, CH₃CO), 3.21 (1 H, d, *J* 2, 6-H), 5.24 + 5.25 (total 1 H, 2 d, *J* 2, 3-H) and 7.12–7.35 (5 H, m, ArH); δ_{C} –3.2, 20.9, 25.7, 29.5, 35.2, 72.8, 79.3, 86.4, 125.1, 127.0, 128.1, 139.1 and 170.2 [Found (HRMS): 316.1850. Calc. for C₁₉H₂₈O₂Si: 316.1859].

2-Methyl-5-phenyl-5-trimethylsilylpent-3-yn-2-yl acetate **3e** (79%): $\nu_{\max}/\text{cm}^{-1}$ 1736 (C=O); δ_{H} 0.12 (9 H, s, SiMe₃), 1.72 (3 H, s, Me), 1.74 (3 H, s, Me), 2.11 (3 H, s, CH₃CO), 3.18 (1 H, s, 5-H) and 7.12–7.33 (5 H, m, ArH); δ_{C} –3.4, 21.9, 29.3, 29.4, 72.8, 84.5, 84.6, 125.0, 127.0, 128.4, 139.3 and 169.3 [Found (HRMS): 288.1540. Calc. for C₁₇H₂₄O₂Si: 288.1546].

1-Phenyl-4-trimethylsilylhept-2-ynyl acetate **3f** (74%): $\nu_{\max}/\text{cm}^{-1}$ 1743 (C=O); δ_{H} 0.14 + 0.15 (total 9 H, 2 s, SiMe₃), 0.98 (3 H, t, *J* 7.5, 7-H), 1.40–1.80 (5 H, m), 2.14 (3 H, s, CH₃CO), 6.56 (1 H, br s, 1-H) and 7.40–7.62 (5 H, m, ArH); δ_{C} –3.2, 13.7, 19.9, 21.0, 22.8, 31.2, 66.5, 77.2, 90.8, 127.6, 128.4, 128.5, 138.3 and 169.8 [Found (HRMS): 302.1704. Calc. for C₁₈H₂₆O₂Si: 302.1702].

4-Trimethylsilyltridec-5-yn-7-yl acetate **3g** (83%): $\nu_{\max}/\text{cm}^{-1}$ 1746 (C=O); δ_{H} 0.04 (9 H, s, SiMe₃), 0.80–0.90 (6 H, m, 1-H and 13-H), 1.20–1.45 (11 H, m), 1.54–1.74 (4 H, m), 2.06 (3 H, s, CH₃CO) and 5.28–5.37 (1 H, m, 7-H); δ_{C} –3.3, 13.7, 14.0, 19.6, 21.1, 22.5, 22.7, 25.1, 28.8, 31.2, 31.7, 35.3, 65.1, 78.3 + 78.4, 88.2 + 88.3 and 170.1 [Found (HRMS): 310.2333. Calc. for C₁₈H₃₄O₂Si: 310.2328].

2,2-Dimethyl-6-trimethylsilylnon-4-yn-3-yl acetate **3h** (78%): $\nu_{\max}/\text{cm}^{-1}$ 1744 (C=O); δ_{H} 0.03 (9 H, s, SiMe₃), 0.85 (3 H, t, *J* 7.2, 9-H), 0.96 (9 H, s, Bu'), 1.31–1.38 (3 H, m), 1.55–1.65 (2 H, m), 2.04 (3 H, s, CH₃CO) and 5.06 + 5.07 (total 1 H, 2 d, *J* 2.6, 3-H); δ_{C} –3.1, 13.7, 19.6, 20.9, 22.7, 25.7, 31.2, 35.1, 72.8, 76.9, 88.4 and 170.2 [Found (HRMS): 282.2020. Calc. for C₁₆H₃₀O₂Si: 282.2015].

2-Methyl-5-trimethylsilyloct-3-yn-2-yl acetate **3i** (92%): $\nu_{\max}/\text{cm}^{-1}$ 1747 (C=O); δ_{H} 0.03 (9 H, s, SiMe₃), 0.82 (3 H, t, *J* 6.7, 8-H), 1.25–1.35 (3 H, m), 1.50–1.65 (2 H, m), 1.55 (6 H, s,

2 × Me) and 1.95 (3 H, s, CH₃CO); δ_{C} –3.3, 13.7, 19.5, 22.0, 22.6, 29.5, 29.6, 31.2, 72.9, 82.1, 86.6 and 169.1 [Found (HRMS): 254.1709. Calc. for C₁₄H₂₆O₂Si: 254.1702].

General Procedure for the Synthesis of Buta-1,2,3-trienes 4.—Tetrabutylammonium fluoride (1.0 mol dm^{–3} in THF; 1.0 cm³, 1.0 mmol) was added dropwise to a stirred solution of the acetate **3** (1.0 mmol) in diethyl ether (20 cm³) under nitrogen at –10 °C. After 5 min, the reaction mixture was poured into saturated aqueous sodium carbonate and extracted with hexane (degassed; 2 × 50 cm³) under nitrogen. The combined extracts were washed with saturated aqueous sodium carbonate, dried (K₂CO₃), filtered and evaporated under reduced pressure to give a yellow oil. This oily residue was chromatographed on Florisil under nitrogen with hexane (degassed) as eluent to give the butatriene **4** as an oil. Unfortunately, owing to the instability of the butatrienes, we were unable to obtain satisfactory high resolution mass data or elemental analysis data of these compounds.

The following butatrienes were prepared.

1,4-Diphenylbuta-1,2,3-triene **4a** (83%): $\nu_{\max}/\text{cm}^{-1}$ 3022, 1945, 1672, 1494, 836, 784, 761 and 696; δ_{H} 6.53 + 6.61 [total 2 H, intensity 1:1, 2 s, 1-H and 4-H of (*E*)- and (*Z*)-isomers] and 7.24–7.60 (10 H, m, ArH); δ_{C} 109.6 (¹*J*_{CH} 164, 1-C and 4-C), 127.9, 128.0 + 128.1, 128.7 + 128.8, 137.0 + 137.2 and 155.7 + 155.8; *m/z* 204 (M⁺, 47%).

1-Phenyldeca-1,2,3-triene **4b** (70%): $\nu_{\max}/\text{cm}^{-1}$ 2956, 2928, 1947, 1680, 1448, 1314, 836, 788, 764 and 699; δ_{H} 0.85–1.00 (3 H, m), 1.20–1.73 (8 H, m), 2.28–2.41 (2 H, m), 5.73 + 5.79 [total 1 H, intensity 1:1, 2 q, *J* 7.4, 4-H of (*E*)- and (*Z*)-isomers], 6.36 + 6.37 [total 1 H, 2 dt, *J* 7.4 and 1.6, 1-H of (*E*)- and (*Z*)-isomers] and 7.18–7.44 (5 H, m, ArH); δ_{C} 14.0, 22.6, 28.8, 31.7, 33.0, 33.5, 106.6 + 106.7 (¹*J*_{CH} 163, 4-C), 111.7 (¹*J*_{CH} 158, 1-C), 127.4, 127.5, 128.6, 137.1, 158.8 and 159.8; *m/z* 212 (M⁺, 41%).

5-Methyl-1-phenylhexa-1,2,3-triene **4c** (89%): $\nu_{\max}/\text{cm}^{-1}$ 2962, 2929, 1920, 1647, 1450, 1314, 835, 751 and 699; δ_{H} 1.14 + 1.21 (total 6 H, intensity 1:1.2, 2 d, *J* 6.7, CMe₂), 2.50–2.72 (1 H, m, 5-H), 5.76 + 5.81 [total 1 H, 2 dd, *J* 7 and 6, 4-H of (*E*)- and (*Z*)-isomers], 6.37 + 6.39 [total 1 H, 2 dd, *J* 7 and 2, 1-H of (*E*)- and (*Z*)-isomers] and 7.16–7.49 (5 H, m, ArH); δ_{C} 22.0 + 22.9, 32.0 + 32.1, 106.6 + 106.7 (¹*J*_{CH} 164, 4-C), 118.5 (¹*J*_{CH} 164, 1-C), 127.4, 127.5, 128.6, 137.0 + 137.2, 157.3 and 160.8; *m/z* 170 (M⁺, 44%).

5,5-Dimethyl-1-phenylhexa-1,2,3-triene **4d** (93%): $\nu_{\max}/\text{cm}^{-1}$ 2968, 2909, 1940, 1679, 1478, 1366, 835, 788, 755 and 696; δ_{H} 1.19 + 1.25 (total 9 H, intensity 1:1.5, 2 s, Bu'), 5.75 + 5.83 [total 1 H, 2 d, *J* 7.7, 4-H of (*E*)- and (*Z*)-isomers], 6.39 + 6.43 [total 1 H, 2 d, *J* 7.7, 1-H of (*E*)- and (*Z*)-isomers] and 7.20–7.50 (5 H, m, ArH); δ_{C} 29.7 + 29.9, 35.5 + 35.7, 106.5 + 106.6 (¹*J*_{CH} 165, 4-C), 122.7 + 122.7 (¹*J*_{CH} 165, 1-C), 127.4, 128.6, 128.7, 137.0 + 137.3, 156.0 + 156.2 and 161.3; *m/z* 184 (M⁺, 52%).

4-Methyl-1-phenylpenta-1,2,3-triene **4e** (71%): δ_{H} 2.05 (3 H, s, Me), 2.12 (3 H, s, Me), 6.20 (1 H, s, 1-H) and 7.16–7.43 (5 H, m, ArH).

1-Phenylhepta-1,2,3-triene **4f** (89%): $\nu_{\max}/\text{cm}^{-1}$ 2990, 2920, 1956, 1423, 1357, 825, 795, 764 and 699; δ_{H} 1.11 + 1.16 (total 3 H, t, *J* 7.3, 7-H), 1.53–1.90 (2 H, m), 2.33–2.51 (2 H, m), 5.85 + 5.92 [total 1 H, intensity 1:1, 2 q, *J* 7.4, 4-H of (*E*)- and (*Z*)-isomers], 6.51 + 6.52 [total 1 H, 2 dt, *J* 7.5 and 1.5, 1-H of (*E*)- and (*Z*)-isomers] and 7.25–7.59 (5 H, m, ArH); δ_{C} 13.6, 22.0 + 22.1, 35.0 + 35.4, 106.6 + 106.7 (¹*J*_{CH} 162, 4-C), 111.3 (¹*J*_{CH} 161, 1-C), 127.3, 127.4, 128.5, 137.0, 158.9 and 159.7; *m/z* 170 (M⁺, 33%).

Trideca-4,5,6-triene **4g** (92%): $\nu_{\max}/\text{cm}^{-1}$ 2966, 2938, 2059, 1744, 1475, 1378 and 842; δ_{H} 0.84–0.98 (6 H, m), 1.22–1.38 (6 H, m), 1.42–1.60 (4 H, m), 2.12–2.25 (4 H, m) and 5.48 + 5.50 [total

2 H, intensity 1:1, 2 q, J 7.4, 4-H and 7-H of (*E*)- and (*Z*)-isomers]; δ_C 13.6, 14.0, 22.0, 22.2, 22.6, 28.7 + 28.8, 31.7, 32.8, 34.8 + 34.9, 107.3 + 107.4 (d, $^1J_{CH}$ 163), 107.6 + 107.8 (d, $^1J_{CH}$ 163), 161.0 and 161.2; m/z 178 (M^+ , 12%).

2,2-Dimethylnona-3,4,5-triene **4h** (91%): ν_{max}/cm^{-1} 2959, 2938, 2000, 1744, 1475, 1378 and 842; δ_H 0.93 + 0.94 (total 3 H, intensity 1:2, J 7.1, 9-H), 1.09 + 1.10 (total 9 H, 2 s, Bu^t), 1.45–1.62 (2 H, m), 2.11–2.23 (2 H, m) and 5.46–5.59 [2 H, m, 3-H and 6-H of (*E*)- and (*Z*)-isomers]; δ_C 13.8, 21.9, 22.2, 29.8, 34.8 + 34.9, 107.0 (d, $^1J_{CH}$ 165), 118.6 + 118.7 (d, $^1J_{CH}$ 168), 158.4 and 162.8; m/z 150 (M^+ , 6%).

2-Methylocta-2,3,4-triene **4i** (83%): ν_{max}/cm^{-1} 2961, 2924, 2062, 1644, 1464, 1375 and 857; δ_H 0.93 (3 H, t, J 7.3, 8-H), 1.50 (2 H, sextet, J 7.4, 7-H), 1.88 (3 H, s, Me), 1.90 (3 H, s, Me), 2.13 (2 H, q, J 7.4, 6-H) and 5.28 (1 H, t, sextet, J 7.2 and 1.3, 5-H); δ_C 13.6, 22.2, 23.9, 24.4, 34.6, 103.0 (d, $^1J_{CH}$ 159, 5-C), 112.2, 156.0 and 157.8.

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