

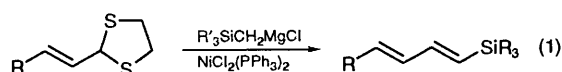
Synthesis of Functionalized 1-Silyl-substituted Dienes by Regioselective Cyclopropanation of 1-Silyl-substituted Butadienes with Dibromocarbene Followed by Ag^I-Promoted Ring-opening of the resulting Dibromocyclopropanes

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The reaction of 1-trimethylsilyl-substituted butadienes with dibromocarbene, generated from CHBr₂ and KOH under phase-transfer conditions gave, regioselectively, the corresponding cyclopropane adduct. The ring formation occurs at the double bond away from the silyl substituent. Ag^I-Promoted ring-opening of these cyclopropanes in the presence of different nucleophiles gave the corresponding functionalized butadienylsilanes.

Despite the extensive and fascinating applications of organo-silicon compounds in organic synthesis, the use of silyl-substituted dienes has been less well explored.¹ Although these dienes can be synthesized by a number of procedures, there seems to be lack of a general method to prepare functionalized silyl-substituted dienes. Our recent discovery of a facile procedure for the preparation of various silyl-substituted dienes [eqn. (1)]² prompted us to investigate the modification of these



compounds to introduce different functionalities. Since it is well documented that bromocyclopropanes undergo ring-opening upon treatment with Ag^I to give allylic products,³ we envisaged that this process might represent a useful approach for the synthesis of functionalized dienes having a silyl substituent. Although cyclopropanation of alkenes with dihalogenocarbenes has been widely used in synthesis and the corresponding cycloadditions with conjugated dienes have been investigated,^{4,5} the silyl substituent on the diene moiety may exert a stereoelectronic effect such that the addition of the dihalogenocarbene group is regioselective. We now report a full account on the cyclopropanation of silyl-substituted dienes and its application to the synthesis of functionalized dienes having a silyl substituent.

Results and Discussion

Addition of CBr₂ to Silyl-substituted Dienes 1.—Under phase-transfer conditions using hexadecyl(trimethyl)ammonium bromide (HTMAB) as the catalyst, a mixture of bromoform and the 1-silyl-substituted butadiene **1** in 33% aqueous KOH/CH₂Cl₂ was stirred at room temperature for 16 h to give, after work-up, the corresponding dibromocyclopropane **2** in satisfactory yield. The results are summarized in Table 1.

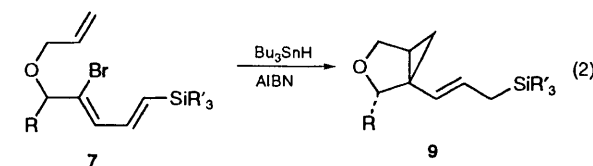
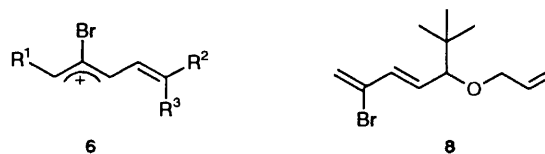
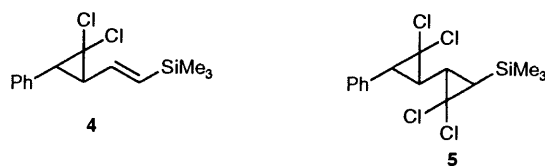
The silyl-substituted dienes **1a–f** gave single regioisomers of the cyclopropanes **2a–f** in satisfactory yields (entries 1–6) a reaction which upon extension to a triene system also gave, regioselectively, one isomer in moderate yield (entry 7).

The reaction became less selective when the silyl-substituted diene **1** had a bulky 4-alkyl group (entries 8 and 9). It is noteworthy that the diene **1i** gave **3i** as the major product which indicated that steric effects play an important role in this cycloaddition, the trimethylsilyl group being less sterically hindered than the *tert*-butyl group. The reactions with dienes without silyl substituents have also been investigated for

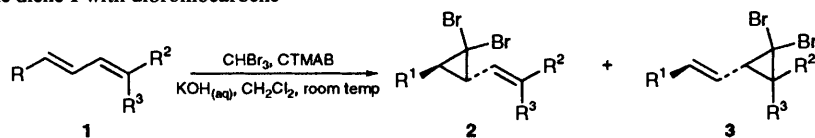
comparison. Treatment of 1-phenylbutadiene **1k** with dibromocarbene under the same conditions gave an 11:1 mixture of the cyclopropanes **2k** and **3k** in 71% yield (entry 11).⁶ It is noted that, when the diene **1l** was allowed to react under similar conditions, a mixture of **2l** and **3l** was obtained (entry 12). This observation and the result from entry 2 indicated that the silyl substituent may exert a mainly steric effect leading to the regioselective cyclopropanation of **1**.

Dichlorocarbene, on the other hand, was too reactive and, therefore, less selective under these conditions. Thus, treatment of **1b** with CHCl₃ under similar conditions afforded a mixture of the mono- and bis-cyclopropane adducts **4** (65%) and **5** (13%), respectively.

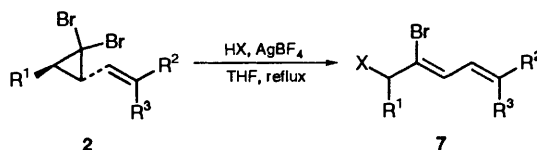
AgBF₄-Promoted Rearrangement of (Vinyl)dibromocyclopropanes 2.—Although the Ag^I-promoted ring-opening of bromocyclopropanes is well-documented,³ the corresponding reactions with vinyl-substituted derivatives have been little explored.^{3d,e} The ring-opening of **2** would generate a penta-dienyl cation **6** which would have different sites for the



nucleophilic attack. The selectivity of the nucleophilic attack on **6** would depend on the nature of the substituent in **6**. Treatment of the silyl-substituted vinylcyclopropanes **2** with AgBF₄ (1.2 equiv.) in the presence of different nucleophiles in refluxing THF gave the corresponding bromo-substituted dienes **7** as the sole

Table 1 The reactions of the diene **1** with dibromocarbene

Entry	Substrate	R ¹	R ²	R ³	Product (% yield)
1	1a	H	SiMe ₃	H	2a (63)
2	1b	Ph	SiMe ₃	H	2b (42)
3	1c	Me	SiMe ₃	H	2c (72)
4	1d	C ₆ H ₁₃	SiMe ₃	H	2d (63)
5	1e	Me	SiMe ₂ Ph	H	2e (68)
6	1f	H	SiMe ₂ Ph	Me	2f (72)
7	1g	Me	CH=CHSiMe ₂ Ph	H	2g (51)
8	1h	Pr ⁱ	SiMe ₃	H	2h (38)
					3h (38)
9	1i	Bu ^t	SiMe ₃	H	2i (11)
					3i (58)
10	1j	H	Bu ^t	H	2j (51)
11	1k	H	Ph	H	2k (65)
					3k (6)
12	1l	Ph	Bu ^t	H	2l (25)
					3l (8)

Table 2 The reactions of **2** with AgBF₄ in the presence of nucleophiles HX

Entry	Substrate	HX	R ¹	R ²	R ³	Product (% yield)
13	2e	HOAc	Me	SiMe ₂ Ph	H	7a (64)
14	2e	H ₂ O	Me	SiMe ₂ Ph	H	7b (78)
15	2e	MeOH	Me	SiMe ₂ Ph	H	7c (51) ^a
16	2e	H ₂ C=CHCH ₂ OH	Me	SiMe ₂ Ph	H	7d (83)
17	2b	H ₂ C=CHCH ₂ OH	Ph	SiMe ₃	H	7e (60)
18	2d	H ₂ C=CHCH ₂ OH	C ₆ H ₁₃	SiMe ₃	H	7f (42)
19	2f	H ₂ C=CHCH ₂ OH	H	SiMe ₂ Ph	Me	7g (52)
20	2e	H ₂ C=CHCH ₂ CH ₂ OH	Me	SiMe ₂ Ph	H	7h (68)
21	2e	H ₂ C=CMeCH ₂ OH	Me	SiMe ₂ Ph	H	7i (53)
22	2e	(E)-MeHC=CHCH ₂ OH	Me	SiMe ₂ Ph	H	7j (58)
23	2e	PhCH ₂ OH	Me	SiMe ₂ Ph	H	7k (70)
24	2e	HC=CCH ₂ OH	Me	SiMe ₂ Ph	H	7l (83)
25	2f	H ₂ C=CHCHMeOH	H	SiMe ₂ Ph	Me	7m (45)
26	2k	H ₂ C=CHCH ₂ OH	H	Ph	H	7n (85)
27	2l	H ₂ C=CHCH ₂ OH	H	Ac	H	7o (54)
28	2j	H ₂ C=CHCH ₂ OH	H	Bu ^t	H	7p (36) ^b

^a The reaction was carried out in MeOH. ^b Isomer **8** was also isolated in 33% yield.

products in moderate to good yields. Representative examples are shown in Table 2. Nucleophiles can be alcohols, water, or even carboxylic acids. The stereochemistry of **7** was determined by NOE experiments. The silyl substituent seemed to play an important role in directing the regioselective nucleophilic attack at C-5 and a phenyl group (entry 26) or electron-withdrawing group (entry 27) behaved similarly. However, an alkyl substituent such as the *tert*-butyl analogue gave a mixture of isomeric products **7p** and **8** (entry 28).

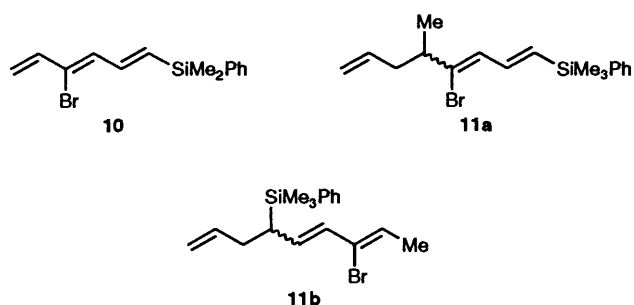
These results demonstrated a useful procedure for the preparation of polyfunctionalized silyl-substituted dienes **7** which are potentially useful in synthesis. The vinyl bromide group will be vulnerable to the radical reactions and the alkene moiety in **7d-p** could serve as an acceptor for radicals and for organo-

metallic intermediates. For example, tandem [2 + 1] radical cyclization of certain compounds **7** afforded the corresponding bicyclo[3.1.0]-skeleton **9** exclusively [eqn. (2)].⁷

In the absence of an appropriate nucleophile, elimination to give a triene occurred. Thus, treatment of **2e** with AgBF₄ in the presence of maleic anhydride gave **10** (41%).

The reactions with carbon nucleophiles yielded a mixture of regioisomers: thus, treatment of **2c** with allylsilane under similar conditions afforded a 2:1 mixture of **11a** (*E:Z* = 1:4) and **11b** (51%).⁸

In summary, we have described the selective cyclopropanation of silyl-substituted dienes, the products from which can undergo regioselective ring-opening to give functionalized silyl-substituted dienes or trienes.



Experimental

General Procedure for the Addition of Dibromocarbene to 1.—A 25-cm³, two-necked flask equipped with a stirrer, a nitrogen inlet, and a serum cap, was charged with bromoform (2.0 mmol), **1** (1.0 mmol), HTMAB (0.08 g, 0.2 mmol) and CH₂Cl₂ (5 cm³). The solution was stirred and aqueous KOH (33%; 4.5 cm³, 40 mmol) was slowly added to it over 1 h from a syringe pump. The reaction mixture was stirred at room temperature for an additional 16 h and then poured into water (20 cm³). The organic layer was separated and the aqueous phase was extracted with CH₂Cl₂ (2 × 20 cm³). The combined extracts were washed with water (2 × 20 cm³), dried (MgSO₄), and concentrated under reduced pressure to give a dark brown oil which was chromatographed on silica gel using hexane as eluent.

(E)-1,1-Dibromo-2-(2-trimethylsilylvinyl)cyclopropane **2a**. To a mixture of **1a** (1.26 g, 10.0 mmol), CHBr₃ (3.95 g, 15.0 mmol) and HTMAB (0.80 g, 2.0 mmol) in CH₂Cl₂ (45 cm³) was slowly added aqueous KOH (33%; 4.5 cm³) to give **2a** (1.88 g, 63%): $\nu_{\max}/\text{cm}^{-1}$ 2956, 1749, 1612, 1412, 1250, 861 and 842; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.07 (s, 9 H), 1.59 (t, *J* 7.6, 1 H), 1.94 (dd, *J* 7.6, 10.4, 1 H), 2.29 (td, *J* 7.6, 10.4, 1 H), 5.66 (dd, *J* 7.6, 18.3, 1 H) and 5.99 (d, *J* 18.3, 1 H); $\delta_{\text{C}}(\text{CDCl}_3, 50 \text{ MHz})$ -1.3, 28.0, 29.7, 36.1, 135.7 and 143.0; *m/z* (rel. intensity) 300 (1), 298 (2), 296 (1), 285 (5), 283 (9), 281 (4), 205 (3), 203 (7), 201 (3), 139 (72), 73 (100) and 65 (51).

(E)-1,1-Dibromo-2-phenyl-3-(2-trimethylsilylvinyl)cyclopropane **2b**. To a mixture of **1b** (202 mg, 1.0 mmol), CHBr₃ (506 mg, 2.0 mmol) and HTMAB (0.20 mmol) in CH₂Cl₂ (5 cm³) was slowly added aqueous KOH (33%; 4.5 cm³) to give **2b** (157 mg, 42%): $\nu_{\max}/\text{cm}^{-1}$ 2955, 2897, 1608, 1496, 1450, 1249, 982, 859, 839, 755, 720 and 695; $\delta_{\text{H}}(\text{CDCl}_3, 200 \text{ MHz})$ 0.09 (s, 9 H), 2.60 (t, *J* 7.6, 1 H), 2.85 (d, *J* 8.2, 1 H), 5.85 (dd, *J* 7.6, 18.3, 1 H), 6.10 (d, *J* 18.3, 1 H) and 7.24–7.35 (m, 5 H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ -1.4, 36.3, 40.6, 42.4, 127.7, 128.3, 128.8, 135.7, 136.3 and 142.5; *m/z* (rel. intensity) 376 (0.1), 374 (0.2), 372 (0.1), 295 (13), 293 (13), 232 (12), 230 (12), 141 (76) and 73 (100) (Found: M, 373.9504. Calc. for C₁₄H₁₈⁷⁹Br⁸¹BrSi: 373.9524).

(E)-1,1-Dibromo-3-methyl-2-(2-trimethylsilylvinyl)cyclopropane **2c**. To a mixture of **1c** (140 mg, 1.0 mmol), CHBr₃ (506 mg, 2 mmol) and HTMAB (80 mg, 0.20 mmol) in CH₂Cl₂ (5 cm³) was slowly added aqueous KOH (33%; 4.5 cm³) to give **2c** (225 mg, 72%): $\nu_{\max}/\text{cm}^{-1}$ 2950, 1713, 1609, 1449, 1249, 982, 840, 754 and 720; $\delta_{\text{H}}(\text{CDCl}_3, 200 \text{ MHz})$ 0.06 (s, 9 H), 1.16 (d, *J* 6.6, 3 H), 1.54 (dq, *J* 6.6, 7.7, 1 H), 1.79 (t, *J* 7.7, 1 H), 5.66 (dd, *J* 7.7, 18.6, 1 H) and 5.95 (d, *J* 18.6, 1 H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ -1.4, 16.9, 33.1, 38.5, 42.7, 135.2 and 143.6; *m/z* (rel. intensity) 241 (2), 239 (M⁺ - SiMe₃, 4), 237 (2), 172 (26), 170 (26), 139 (12), 137 (12) and 73 (100) [Found: M, 238.8911. Calc. for C₆H₇⁷⁹Br⁸¹Br (M - Me₃Si): 238.8914].

(E)-1,1-Dibromo-3-hexyl-2-(2-trimethylsilylvinyl)cyclopropane **2d**. To a mixture of **1d** (4.20 g, 20.0 mmol), CHBr₃ (10.52 g, 40 mmol) and HTMAB (1.60 g, 4.0 mmol) in CH₂Cl₂ (90 cm³) was slowly added aqueous KOH (33%; 44.8 cm³) to give **2d** (4.81 g, 63%): $\nu_{\max}/\text{cm}^{-1}$ 2956, 2928, 2857, 1609, 1462, 1249, 981, 861, 838 and 720; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.06 (s, 9 H), 0.75–0.90 (m, 3 H),

1.15–1.70 (m, 11 H), 1.82 (t, *J* 7.6, 1 H), 5.67 (dd, *J* 7.6, 18.2, 1 H) and 5.92 (d, *J* 18.2, 1 H); $\delta_{\text{C}}(\text{CDCl}_3, 50 \text{ MHz})$ -1.3, 14.1, 22.6, 28.1, 28.8, 31.6, 31.7, 32.4, 32.6, 42.0, 134.9 and 143.6; *m/z* (rel. intensity) 384 (0.1), 382 (0.2), 380 (0.1), 369 (0.5), 367 (1), 365 (0.5), 302 (16), 300 (12), 159 (23), 157 (24) and 73 (100) (Found: M, 379.9966. Calc. for C₁₄H₂₆⁷⁹Br₂Si: 380.0171).

(E)-1,1-Dibromo-2-(2-dimethylphenylsilylvinyl)-3-methylcyclopropane **2e**. To a mixture of **1e** (202 mg, 1.0 mmol), CHBr₃ (506 mg, 2 mmol) and HTMAB (80 mg, 0.20 mmol) in CH₂Cl₂ (5 cm³) was slowly added aqueous KOH (33%; 4.5 cm³) to give **2e** (254 mg, 68%): $\nu_{\max}/\text{cm}^{-1}$ 2958, 1609, 1250, 1114, 1041, 983, 835, 819, 783, 730 and 699; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.35 (s, 6 H), 1.30 (d, *J* 6.2, 3 H), 1.56 (qd, *J* 6.2, 7.7, 1 H), 1.84 (t, *J* 7.7, 1 H), 5.76 (dd, *J* 7.7, 18.6, 1 H), 6.05 (d, *J* 18.6, 1 H), 7.30–7.40 (m, 3 H), 7.45–7.55 (m, 2 H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ -2.6, 16.9, 33.1, 38.3, 42.7, 127.8, 129.0, 132.8, 133.8, 138.2 and 145.4; *m/z* (rel. intensity) 376 (0.1), 374 (0.2), 372 (0.1), 361 (0.4), 359 (0.8), 357 (0.4), 295 (24), 293 (24), 201 (45), 199 (45), 155 (81), 140 (100) and 135 (93); (Found: M, 373.9525. Calc. for C₁₄H₁₈⁷⁹Br⁸¹BrSi: 373.9524).

(E)-1,1-Dibromo-2-(2-dimethylphenylsilyl-2-methylvinyl)cyclopropane **2f**. To a mixture of **1f** (202 mg, 1.0 mmol), CHBr₃ (506 mg, 2 mmol) and HTMAB (80 mg, 0.20 mmol) in CH₂Cl₂ (5 cm³) was slowly added aqueous KOH (33%; 4.5 cm³) to give **2f** (269 mg, 72%): $\nu_{\max}/\text{cm}^{-1}$ 3068, 2958, 1615, 1428, 1250, 1110, 833, 815, 774, 732, 700 and 682; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.34 (s, 6 H), 1.52 (t, *J* 7.5, 1 H), 1.82 (s, 3 H), 2.00 (dd, *J* 7.5, 10.4, 1 H), 2.48 (ddd, *J* 7.5, 9.4, 10.4, 1 H), 5.40 (d, *J* 9.4, 1 H), 7.30–7.36 (m, 3 H) and 7.45–7.55 (m, 2 H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ -3.6, 16.1, 29.2, 29.8, 30.6, 127.8, 129.1, 134.0, 137.7, 138.0 and 140.7; *m/z* (rel. intensity) 376 (0.3), 374 (0.6), 372 (0.3), 361 (3), 359 (6), 357 (3), 295 (11), 293 (11), 213 (92) and 139 (100) (Found: M, 373.9526. Calc. for C₁₄H₁₈⁷⁹Br⁸¹BrSi: 373.9524).

(E,E)-1,1-Dibromo-2-(4-dimethylphenylsilylbuta-1,3-dienyl)-3-methylcyclopropane **2g**. To a mixture of **1g** (222 mg, 1.0 mmol), CHBr₃ (253 mg, 1 mmol) and HTMAB (80 mg, 0.20 mmol) in CH₂Cl₂ (5 cm³) was slowly added aqueous KOH (33%; 4.5 cm³) to give, in addition to recovered **1g** (48 mg, 22%), **2g** (157 mg, 51% based on the unrecovered **1g**): $\nu_{\max}/\text{cm}^{-1}$ 2956, 2920, 1577, 1426, 1248, 1113, 998, 838, 825, 730, 698 and 668; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.32 (s, 6 H), 1.31 (d, *J* 6.1, 3 H), 1.51 (qd, *J* 6.1, 7.8, 1 H), 1.78 (dd, *J* 7.8, 8.7, 1 H), 5.44 (dd, *J* 8.7, 14.9, 1 H), 5.95 (d, *J* 18.1, 1 H), 6.31 (dd, *J* 10.1, 14.9, 1 H), 6.56 (dd, *J* 10.1, 18.1, 1 H), 7.30–7.36 (m, 3 H) and 7.45–7.55 (m, 2 H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ -2.6, 17.0, 33.8, 39.0, 40.2, 127.8, 129.0, 131.5, 132.9, 133.8, 136.3, 138.5 and 144.6; *m/z* (rel. intensity) 400 (0.1), 321 (6), 319 (6), 239 (12), 199 (20), 135 (100) and 105 (27) (Found: M, 399.9678. Calc. for C₁₆H₂₀⁷⁹Br⁸¹BrSi: 399.9681).

(E)-1,1-Dibromo-3-isopropyl-2-(2-trimethylsilylvinyl)cyclopropane **2h** and (E)-1,1-dibromo-3-(2-isopropylvinyl)-2-(trimethylsilyl)cyclopropane **3h**. To a mixture of **1h** (168 mg, 1.0 mmol), CHBr₃ (506 mg, 2 mmol) and HTMAB (80 mg, 0.20 mmol) in CH₂Cl₂ (5 cm³) was slowly added aqueous KOH (33%; 4.5 cm³) to give a mixture of **2h** and **3h** (258 mg, 76%; **2h**:**3h** = 1:1). The isomers were separated by preparative HPLC: **2h**: $\nu_{\max}/\text{cm}^{-1}$ 2959, 2869, 1485, 1250, 1012, 963, 942, 860, 842 and 721; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.05 (s, 9 H), 1.00 (d, *J* 6.7, 3 H), 1.13 (d, *J* 6.5, 3 H), 1.20 (dd, *J* 7.7, 10.0, 1 H), 1.30–1.50 (m, 1 H), 1.84 (t, *J* 7.7, 1 H), 5.68 (dd, *J* 7.7, 18.3, 1 H) and 5.91 (d, *J* 18.3, 1 H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ -1.3, 20.8, 21.2, 33.2, 41.5, 45.3, 134.7 and 143.6; *m/z* (rel. intensity) 342 (0.1), 340 (0.2), 338 (0.1), 281 (6), 279 (12), 277 (6), 267 (4), 265 (8), 263 (4), 200 (24), 198 (24) and 73 (100) (Found: M, 339.9647. Calc. for C₁₁H₂₀⁷⁹Br⁸¹BrSi: 339.9681). **3h**: $\nu_{\max}/\text{cm}^{-1}$ 2958, 1610, 1459, 1249, 1029, 980, 860, 838, 751 and 720; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.16 (s, 9 H), 0.88 (d, *J* 9.9, 1 H), 1.00 (d, *J* 6.8, 6 H), 2.05 (dd, *J* 7.7, 9.9, 1 H), 2.30 (d of heptet, *J* 6.5, 6.8, 1 H), 5.16 (dd, *J* 7.7, 15.4, 1 H) and 5.67 (dd, *J* 6.5, 15.4, 1 H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ -1.3, 22.3, 30.2,

31.2, 35.7, 36.7, 126.3 and 141.7; m/z (rel. intensity) 342 (0.4), 340 (0.8), 338 (0.4), 269 (12), 267 (24), 265 (12), 200 (10), 198 (10), 187 (12), 139 (26), 137 (28), 125 (18), 107 (24) and 73 (100) (Found: M, 339.9668. Calc. for $C_{11}H_{20}^{79}Br^{81}BrSi$: 339.9681).

(E)-1,1-Dibromo-2-tert-butyl-3-(2-trimethylsilylvinyl)cyclopropane **2i** and (E)-1,1-dibromo-2-trimethylsilyl-3-(2-tert-butylvinyl)cyclopropane **3i**. To a mixture of **1i** (182 mg, 1.0 mmol), $CHBr_3$ (506 mg, 2.0 mmol) and HTMAB (80 mg, 0.20 mmol) in CH_2Cl_2 (5 cm^3) was slowly added aqueous KOH (33%; 4.5 cm^3) to give a mixture of **2i** and **3i** (244 mg, 69%; **2i**:**3i** = 16:84); **3i** was purified by preparative HPLC. **2i**: δ_H ($CDCl_3$, 300 MHz) 0.05 (s, 9 H), 1.07 (s, 9 H), 1.52 (d, J 9.4, 1 H), 2.13 (dd, J 7.1, 9.4, 1 H), 5.75 (dd, J 7.1, 18.5, 1 H) and 5.94 (d, J 18.5, 1 H); δ_C ($CDCl_3$, 75 MHz) -1.3, 28.6, 32.3, 34.2, 38.3, 48.6, 134.8 and 144.1. **3i**: ν_{max}/cm^{-1} 2958, 2902, 2867, 1476, 1364, 1251, 1178, 1013, 862, 843 and 775; δ_H ($CDCl_3$, 300 MHz) 0.06 (s, 9 H), 0.71 (d, J 10.1, 1 H), 1.46 (s, 9 H), 1.97 (dd, J 7.6, 10.1, 1 H), 5.04 (dd, J 7.6, 15.5, 1 H), 5.63 (d, J 15.5, 1 H); δ_C ($CDCl_3$, 75 MHz) -1.3, 29.5, 30.1, 33.4, 35.8, 36.8, 124.2 and 145.4; m/z (rel. intensity) 356 (0.1), 354 (0.2), 352 (0.1), 296 (3), 294 (6), 292 (3), 274 (8), 272 (8), 201 (16), 199 (16) and 120 (100) (Found: M, 353.9825. Calc. for $C_{12}H_{22}^{79}Br^{81}BrSi$: 353.9837).

(E)-1,1-Dibromo-2-(2-tert-butylvinyl)cyclopropane **2j**. To a mixture of **1j** (220 mg, 2.0 mmol), $CHBr_3$ (789 mg, 3.0 mmol) and HTMAB (160 mg, 0.40 mmol) in CH_2Cl_2 (9 cm^3) was slowly added aqueous KOH (33%; 9.0 cm^3) to give **2j** (288 mg, 51%); δ_H ($CDCl_3$, 300 MHz) 1.01 (s, 9 H), 1.49 (t, J 7.6, 1 H), 1.90 (dd, J 7.6, 10.4, 1 H), 2.21 (td, J 7.6, 10.4, 1 H), 5.07 (dd, J 7.6, 15.5, 1 H) and 5.71 (d, J 15.5, 1 H); δ_C ($CDCl_3$, 50 MHz) 29.3, 29.4, 31.0, 33.4, 33.5, 122.6 and 146.4; m/z (rel. intensity) 284 (1), 282 (2), 280 (1), 203 (13), 201 (13), 121 (82), 107 (39) and 57 (100) [Found: (M + 1), 282.9521. Calc. for $C_9H_{15}^{79}Br^{81}Br$: (M + 1) 282.9520].

(E)-1,1-Dibromo-2-(2-phenylvinyl)cyclopropane **2k**. To a mixture of **1k** (3.90 g, 30.0 mmol), $CHBr_3$ (11.84 g, 45.0 mmol) and HTMAB (2.40 g, 0.60 mmol) in CH_2Cl_2 (135 cm^3) was slowly added aqueous KOH (33%; 135.0 cm^3) to give **2k** (5.85 g, 65%) and **3k** (0.58 g, 6%). **2k**: ν_{max}/cm^{-1} 3027, 1596, 1493, 1449, 1426, 1100, 1007, 960, 749 and 684; δ_H ($CDCl_3$, 300 MHz) 1.68 (t, J 7.6, 1 H), 2.05 (dd, J 7.6, 10.2, 1 H), 2.44 (td, J 7.6, 7.6, 10.2, 1 H), 5.93 (dd, J 7.6, 15.7, 1 H), 6.67 (d, J 15.7, 1 H) and 7.20–7.50 (m, 5 H); δ_C ($CDCl_3$, 50 MHz) 28.7, 30.1, 34.0, 126.2, 127.7, 128.3, 128.6, 133.8 and 136.6.

(E)-1,1-Dibromo-3-(2-tert-butylvinyl)-2-phenylcyclopropane **2l** and (E)-1,1-dibromo-3-tert-butyl-2-(2-phenylvinyl)cyclopropane **3l**. To a mixture of **1l** (186 mg, 1.0 mmol), $CHBr_3$ (506 mg, 2 mmol) and HTMAB (80 mg, 0.20 mmol) in CH_2Cl_2 (5 cm^3) was slowly added aqueous KOH (33%; 4.5 cm^3) to give a mixture of **2l** and **3l** (119 mg, 33%; **2l**:**3l** = 76:24). The two isomers were separated by preparative HPLC. **2l**: ν_{max}/cm^{-1} 3085, 2960, 2867, 1496, 1448, 1364, 1262, 1081, 1029, 964, 860, 737 and 694; δ_H ($CDCl_3$, 300 MHz) 0.04 (s, 9 H), 2.51 (dd, J 8.0, 8.3, 1 H), 2.75 (d, J 8.3, 1 H), 5.26 (dd, J 8.0, 15.5, 1 H), 5.85 (d, J 15.5, 1 H) and 7.23–7.40 (m, 5 H); δ_C ($CDCl_3$, 50 MHz) 29.4, 33.5, 37.6, 37.9, 42.0, 122.2, 127.6, 128.2, 128.8, 135.9 and 146.7; m/z (rel. intensity) 360 (3), 358 (6), 356 (3), 303 (1), 301 (2), 299 (1), 279 (64), 277 (62), 237 (8), 235 (8), 197 (100), 183 (22) and 91 (36) (Found: M, 357.9757. Calc. for $C_{15}H_{18}^{79}Br^{81}Br$: 357.9756). **3l**: ν_{max}/cm^{-1} 3081, 2960, 2669, 1598, 1494, 1449, 1365, 1262, 1197, 1061, 1018, 958, 778, 741, 713 and 691; δ_H ($CDCl_3$, 300 MHz) 1.11 (s, 9 H), 1.60 (d, J 8.6, 1 H), 2.26 (t, J 8.6, 1 H), 6.00 (dd, J 8.6, 15.8, 1 H), 6.62 (d, J 15.8, 1 H) and 7.23–7.40 (m, 5 H); δ_C ($CDCl_3$, 75 MHz) 28.6, 32.4, 34.8, 36.2, 49.2, 126.2, 127.6, 128.7, 129.0, 133.2 and 136.8; m/z (rel. intensity) 360 (2), 358 (5), 356 (2), 279 (100), 277 (90), 237 (20), 235 (15), 197 (46) and 57 (56) (Found: M, 355.9746. Calc. for $C_{15}H_{18}^{79}Br_2$: 355.9756).

(E)-2-(Acetylvinyl)-1,1-dibromo-3-methylcyclopropane **2m**.—To a solution of **2e** (3.74 g, 10.0 mmol) in CH_2Cl_2 (80 cm^3) under N_2 at 0 °C was added dropwise a slurry of acetyl chloride (0.94 g, 12.0 mmol) and $AlCl_3$ (1.60 g, 12.0 mmol) in CH_2Cl_2 (20 cm^3), and the solution was stirred at 0 °C for 20 min. It was then quenched with ice-water (100 cm^3) and extracted with CH_2Cl_2 (50 $cm^3 \times 2$). The combined extracts were dried ($MgSO_4$) and evaporated and the residue was chromatographed on silica gel to give **2m** (1.52 g, 54%); δ_H ($CDCl_3$, 200 MHz) 1.35 (d, J 6.1, 3 H), 1.72 (qd, J 6.1, 7.4, 1 H), 1.88 (dd, J 7.4, 8.6, 1 H), 6.26 (d, J 15.8, 1 H) and 6.44 (dd, J 8.6, 15.8, 1 H); δ_C ($CDCl_3$, 50 MHz) 16.8, 27.2, 34.9, 36.6, 39.6, 133.1, 145.3 and 197.1; m/z (rel. intensity) 284 (1), 282 (2), 280 (1), 203 (12), 201 (12), 121 (80) and 43 (100) (Found: M, 281.9085. Calc. for $C_8H_{10}^{79}Br^{81}BrO$: M, 281.9078).

AgBF₄-Catalysed Rearrangement of 1,1-Dibromo(vinyl)cyclopropane.—To a mixture of alcohol or acid (2 equiv.) and AgBF₄ (1.2–1.5 equiv.) in THF was added **2** (1.0 equiv.). The mixture was stirred at room temperature or refluxed for 5–16 h. After being cooled, the mixture was diluted with ether added and the slurry was filtered through Florisil. The filtrate was dried ($MgSO_4$) and evaporated under reduced pressure to give a yellow residue which was chromatographed on silica gel to give the product.

(3Z,5E)-2-Acetoxy-3-bromo-6-(dimethylphenylsilyl)hexa-3,5-diene **7a**.—A solution of **2a** (374 mg, 1.0 mmol), acetic acid (120 mg, 2.0 mmol) and AgBF₄ (233 mg, 1.2 mmol) in THF (10 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2% EtOAc–hexane) to afford **7a** (191 mg, 64%); ν_{max}/cm^{-1} 3086, 2958, 1743, 1628, 1571, 1371, 1232, 1112, 1047, 842, 735 and 700; δ_H ($CDCl_3$, 300 MHz) 0.38 (s, 6 H), 1.42 (d, J 6.5, 3 H), 2.07 (s, 3 H), 5.42 (q, J 6.5, 1 H), 6.27 (d, J 18.2, 1 H), 6.62 (d, J 9.9, 1 H), 6.85 (dd, J 9.9, 18.2, 1 H), 7.30–7.40 (m, 3 H) and 7.45–7.50 (m, 2 H); δ_C ($CDCl_3$, 50 MHz) -2.9, 19.7, 21.1, 73.6, 127.6, 127.8, 129.1, 131.8, 133.8, 137.8, 138.4, 141.4 and 169.8; m/z (rel. intensity) 354 (0.1), 352 (0.1), 273 (19), 242 (3), 240 (3), 230 (24), 152 (31), 141 (100), 137 (22) and 106 (64) (Found: M, 352.0469. Calc. for $C_{16}H_{21}^{79}BrSiO_2$: M, 352.0457).

(3Z,5E)-3-Bromo-6-(dimethylphenylsilyl)-2-hydroxyhexa-3,5-diene **7b**. A solution of **2e** (187 mg, 0.5 mmol), water (36 mg, 2.00 mmol) and AgBF₄ (146 mg, 0.75 mmol) in THF (5 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (7% EtOAc–hexane) to afford **7b** (121 mg, 78%); ν_{max}/cm^{-1} 3564, 3374, 3069, 2957, 1626, 1569, 1427, 1251, 1114, 991, 840, 824, 734 and 700; δ_H ($CDCl_3$, 300 MHz) 0.38 (s, 6 H), 1.38 (d, J 6.4, 3 H), 1.93 (d, J 5.0, 1 H), 4.35 (dq, J 5.0, 6.4, 1 H), 16% enhancement upon irradiation at δ 6.68), 6.21 (d, J 18.3, 1 H), 6.58 (d, J 9.8, 1 H), 6.85 (dd, J 9.8, 18.3, 1 H), 22% enhancement upon irradiation at δ 6.68), 7.30–7.40 (m, 3 H) and 7.45–7.50 (m, 2 H); δ_C ($CDCl_3$, 75 MHz) -2.8, 22.3, 72.6, 127.9, 129.1, 129.3, 133.3, 133.8, 137.5, 138.0 and 141.7; m/z (rel. intensity) 311 (1), 309 (1), 297 (17), 295 (15), 242 (28), 240 (26), 227 (25), 225 (23), 155 (48), 41 (100) and 91 (22) [Found: (M - 1), 309.0312. Calc. for $C_{14}H_{18}^{79}BrSiO$: (M - 1) 309.0310].

(4Z,6E)-4-Bromo-7-(dimethylphenylsilyl)-3-methyl-2-oxahepta-4,6-diene **7c**. A solution of **2e** (187 mg, 0.5 mmol) and AgBF₄ (146 mg, 0.75 mmol) in MeOH (5 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (5% EtOAc–hexane) to afford **7c** (83 mg, 51%); ν_{max}/cm^{-1} 2985, 2933, 2900, 2821, 1623, 1569, 1454, 1427, 1260, 1250, 1113, 991, 840, 824, 734 and 699; δ_H ($CDCl_3$, 300 MHz) 0.38 (s, 6 H), 1.32 (d, J 6.4, 3 H), 3.25 (s, 3 H), 3.79 (q, J 6.4, 1 H), 6.21 (d, J 18.2, 1 H), 6.56 (d, J 9.8, 1 H), 6.91 (dd, J 9.8, 18.2, 1 H), 7.30–7.40 (m, 3 H) and 7.45–7.50 (m, 2 H); δ_C ($CDCl_3$, 50 MHz) -2.8, 20.8, 56.3, 81.4, 127.9, 129.2, 131.2, 131.3, 133.8,

137.2, 138.0 and 141.6; m/z (rel. intensity) 326 (1), 324 (1), 311 (18), 309 (16), 242 (28), 240 (26), 187 (51), 155 (82), 141 (100), 89 (80) and 59 (68) (Found: M , 324.0526. Calc. for $C_{15}H_{21}^{79}BrSiO$: 324.0524).

(6Z,8E)-6-Bromo-9-(dimethylphenylsilyl)-5-methyl-4-oxanona-1,6,8-triene **7d**. A solution of **2e** (374 mg, 1.0 mmol), 2-propen-1-ol (116 mg, 2.0 mmol) and $AgBF_4$ (291 mg, 1.5 mmol) in THF (10 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2%, EtOAc-hexane) to afford **7d** (291 mg, 83%); ν_{max}/cm^{-1} 3069, 2958, 2860, 1224, 1570, 1427, 1262, 1115, 1098, 992, 840, 823, 734 and 699; $\delta_C(CDCl_3, 300\text{ MHz})$ 0.41 (s, 6 H), 1.36 (d, J 5.9, 3 H), 3.79 (dd, J 6.4, 12.6, 1 H), 4.00 (q, J 5.9, 1 H), 4.03 (dd, J 5.0, 12.6, 1 H), 5.18 (d, J 11.5, 1 H), 5.28 (d, J 17.1, 1 H), 5.80–6.00 (m, 1 H), 6.22 (d, J 18.2, 1 H), 6.57 (d, J 9.7, 1 H), 6.93 (dd, J 9.7, 18.2, 1 H), 7.30–7.40 (m, 3 H) and 7.50–7.60 (m, 2 H); $\delta_C(CDCl_3, 75\text{ MHz})$ –2.8, 20.9, 69.3, 78.9, 117.2, 127.8, 129.1, 131.0, 131.5, 133.8, 134.4, 137.1, 138.0 and 141.7; m/z (rel. intensity) 352 (0.3), 350 (0.3), 337 (4), 335 (4), 311 (13), 309 (13), 242 (30), 240 (30), 154 (100) and 105 (61) (Found: M , 350.0713. Calc. for $C_{17}H_{23}^{79}BrOSi$: M , 350.0702).

(6Z,8E)-6-Bromo-5-phenyl-9-(trimethylsilyl)-4-oxanona-1,6,8-triene **7e**. A solution of **2b** (374 mg, 1.0 mmol), 2-propen-1-ol (116 mg, 2.0 mmol) and $AgBF_4$ (291 mg, 1.5 mmol) in THF (10 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2%, EtOAc-hexane) to afford **7e** (211 mg, 60%); ν_{max}/cm^{-1} 2956, 2863, 1683, 1492, 1451, 1250, 1091, 1070, 853, 840, 757 and 698; $\delta_H(CDCl_3, 200\text{ MHz})$ 0.11 (s, 9 H), 3.97 (dd, J 5.8, 12.8, 1 H), 4.12 (dd, J 5.2, 12.8, 1 H), 4.98 (s, 1 H), 5.22 (d, J 10.3, 1 H), 5.36 (d, J 17.2, 1 H), 5.80–6.05 (m, 1 H), 6.17 (d, J 17.2, 1 H), 6.74 (d, J 9.5, 1 H), 6.84 (dd, J 9.5, 17.2, 1 H) and 7.24–7.50 (m, 5 H); $\delta_C(CDCl_3, 50\text{ MHz})$ –1.5, 69.6, 84.2, 117.5, 127.0, 128.0, 128.2, 128.4, 131.9, 134.2, 139.0 and 140.2; m/z (rel. intensity) 352 (6), 350 (6), 337 (3), 335 (3), 271 (59), 230 (20), 105 (28) and 73 (100) (Found: M , 350.0713. Calc. for $C_{17}H_{23}^{79}BrOSi$: M , 350.0702).

(1E,3Z)-5-Allyloxy-4-bromo-1-(trimethylsilyl)undeca-1,3-diene **7f**. A solution of **2d** (382 mg, 1.0 mmol) allyl alcohol (116 mg, 2.0 mmol) and $AgBF_4$ (291 mg, 1.5 mmol) in THF (10 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2% EtOAc-hexane) to afford **7f** (151 mg, 42%); ν_{max}/cm^{-1} 2956, 2858, 1459, 1249, 1127, 1084, 991, 864, 840 and 732; $\delta_C(CDCl_3, 300\text{ MHz})$ 0.11 (s, 9 H), 0.75–0.85 (m, 3 H), 1.15–1.30 (br, 8 H), 1.60–1.70 (m, 2 H), 3.65–3.75 (m, 2 H), 4.01 (dd, J 5.0, 11.1, 1 H), 5.16 (d, J 10.4, 1 H), 5.24 (d, J 17.3, 1 H), 5.75–5.95 (m, 1 H), 6.08 (d, J 18.3, 1 H), 6.47 (d, J 9.5, 1 H) and 6.81 (dd, J 9.5, 18.3, 1 H); $\delta_C(CDCl_3, 75\text{ MHz})$ –1.5, 14.0, 22.6, 25.2, 29.1, 31.7, 34.3, 69.3, 83.2, 117.2, 129.9, 132.1, 134.6, 139.5 and 140.2; m/z (rel. intensity) 360 (9), 358 (9), 345 (8), 343 (8), 275 (98), 273 (100) and 73 (45) (Found: M , 360.1324. Calc. for $C_{17}H_{31}^{81}BrOSi$: M , 360.1307).

(6Z,8E)-6-Bromo-9-(dimethylphenylsilyl)-4-oxadeca-1,6,8-triene **7g**. A solution of **2f** (1.12 g, 3.0 mmol), allyl alcohol (348 mg, 6.0 mmol) and $AgBF_4$ (698 mg, 3.6 mmol) in THF (30 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2% EtOAc-hexane) to afford **7g** (537 mg, 52%); ν_{max}/cm^{-1} 2959, 2921, 2852, 1648, 1629, 1427, 1250, 1110, 926, 815, 775, 732 and 701; $\delta_H(CDCl_3, 200\text{ MHz})$ 0.41 (s, 6 H), 1.83 (s, 3 H), 4.03 (dd, J 1.0, 6.0, 2 H), 4.24 (s, 2 H), 5.23 (d, J 10.2, 1 H), 5.31 (d, J 17.2, 1 H), 5.80–6.00 (m, 1 H), 6.69 (d, J 10.1, 1 H), 6.93 (d, J 10.1, 1 H), 7.30–7.40 (m, 3 H) and 7.50–7.60 (m, 2 H); $\delta_C(CDCl_3, 50\text{ MHz})$ –3.7, 16.4, 70.9, 75.0, 117.5, 124.4, 125.8, 127.8, 129.1, 133.0, 134.2, 134.6, 137.5 and 143.5; m/z (rel. intensity) 352 (8), 350 (8), 311 (8), 309 (10), 295 (48), 293 (47), 286 (39), 271 (85), 213 (71) and 156 (100); (Found: M , 350.0694. $C_{17}H_{23}^{79}BrOSi$: M , 350.0702).

(7Z,9E)-7-Bromo-10-(dimethylphenylsilyl)-6-methyl-5-oxadeca-1,7,9-triene **7h**. A solution of **2e** (748 mg, 2.0 mmol), but-3-

en-1-ol (288 mg, 4.0 mmol) and $AgBF_4$ (582 mg, 3.0 mmol) in THF (20 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2%, EtOAc-hexane) to afford **7h** (496 mg, 68%); ν_{max}/cm^{-1} 3070, 2982, 1624, 1570, 1428, 1261, 1104, 991, 840, 823, 733 and 699; $\delta_H(CDCl_3, 300\text{ MHz})$ 0.38 (s, 6 H), 1.33 (d, J 6.5, 3 H), 2.25–2.40 (m, 2 H), 3.15–3.30 (m, 1 H), 3.45–3.55 (m, 1 H), 3.91 (q, J 6.5, 1 H), 5.04 (d, J 10.8, 1 H), 5.08 (d, J 18.8, 1 H), 5.70–5.90 (m, 1 H), 6.20 (d, J 18.3, 1 H), 6.56 (d, J 9.5, 1 H), 6.90 (dd, J 9.5, 18.3, 1 H), 7.30–7.40 (m, 3 H) and 7.50–7.60 (m, 2 H); $\delta_C(CDCl_3, 50\text{ MHz})$ –2.8, 20.9, 34.2, 68.0, 79.9, 116.4, 127.8, 129.1, 130.7, 131.8, 133.8, 135.2, 136.9, 138.0 and 141.7; m/z (rel. intensity) 366 (2), 364 (2), 354 (11), 352 (11), 242 (43), 240 (43), 228 (52), 155 (100), 141 (76) and 129 (70) (Found: M , 364.0848. Calc. for $C_{18}H_{25}^{79}BrOSi$: M , 364.0859).

(6Z,8E)-6-Bromo-9-(dimethylphenylsilyl)-2,5-dimethyl-4-oxanona-1,6,8-triene **7i**. A solution of **2e** (1.50 g, 4.0 mmol), 2-methylprop-2-en-1-ol (576 mg, 8.0 mmol) and $AgBF_4$ (931 mg, 4.8 mmol) in THF (40 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2% EtOAc-hexane) to afford **7i** (774 mg, 53%); ν_{max}/cm^{-1} 2981, 2857, 1624, 1570, 1428, 1261, 1112, 840, 823 and 734; $\delta_C(CDCl_3, 300\text{ MHz})$ 0.39 (s, 6 H), 1.35 (d, J 6.4, 3 H), 1.74 (s, 3 H), 3.69 (d, J 12.4, 1 H), 3.92 (d, J 12.4, 1 H), 3.95 (q, J 6.4, 1 H), 4.89 (s, 1 H), 4.96 (s, 1 H), 6.21 (d, J 18.6, 1 H), 6.56 (d, J 9.8, 1 H), 6.92 (dd, J 9.8, 18.6, 1 H), 7.30–7.40 (m, 3 H) and 7.50–7.60 (m, 2 H); $\delta_C(CDCl_3, 75\text{ MHz})$ –2.8, 19.6, 20.9, 72.2, 78.6, 112.5, 127.9, 129.1, 131.0, 131.6, 133.8, 137.0, 138.0, 141.7 and 141.9; m/z (rel. intensity) 366 (1), 364 (1), 351 (9), 349 (9), 311 (15), 309 (16), 227 (32), 155 (100), 137 (70) and 129 (60) (Found: M , 366.0844. Calc. for $C_{18}H_{25}^{81}BrOSi$: 366.0839).

(2E,7Z,9E)-7-Bromo-10-(dimethylphenylsilyl)-6-methyl-5-oxadeca-2,7,9-triene **7j**. A solution of **2e** (374 mg, 1.0 mmol), (E)-3-methylprop-2-en-1-ol (144 mg, 2.0 mmol) and $AgBF_4$ (291 mg, 1.5 mmol) in THF (10 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2%, EtOAc-hexane) to afford **7j** (212 mg, 58%); ν_{max}/cm^{-1} 2959, 1448, 1255, 1119, 1058, 832, 792, 734 and 700; $\delta_H(CDCl_3, 300\text{ MHz})$ 0.40 (s, 6 H), 1.33 (d, J 6.3, 3 H), 1.69 (d, J 6.0, 3 H), 3.70 (dd, J 6.6, 11.5, 1 H), 3.91 (dd, J 7.2, 11.5, 1 H), 3.97 (q, J 6.3, 1 H), 5.54–5.80 (m, 2 H), 6.20 (d, J 18.3, 1 H), 6.55 (d, J 9.6, 1 H), 6.90 (dd, J 9.6, 18.3, 1 H), 7.30–7.40 (m, 3 H) and 7.50–7.60 (m, 2 H); $\delta_C(CDCl_3, 75\text{ MHz})$ –2.8, 17.8, 21.0, 69.1, 78.7, 127.2, 127.8, 129.1, 130.0, 130.9, 131.8, 133.8, 136.9, 138.0 and 141.7; m/z (rel. intensity) 366 (0.1), 364 (0.1), 351 (2), 349 (2), 311 (5), 309 (4), 226 (33), 271 (100), 193 (24) and 155 (40) (Found: M , 364.0869. Calc. for $C_{18}H_{25}^{79}BrOSi$: M , 364.0859).

(4Z,6E)-4-Bromo-7-(dimethylphenylsilyl)-3-methyl-1-phenyl-2-oxahepta-4,6-heptadiene **7k**. A solution of **2e** (374 mg, 1.0 mmol), benzyl alcohol (216 mg, 2.0 mmol) and $AgBF_4$ (291 mg, 1.5 mmol) in THF (10 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2% EtOAc-hexane) to afford **7k** (281 mg, 70%); ν_{max}/cm^{-1} 2950, 1723, 1454, 1255, 1180, 1068, 832, 792, 736 and 699; $\delta_H(CDCl_3, 200\text{ MHz})$ 0.44 (s, 6 H), 1.40 (d, J 6.3, 3 H), 4.03 (q, J 6.3, 3 H), 4.30 (d, J 11.7, 1 H), 4.61 (d, J 11.7, 1 H), 6.25 (d, J 18.2, 1 H), 6.61 (d, J 9.5, 1 H), 6.97 (dd, J 9.5, 18.2, 1 H), 7.30–7.45 (m, 8 H) and 7.50–7.65 (m, 2 H); $\delta_C(CDCl_3, 50\text{ MHz})$ –2.8, 21.0, 70.2, 78.8, 127.7, 127.8, 128.4, 129.2, 131.3, 131.5, 133.8, 137.3, 137.9 and 141.7; m/z (rel. intensity) 402 (0.1), 400 (0.1), 387 (3), 385 (3), 372 (7), 370 (7), 242 (17), 240 (17), 233 (48), 155 (51), 136 (53) and 91 (100) (Found: M , 400.0854. Calc. for $C_{21}H_{25}^{79}BrOSi$: 400.0859).

(6Z,8E)-6-Bromo-9-(dimethylphenylsilyl)-5-methyl-4-oxanona-6,8-diene-1-yne **7l**. A solution of **2e** (374 mg, 1.0 mmol), prop-2-ynyl alcohol (116 mg, 2.0 mmol) and $AgBF_4$ (291 mg, 1.5 mmol) in THF (10 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel

(2%, EtOAc-hexane) to afford **7l** (291 mg, 83%); $\nu_{\max}/\text{cm}^{-1}$ 3300, 2957, 1569, 1441, 1252, 1115, 1092, 1073, 892, 992, 841, 823, 734 and 699; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.41 (s, 6 H), 1.37 (d, J 6.4, 3 H), 2.42 (s, 1 H), 3.97 (d, J 15.9, 1 H), 4.20 (d, J 15.9, 1 H), 4.23 (q, J 6.4, 1 H), 6.26 (d, J 18.2, 1 H), 6.62 (d, J 9.4, 1 H), 6.91 (dd, J 9.4, 18.2, 1 H), 7.35–7.45 (m, 3 H) and 7.50–7.60 (m, 2 H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ –2.9, 20.7, 55.3, 74.6, 78.0, 127.9, 129.2, 130.0, 132.2, 133.8, 137.9 and 141.4; m/z (rel. intensity) 350 (0.3), 348 (0.3), 335 (5), 333 (5), 311 (5), 309 (5), 242 (20), 240 (20), 155 (75), 141 (100) and 83 (80) (Found: M, 348.0533. Calc. for $\text{C}_{17}\text{H}_{21}^{79}\text{BrOSi}$: M, 348.0545).

(6Z,8E)-6-Bromo-10-(dimethylphenylsilyl)-3-methyl-4-oxadeca-1,6,8-triene **7m**. A solution of **2f** (1.12 g, 3.0 mmol), allyl alcohol (0.43 g, 6.0 mmol) and AgBF_4 (0.70 g, 3.6 mmol) in THF (30 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2%, EtOAc-hexane) to afford **7m** (0.49 g, 45%); $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.40 (s, 6 H), 1.28 (d, J 7.0, 3 H), 1.81 (s, 3 H), 3.93 (qd, J 6.5, 6.8, 1 H), 4.13 (d, J 14.3, 1 H), 4.25 (d, J 14.3, 1 H), 5.16 (d, J 10.2, 1 H), 5.19 (d, J 17.5, 1 H), 5.74 (ddd, J 6.8, 10.2, 17.5, 1 H), 6.67 (d, J 10.2, 1 H), 6.91 (d, J 10.2, 1 H), 7.30–7.40 (m, 3 H) and 7.50–7.60 (m, 2 H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ –3.7, 16.3, 21.2, 73.0, 72.2, 116.4, 123.9, 126.4, 127.7, 129.0, 133.9, 134.7, 137.5, 139.6 and 143.0; m/z (rel. intensity) 366 (0.1), 364 (0.3), 286 (21), 271 (45), 208 (29), 193 (27) and 135 (100) (Found: M, 366.0835. Calc. for $\text{C}_{18}\text{H}_{25}^{81}\text{BrOSi}$: M, 366.0839).

(6Z,8E)-6-Bromo-9-phenyl-4-oxanona-1,6,8-triene **7n**. A solution of **2k** (1.21 g, 4 mmol), allyl alcohol (0.46 g, 8 mmol) and AgBF_4 (0.93 g, 4.8 mmol) in THF (40 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2%, EtOAc-hexane) to afford **7n** (189 mg, 85%); $\nu_{\max}/\text{cm}^{-1}$ 2902, 1685, 1453, 1275, 1158, 1103, 931, 751 and 694; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 4.03 (d, J 5.6, 2 H), 4.24 (s, 2 H), 5.23 (d, J 10.4, 1 H), 5.32 (d, J 17.3, 1 H), 5.80–6.00 (m, 1 H), 6.72 (d, J 10.5, 1 H), 6.73 (d, J 15.6, 1 H), 7.06 (dd, J 10.5, 15.6, 1 H), 7.20–7.40 (m, 3 H) and 7.46 (d, J 4.0, 2 H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ 70.9, 74.8, 117.6, 124.3, 125.4, 126.8, 128.3, 128.7, 129.6, 134.2, 136.1 and 136.7; m/z (rel. intensity) 280 (16), 278 (15), 223 (5), 221 (5), 199 (13), 141 (71), 115 (84), 91 (46) and 41 (100) (Found: M, 278.0311. Calc. for $\text{C}_{14}\text{H}_{15}^{79}\text{BrO}$: M, 278.0306).

(6Z,8E)-6-Bromo-5-methyl-4-oxaundeca-1,6,8-trien-2-one **7o**. A solution of **2m** (141.0 mg, 0.5 mmol), allyl alcohol (58 mg, 1.0 mmol) and AgBF_4 (116 mg, 0.6 mmol) in THF (10 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2%, EtOAc-hexane) to afford **7o** (70 mg, 54%); $\nu_{\max}/\text{cm}^{-1}$ 2985, 2862, 1673, 1621, 1592, 1361, 1254, 1097 and 980; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 1.36 (d, J 6.5, 3 H), 2.31 (s, 3 H), 3.82 (dd, J 6.2, 11.2, 1 H), 4.00–4.20 (m, 2 H), 5.18 (d, J 10.4, 2 H), 5.24 (d, J 17.4, 2 H), 5.80–6.00 (m, 1 H), 6.25 (d, J 15.9, 1 H), 6.68 (d, J 10.4, 1 H), 7.40 (dd, J 10.4, 15.9, 1 H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ 20.7, 27.0, 69.6, 79.0, 117.4, 126.5, 133.4, 133.9, 139.1, 140.5 and 198.3; m/z (rel. intensity) 260 (23), 258 (24), 179 (31), 137 (23) and 43 (100) (Found: M, 260.0237. Calc. for $\text{C}_{11}\text{H}_{15}^{81}\text{BrO}_2$: M, 260.0235).

(6Z,8E)-6-Bromo-9,9-dimethyl-4-oxaundeca-1,6,8-triene **7p**. A solution of **2j** (564 mg, 2.0 mmol), allyl alcohol (232 mg, 4.0 mmol) and AgBF_4 (466 mg, 2.4 mmol) in THF (20 cm^3) was allowed to reflux for 5 h. After work-up, the crude product was chromatographed on silica gel (2%, EtOAc-hexane) to afford **7p** (189 mg, 36%) and **8** (171 mg, 33%). **7p**: $\nu_{\max}/\text{cm}^{-1}$ 2962, 1647, 1362, 1261, 1104, 974, 925 and 805; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 1.04 (s, 9 H), 3.97 (d, J 5.6, 2 H), 4.16 (s, 2 H), 5.19 (d, J 11.5, 1 H), 5.29 (d, J 17.0, 1 H), 5.80–6.00 (m, 2 H), 6.24 (dd, J 9.8, 15.5, 1 H) and 6.59 (d, J 9.8, 1 H); $\delta_{\text{C}}(\text{CDCl}_3, 50 \text{ MHz})$ 29.2, 33.7, 70.6, 74.8, 117.3, 121.5, 122.0, 130.3, 134.3 and 150.4; m/z (rel. intensity) 260 (18), 258 (17), 187 (38), 185 (36), 179 (39), 121 (90), 95 (100), 81

(67) and 57 (47) (Found: M, 258.0602. Calc. for $\text{C}_{12}\text{H}_{19}^{79}\text{BrO}$: M, 258.0619). **8**: $\nu_{\max}/\text{cm}^{-1}$ 2861, 2865, 1646, 1362, 1261, 1105, 1056 and 805; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.88 (s, 9 H), 3.43 (d, J 6.8, 1 H), 3.74 (dd, J 5.9, 13.1, 1 H), 4.02 (dd, J 4.9, 13.1, 1 H), 5.12 (d, J 10.2, 1 H), 5.24 (d, J 17.2, 1 H), 5.60 (s, 1 H), 5.77 (s, 1 H), 5.80–6.00 (m, 1 H), 5.98 (dd, J 6.6, 14.9, 1 H) and 6.12 (d, J 14.9, 1 H); $\delta_{\text{C}}(\text{CDCl}_3, 50 \text{ MHz})$ 26.1, 35.3, 70.0, 86.5, 116.2, 119.5, 129.4, 130.7, 135.2 and 135.8; m/z (rel. intensity) 260 (28), 258 (26), 179 (36), 121 (91), 95 (100), 81 (67) and 57 (43) (Found: M, 258.0623. Calc. for $\text{C}_{12}\text{H}_{19}^{79}\text{BrO}$: M, 258.0619).

(3Z,5E)-3-Bromo-6-dimethylphenylsilylhexa-1,3,5-triene **10**. A solution of **2e** (187 mg, 0.5 mmol), maleic anhydride (49 mg, 0.5 mmol) and AgBF_4 (146 mg, 0.75 mmol) in ether (5 cm^3) was stirred at room temperature for 16 h. After work-up, the crude product was chromatographed on silica gel (hexane) to afford **10** (60 mg, 41%); $\nu_{\max}/\text{cm}^{-1}$ 3016, 2957, 2927, 2854, 1594, 1427, 1268, 1250, 1115, 989, 910, 840, 823, 733 and 698; $\delta_{\text{H}}(\text{CDCl}_3, 300 \text{ MHz})$ 0.38 (s, 6 H), 5.27 (d, J 10.4, 1 H), 5.67 (d, J 16.2, 1 H), 6.26 (d, J 18.3, 1 H), 6.34 (dd, J 10.4, 16.2, 1 H), 6.51 (d, J 9.7, 1 H), 7.02 (dd, J 9.7, 18.3, 1 H), 7.30–7.40 (m, 3 H) and 7.45–7.50 (m, 2 H); $\delta_{\text{C}}(\text{CDCl}_3, 75 \text{ MHz})$ –2.8, 119.7, 125.8, 127.9, 129.1, 133.8, 134.3, 135.9, 138.0, 138.2 and 142.5.

Acknowledgements

Support from the National Science Council of the Republic of China is gratefully acknowledged.

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Paper 3/03863G

Received 5th July 1993

Accepted 29th July 1993