Radical Cyclizations of Geminal Radical Precursors

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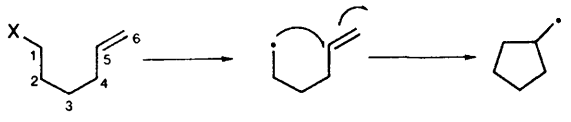
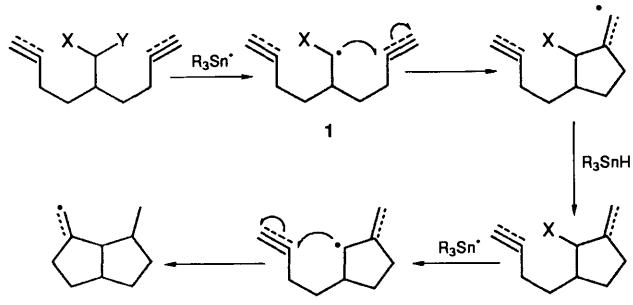
Polycyclic structures can be generated by double radical cyclization, using compounds having two groups, capable of being homolysed, attached to a single carbon that is suitably located with respect to two unsaturated pendants.

The literature on the cyclization of hex-5-enyl radicals deals almost exclusively with those cases in which the potential radical centre (C-1) carries only one substituent, X, which is capable of being homolysed (eqn. 1). If a pair of such groups



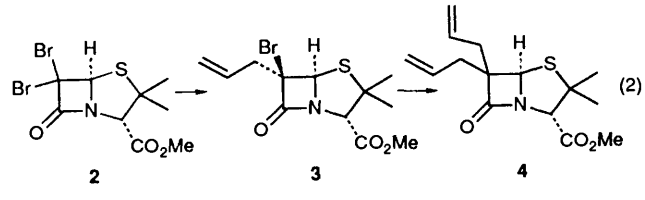
(1)

(X, Y) are attached to the same carbon, and the structure also contains two unsaturated pendants (as in Scheme 1), then, in principle, two successive radical cyclizations could take place and the process would constitute a method for making bicyclic compounds. We report our observations on the synthetic possibilities of such a scheme.



Scheme 1

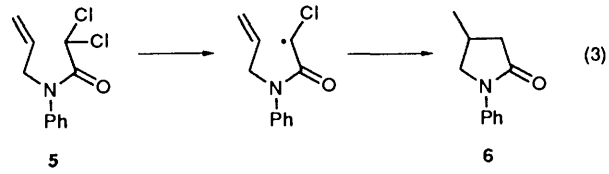
At the outset of our work little was available by way of background information on the behaviour of compounds with geminal groups that can be homolysed. It was known that penicillin derivatives such as **2** react smoothly with allyl tins leading either to adducts **3** or **4**, depending on the stoicheometry used (eqn. 2).[1]



(2)

2 **3** **4**

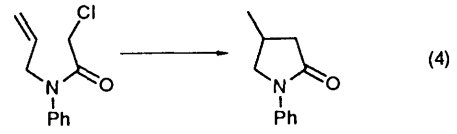
In Scheme 1, the rate of formation and the behaviour of the first radical **1** will be influenced, electronically and sterically (among other factors), by the nature of the remaining substituent X, and a number of cases have been reported where the results of such effects are observed. For example, the



(3)

5 **6**

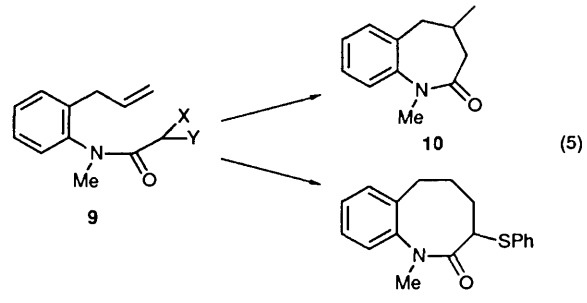
dichloroamide **5** (eqn. 3) undergoes efficient (85%) ring closure, **5** → **6**, on treatment with a stannane,[2] whereas the monochloroamide **7** (eqn. 4) gives only a small amount (12%) of the desired cyclized product **8**.[3]



(4)

7 **8**

The regiochemistry of radical cyclization can also be influenced by the nature of the substituent at the radical centre. In the case of compound **9** (X = Y = Cl), the main product (49%) is the lactam **10** (if 2.2 equiv. of tributylstannane are used), but when X = Y = SPh, the main product (47%) is the phenylthio lactam **11**—the result of *endo* closure (eqn. 5).[4]



(5)

9 **10** **11**

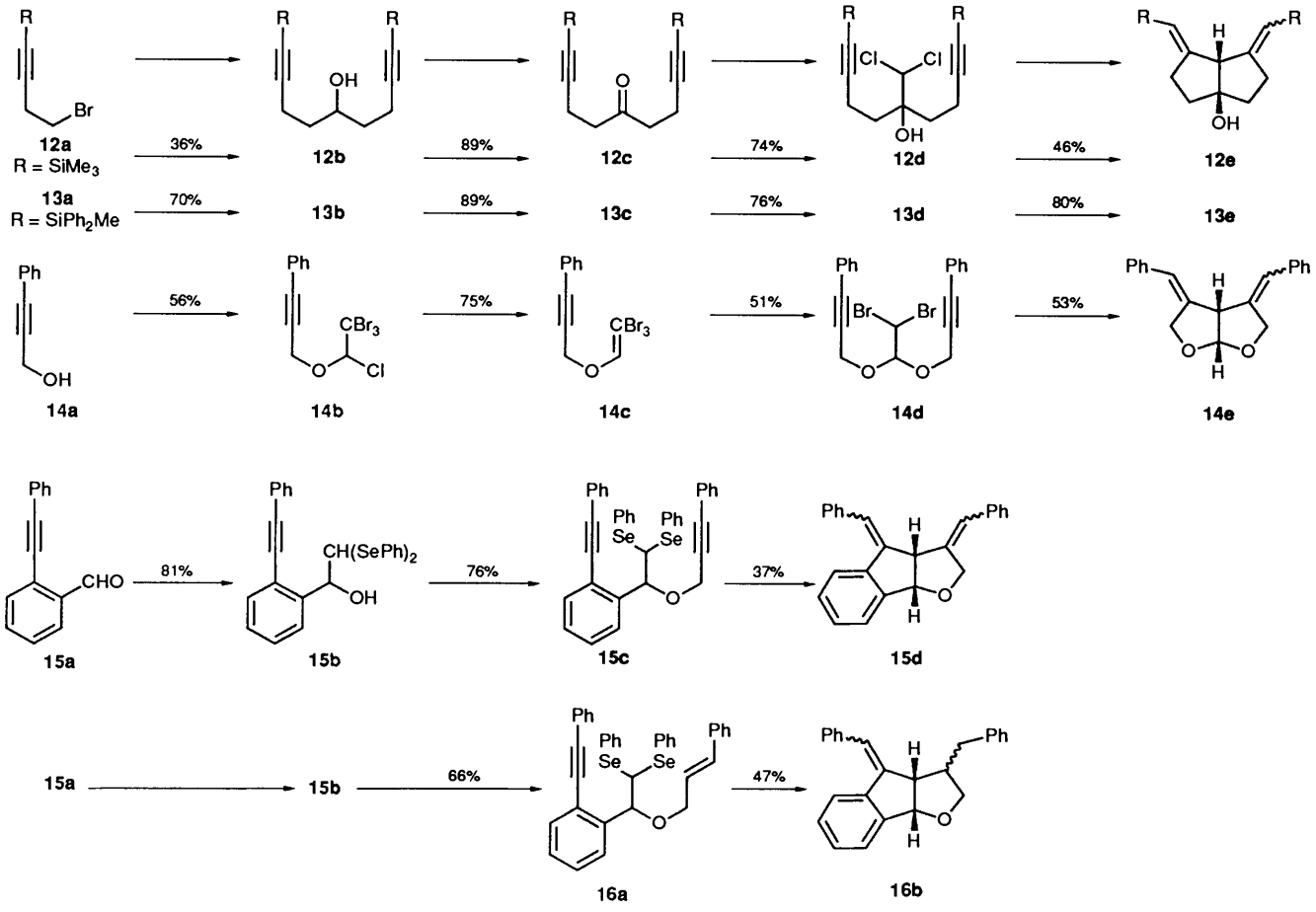
The above examples summarize the empirical observations in the area of geminal radical precursors and, as indicated above, our interest in such species was to evaluate their use for making bicyclic compounds. Such an application† involves two stages: (a) the preparation of the geminal radical precursor with suitably located radical traps, such as double and/or triple bonds, and (b) the double radical cyclization itself.

We initially found some difficulties in making appropriate starting materials that would let us examine the double radical closure, but we were eventually able to prepare suitable test cases.

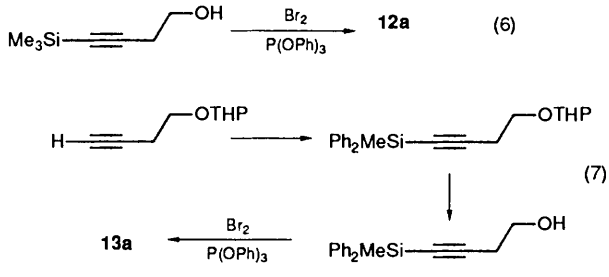
We first made the symmetrical ketones **12c** and **13c** (see Table 1) with the intention of treating them with (dichloro-

† During the course of this work [Canadian Institute of Chemistry, Halifax, July, 1990, Abstracts. D. Cole and D. L. J. Clive, Abstract No. 864] two such applications were reported: See ref. 5.

Table 1



methyl)lithium.[6] The ketones were accessible from the corresponding alcohols **12b** and **13b**, respectively, and these, in turn, were prepared by double Grignard addition to ethyl formate.[7] The bromides **12a** and **13a** (Table 1), needed for these reactions, were formed as shown in eqns. 6 and 7. Although the Grignard

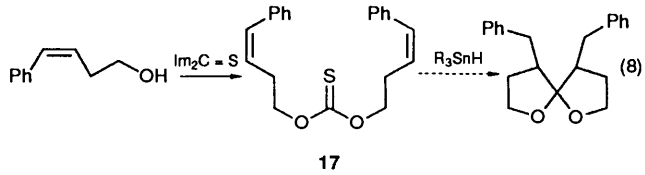


addition provided the desired products, only the formation of alcohol **13b** was efficient (70%). Jones oxidation to ketones **12c** and **13c** was straightforward, and both ketones reacted smoothly with (dichloromethyl)lithium[6] at −78 °C.

The next substrate for double radical closure that we made was the ketal **14d**, and this was prepared as shown in Table 1. Treatment of phenylprop-2-ynyl alcohol with bromal, in the presence of thionyl chloride and pyridine, gave chloro ether **14b**.[8] This was then partially dehalogenated, **14b** → **14c**, by the action of zinc dust. The bromine substitution of the vinyl ether **14c** made it less reactive than simple vinyl ethers, but the compound did condense (51% yield) with phenylprop-2-ynyl alcohol in the presence of concentrated hydrochloric acid (**14c** → **14d**).

The remaining radical precursors, **15c** and **16a**, were assembled quite easily. Condensation of the known aldehyde **15a**[9] with bis(phenylseleno)methylpotassium[10] afforded alcohol **15b**. In this condensation it was advantageous to use potassium diisopropylamide/lithium *tert*-butoxide (81% yield) rather than lithium diisopropylamide (< 10% yield).[11] Alkylation on oxygen was then achieved by treatment with phenylprop-2-ynyl bromide (for **15c**) or cinnamyl bromide (for **16a**) in the presence of sodium hydride.

We also prepared the thiocarbonate **17** (eqn. 8) and the bis(phenylseleno) ketal **18** (eqn. 9) as potential precursors to spiro compounds.



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All of the geminal radical precursors shown in Table 1 underwent double radical cyclization, the yields being in the range 37–80%, *i.e.* 60–89% per carbon–carbon bond being formed. For the radical cyclization, we used standard thermal conditions for the dihalogeno compounds, the reactions being carried out by adding benzene solutions of tributyltin hydride (0.09–0.2 mol dm^{-3}) and azoisobutyronitrile (AIBN) (0.007–0.02 mol dm^{-3}) to a refluxing solution of the substrate (0.007–0.01 mol dm^{-3}), also in benzene.

Examples **12e** and **13e** are very similar, and it is not clear why formation of the latter is much more efficient; neither compound is unduly volatile.

For the bis(phenylseleno) ketals we prefer to conduct the reactions at room temperature and initiate them with tri-

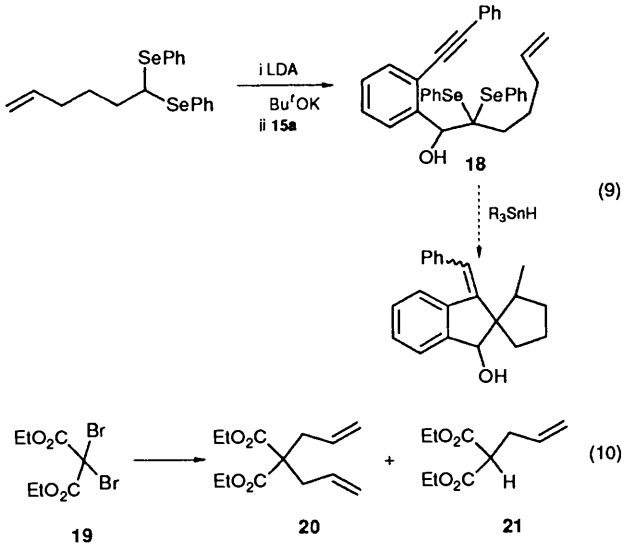
ethylborane and oxygen.[12] This procedure gave better results than the thermal method.

The cyclizations of the bis(acetylenes) must involve, in their second step, closure of an allyl radical onto a triple bond, and so these examples extend the small number of cases of allyl radical cyclization.[13]

Cyclization products **12e** and **13e** were each mixtures of two isomers, one being symmetrical (*E* geometry for both double bonds), and the other having one *E* and one *Z* double bond. Compound **14e** was a mixture of *Z,Z* and *E,Z* isomers. Compounds **15d** and **16b** were obtained as mixtures of three and two isomers, respectively. The stereochemistry of the double bonds in the case of **12e**, **13e** and **14e** was established by NOE observations involving the vinyl hydrogen(s) and the adjacent bridgehead hydrogen in each case. One of the isomers of **15d** was shown by NOE measurements to have the *Z,Z* geometry, but our NOE measurements on the other two isomers of **15d** and on both isomers of **16b** were inconclusive. The ring fusion geometry was proved (by NOE observations) to be *cis* in **13e**, **14e**, **15d** and **16b**, and taken for granted[14] as *cis* in the case of **12e**.

Extension of the method to spiro compounds by radical closures with thiocarbonate **17** or bis(phenylseleno) ketal **18** was not successful.

Finally, we examined reaction of the dibromomalonate **19** with allyltributyltin (eqn. 10). However, even in the presence of an excess of allylstannane, some mono alkylated product was always obtained.



We conclude from these and other[5] results, that double radical cyclization can be used to make polycyclic compounds, but that access to the precursors is sometimes difficult.

Experimental

Argon was purified by passage through a column (3.5 × 42 cm) of R-311 catalyst* and then through a similar column of Drierite. Glassware was dried in an oven for at least 3 h before use (120 °C) and either cooled in a desiccator over Drierite, or assembled quickly, sealed with rubber septa, and allowed to cool under a slight static pressure of argon. Reaction mixtures were stirred by Teflon-coated magnetic stirring bars.

Solvents for chromatography or extractions were distilled before use. Light petroleum refers to the fraction b.p. 35–60 °C.

Products were isolated from solution by evaporation under water-pump vacuum at, or below, 30 °C using a rotary evaporator. HPLC separations were carried out using a Hewlett-Packard 1082B instrument fitted with a Whatman 22 mm (i.d.) × 25 cm Partisil silica column.

M.p.s were determined on a Kofler block melting point apparatus.

Commercial TLC plates (silica gel, Merck 60F-254) were used. Spots were detected by spraying the plate with 3 mol dm^{-3} sulphuric acid in methanol, followed by charring on a hot plate, or by examination under UV light. Silica gel for flash chromatography was Merck type 60 (230–400 mesh).

Dry solvents were prepared under an inert atmosphere and transferred by oven-dried syringes. Dry tetrahydrofuran (THF) and diethyl ether were distilled from sodium and benzophenone ketyl. Dry benzene (which was used for the radical cyclizations) was distilled from sodium. Dry diisopropylamine, dichloromethane, pyridine, and *N,N*-dimethylformamide (DMF) were distilled from calcium hydride, the last solvent being distilled under water-pump vacuum. Commercial (Aldrich) solutions of butyllithium and methyllithium (both in hexanes) were assumed to have the stated molarity.

IR spectra were recorded on a Nicolet 7000 FT-IR model. Measurements were made as casts from the specified solvent and using potassium bromide plates.

^{1}H NMR spectra were recorded with Bruker WP-200 (at 200 MHz), Bruker AM-300 (at 300 MHz), or Bruker AM-400 (at 400 MHz) spectrometers in the specified deuteriated solvent with tetramethylsilane as an internal standard, *J* values are given in Hz. ^{13}C NMR spectra were recorded with Bruker WP-200 (at 50.323 MHz), Bruker AM-300 (at 75.469 MHz), or Bruker AM-400 (at 100.614 MHz) spectrometers using deuteriochloroform as an internal standard. The symbols s′, d′, t′, and q′ used for ^{13}C NMR signals indicate 0, 1, 2, or 3 attached hydrogens, respectively.

Mass spectra were recorded with an AEI Model MS-12 or MS-50 mass spectrometer at an ionizing voltage of 70 eV.

Microanalyses were performed by the micronanalytical laboratory of this Department.

(4-Bromobut-1-ynyl)trimethylsilane **12a**.[15]—Bromine (6.20 g, 38.79 mmol) was added to a stirred solution of triphenyl phosphite (13.10 g, 42.20 mmol) in diethyl ether (40 cm^3). The mixture was cooled to 0 °C and a solution of 4-(trimethylsilyl)-but-3-yn-1-ol[16] (5.00 g, 35.21 mmol) and dry pyridine (2.79 g, 35.21 mmol) in diethyl ether (20 cm^3) was added over 10 min. Stirring at room temperature was continued for 8 h and the mixture was poured into water (100 cm^3). The ether layer was separated and the aqueous phase was extracted with diethyl ether (1 × 20 cm^3). The combined ether layers were dried ($MgSO_4$) and evaporated. Kugelrohr distillation (110 °C, 30 mmHg) of the residue gave bromosilane **12a** (4.5 g, 63%) as a homogeneous [^{1}H NMR (200 MHz)] clear oil: ν_{max}($CDCl_3$ cast)/cm^{-1} (FT) 1645 and 1506; δ_H($CDCl_3$; 200 MHz) 0.12 (s, 9 H), 2.72 (t, *J* 7.5, 2 H) and 3.37 (t, *J* 7.5, 2 H); δ_C($CDCl_3$; 100.6 MHz) −0.07, 24.27, 28.98, 86.83 and 103.13 (Found: M$^+$, 203.9954. Calc. for $C_7H_{13}{}^{79}BrSi$: *M*, 203.9970).

1,9-Bis(trimethylsilyl)nona-1,8-diyn-5-ol **12b**.—Magnesium turnings (0.35 g, 14.40 mmol), contained in a round-bottomed flask, were activated by heating and cooling under argon, by crushing of a few turnings with a spatula, and by addition of several drops of 1,2-dibromoethane.[17] THF (1 cm^3) was then added, followed by (4-bromobut-1-ynyl)trimethylsilane (2.50 g, 12.19 mmol) in THF (5 cm^3), which was introduced dropwise at a rate to maintain a modest exotherm. The mixture was refluxed for 1 h and then cooled in an ice bath. Ethyl formate (0.54 cm^3,

* Supplied by Chemical Dynamics Corporation, South Plainfield, N.J., USA.

6.68 mmol) in THF (5 cm^3) was added dropwise with stirring over 20 min, the ice bath was removed and stirring was continued for 30 min. Aqueous NaOH (3 mol dm^{-3}; 20 cm^3) was added and the mixture was stirred for 10 h. The organic layer was separated and washed with saturated aqueous sodium hydrogencarbonate (1 × 10 cm^3) and water (1 × 10 cm^3), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 18 cm) with 10% ethyl acetate–hexane gave *alcohol* **12b** (616 mg, 36%) as a homogeneous [^1H NMR (300 MHz)] colourless oil: $\nu_{max}(CDCl_3$ cast)/cm^{-1} (FT) 3120–3560, 2958, 2175 and 1250; $\delta_H(CDCl_3$; 300 MHz) 0.14 (s, 18 H), 1.58–1.77 (m, 4 H), 2.19 (d, *J* 4.4, 1 H), 2.37 (t, *J* 7, 4 H) and 3.61–3.92 (m, 1 H); $\delta_C(CDCl_3$; 75.469 MHz) 0.15 (q′), 16.49 (t′), 17.84 (t′), 70.51 (d′), 85.39 (s′) and 106.92 (s′) [Found: C, 64.65; H, 10.3; (M^+ + 18) (CI), 298. $C_{15}H_{28}OSi_2$ requires C, 64.22; H, 10.06%; *M*, 280].

1,9-*Bis*(*trimethylsilyl*)*nona*-1,8-*diyn*-5-*one* **12c**.—Jones reagent [18] was added dropwise with stirring to a solution of alcohol **12b** (408 mg, 1.454 mmol) in acetone (5 cm^3) until the orange colour of the reagent persisted for 30 min. Isopropyl alcohol was then added until the green colour returned. The solvent was then evaporated and the residue was extracted with diethyl ether (1 × 10 cm^3) and washed with water (1 × 10 cm^3). The aqueous phase was re-extracted with diethyl ether (1 × 10 cm^3), and the combined organic phases were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica (2 × 18 cm) with 5% ethyl acetate–hexane gave *ketone* **12c** (361 mg, 89%) as a homogeneous [^1H NMR (300 MHz)] clear oil: $\nu_{max}(CH_2Cl_2$ cast)/cm^{-1} (FT) 2959, 2178, 1719 and 1250; $\delta_H(CDCl_3$; 300 MHz) 0.15 (s, 18 H), 2.45–2.52 (m, 4 H) and 2.64–2.71 (m, 4 H); $\delta_C(CDCl_3$; 75.469 MHz) 0.07 (q′), 14.49 (t′), 41.75 (t′), 85.33 (s′) and 105.47 (s′) [Found: C, 64.55; H, 9.5; (M^+ + 18) (CI), 296. $C_{15}H_{26}OSi_2$ requires C, 64.68; H, 9.41%; *M*, 278].

5-(*Dichloromethyl*)-1,9-*bis*(*trimethylsilyl*)*nona*-1,8-*diyn*-5-*ol* **12d**.—A solution of lithium dicyclohexylamide [prepared by addition of butyllithium (1.6 mol dm^{-3} in hexanes; 0.429 cm^3, 0.686 mmol) to a stirred and cooled (0 °C) solution of dicyclohexylamine (0.137 cm^3, 0.69 mmol) in THF (3 cm^3)] was added by syringe over 20 min to a stirred and cooled (−78 °C) solution of ketone **12c** (95.6 mg, 0.343 mmol) in dichloromethane (3 cm^3). The mixture was stirred at −78 °C for 2 h, quenched by addition of saturated aqueous ammonium chloride (10 cm^3), allowed to warm to room temperature, and then extracted with diethyl ether (2 × 20 cm^3). The ether extract was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (1.5 × 18 cm) with 2% ethyl acetate–hexane gave *dichloromethyl alcohol* **12d** (92.5 mg, 74%) as a homogeneous (TLC, silica, 5% ethyl acetate–light petroleum) colourless oil: $\nu_{max}(CHCl_3$ cast)/cm^{-1} (FT) 3360–3600, 2958, 2177 and 1250; $\delta_H(CDCl_3$; 300 MHz) 0.15 (s, 18 H), 2.01 (dt, *J* 14.0, 7.5, 2 H), 2.09 (dt, *J* 14.0, 7.5, 2 H), 2.41 (t, *J* 7.5, 4 H), 2.73 (s, 1 H) and 5.96 (s, 1 H); $\delta_C(CDCl_3$; 75.469 MHz) 0.02 (q′), 14.08 (t′), 33.29 (t′), 77.28 (s′), 78.61 (d′), 86.10 (s′) and 106.24 (s′) [Found: C, 53.55; H, 7.7; (M^+ + 18) (CI), 381. $C_{16}H_{28}Cl_2OSi_2$ requires C, 52.87; H, 7.76%; *M*, 363].

cis-*Octahydro*-1,6-*bis*(*trimethylsilylmethylene*)*pentalen*-3a-*ol* **12e**.—Tributyltin hydride (0.135 cm^3, 0.507 mmol) in benzene (5 cm^3), and AIBN (5.5 mg, 0.034 mmol) in benzene (5 cm^3) were injected simultaneously over 8 h (double syringe pump) into a refluxing solution of dichloromethyl alcohol **12d** (61.4 mg, 0.169 mmol) in benzene (20 cm^3). Refluxing was continued for 4 h after the addition, and the mixture was then cooled and evaporated. Flash chromatography of the residue over silica gel (2 × 18 cm) with 5% ethyl acetate–hexane gave the *pentalenol* **12e** (23 mg, 46%) as a mixture of two isomers [55:45; *E,E*:*Z,E*]. The isomers were separated by HPLC (refractive index detector; 50% diethyl ether–hexane at a flow rate of 3.0 cm^3 min^{-1}). The *E,E* isomer had: $\nu_{max}(CHCl_3$ cast)/cm^{-1} (FT) 3040–3340, 2953, 1635 and 1248; $\delta_H(CDCl_3$; 200 MHz) 0.10 (s, 18 H), 1.62 (br s, 1 H), 1.79–1.91 (m, 4 H), 2.30–2.68 (m, 4 H), 2.95 (br s, 1 H) and 5.43 (q, *J* 2.2, 2 H); $\delta_C(CDCl_3$; 50.323 MHz) −0.20, 31.23, 37.37, 68.30, 88.39, 121.87 and 160.95 (Found: M^+, 294.1840. $C_{16}H_{28}Cl_2OSi_2$ requires *M*, 294.1835).

Irradiation of the signal at δ 2.95 in the ^1H NMR spectrum produced enhancements of 17 and 6% in the signals at δ 5.43 and 1.6, respectively.

The *Z,E* isomer had: $\nu_{max}(CDCl_3$ cast)/cm^{-1} (FT) 3040–3400, 2760–3000, 1530 and 1245; $\delta_H(CDCl_3$; 400 MHz) 0.08 (s, 9 H), 0.10 (s, 9 H), 1.55 (br s, 1 H), 1.64–1.86 (m, 2 H), 1.96 (t, *J* 7.8, 2 H), 2.39–2.51 (m, 3 H), 2.57–2.68 (m, 1 H), 3.10 (br s, 1 H), 5.39 (q, *J* 2.3, 1 H) and 5.48–5.51 (m, 1 H); $\delta_C(CDCl_3$; 50.323 MHz) −0.39, 0.24, 31.06, 35.30, 36.93, 37.18, 64.49, 89.37, 121.84, 123.15, 159.76 and 160.39 (Found: M^+, 294.1840. $C_{16}H_{28}Cl_2OSi_2$ requires M, 294.1835).

Irradiation of the signal at δ 3.10 in the ^1H NMR spectrum produced enhancements of 6 and 5% in the signals at δ 5.39 and 1.5, respectively.

2-*But*-3-*ynyloxytetrahydro*-2H-*pyran*.[19,20]—3,4-Dihydro-2*H*-pyran (12.954 g, 154 mmol) and phosphorus oxychloride (0.060 cm^3) were added to a stirred and cooled (0 °C) solution of but-3-yn-1-ol (10.787 g, 154 mmol). The ice bath was removed and, after 2 h, aqueous potassium hydroxide (1 mol dm^{-3}; 5 cm^3) was added. The mixture was extracted with diethyl ether and the combined extracts were dried ($MgSO_4$) and evaporated. Distillation of the residue gave the title compound (20.6 g, 87%) as a homogeneous [^1H NMR (400 MHz)] clear oil: b.p. 53–57 °C (0.8 mmHg) [lit.,[19] 51 °C (2 mmHg)]; ν_{max}/cm^{-1} (FT) (neat) 3285, 2940, 1120 and 1094; $\delta_H(CDCl_3$; 300 MHz) 1.44–1.90 (m, 6 H), 1.99 (br t, *J* 2.6, 1 H), 2.49 (dt, *J* 7.0, 2.8, 2 H), 3.46–3.52 (m, 2 H), 3.77–3.94 (m, 2 H) and 4.65 (t, *J* 3.3, 1 H); $\delta_C(CDCl_3$; 100.6 MHz) 19.06, 19.65, 25.18, 30.24, 61.72, 65.22, 69.15, 81.08 and 98.35 (Found: M^+, 153.0915. Calc. for $C_9H_{13}O_2$: *M*, 153.0916).

Methyldiphenyl[4-(*tetrahydro*-2H-*pyran*-2-*yloxy*)*but*-1-*ynyl*]-*silane*.—Methyllithium (1.4 mol dm^{-3} in diethyl ether; 20.4 cm^3, 28.5 mmol) was added dropwise over 10 min to a stirred and cooled (−78 °C) solution of 2-but-3-ynyloxytetrahydro-2*H*-pyran (3.67 g, 23.9 mmol) in a mixture of diethyl ether (20 cm^3) and THF (10 cm^3). Stirring was continued for 1.5 h and then methyldiphenylsilyl chloride (6.09 g, 26.18 mmol) was added over 20 min (syringe pump). Stirring at −78 °C was continued for a further 1 h, the cooling bath was removed and, after a further 3 h, water (10 cm^3) was added. The organic layer was separated and the aqueous phase was extracted with diethyl ether (2 × 20 cm^3). The combined organic layers were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (4 × 18 cm) with 10% ethyl acetate–hexane gave the *title compound* (6.42 g, 77%) as a homogeneous [^1H NMR (400 MHz)] colourless liquid: ν_{max}(film)/cm^{-1} (FT) 2840–3080, 2165 and 1430; $\delta_H(CDCl_3$; 400 MHz) 0.67 (m, 1 H), 1.42–1.91 (m, 6 H), 2.65 (t, *J* 7, 2 H), 3.45–3.52 (s, 3 H), 3.62 (dt, *J* 9.4, 7, 1 H), 3.85–3.93 (m, 2 H), 4.68 (t, *J* 3.5, 1 H), 7.32–7.42 (m, 6 H) and 7.61–7.67 (m, 4 H); $\delta_C(CDCl_3$; 100.614 MHz) −1.5 (q′), 19.61 (t′), 22.04 (t′), 25.82 (t′), 30.92 (t′), 62.34 (t′), 65.84 (t′), 82.32 (s′), 99.01 (d′), 106.17 (s′), 128.24 (d′), 129.92 (d′), 134.85 (d′) and 136.06 (s′) (Found: M^+, 350.1693. $C_{22}H_{26}O_2Si$ requires *M*, 350.1702).

4-(*Methyldiphenylsilyl*)*but*-3-*yn*-1-*ol*.—A catalytic amount of toluene-*p*-sulphonic acid monohydrate was added to a solution

of methyldiphenyl[4-(tetrahydro-2*H*-pyran-2-yloxy)but-1-ynyl]silane (6.41 g, 18.29 mmol) in methanol (50 cm^3). The mixture was stirred and refluxed for 24 h, and the methanol was then evaporated. The residue was dissolved in diethyl ether (20 cm^3) and the solution was washed with saturated aqueous sodium hydrogen carbonate (1 × 10 cm^3), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (3.5 × 18 cm) with 20% ethyl acetate–hexane gave the *title compound* (3.90 g, 80%) as a homogeneous [^1H NMR (400 MHz)] clear liquid: ν_{max}(neat)/cm^{-1} (FT) 3120–3600, 2840–2940, 2176, 1576, 1429, 1115, 792, 727 and 698; δ_H($CDCl_3$; 400 MHz) 0.80 (s, 3 H), 2.42 (t, *J* 5.5, 1 H), 2.65 (t, *J* 6.5, 2 H), 3.80 (dt, *J* 6.5, 5.5, 2 H), 7.41–7.51 (m, 6 H) and 7.73–7.89 (m, 4 H); δ_C($CDCl_3$; 100.6 MHz) −1.94, 24.35, 60.81, 83.05; 107.21, 127.92, 129.63, 134.40 and 135.40 (Found: M^+, 266.1123. $C_{17}H_{18}OSi$ requires *M*, 266.1127).

(4-*Bromobut*-1-*ynyl*)*methyldiphenylsilane* **13a**.—The procedure for the preparation of bromide **12a** was followed, using bromine (4.34 g, 27.14 mmol), triphenylphosphine (9.12 g, 28.82 mmol) in diethyl ether (30 cm^3), and 4-(methyldiphenylsilyl)-but-3-yn-1-ol (6.50 g, 24.40 mmol) and dry pyridine (2.0 cm^3, 25.80 mmol) in diethyl ether (15 cm^3). Flash chromatography of the crude product over silica gel (5 × 18 cm) with 10% ethyl acetate–hexane gave *bromide* **13a** (7.22 g, 90%) as a homogeneous [^1H NMR (400 MHz)] clear oil: ν_{max}($CDCl_3$ cast)/cm^{-1} (FT) 3059, 2179, 1429 and 1115; δ_H($CDCl_3$; 400 MHz) 0.76 (s, 3 H), 2.94 (t, *J* 7.2, 2 H), 3.54 (t, *J* 7.2, 2 H) and 7.39–7.50 (m, 4 H); δ_C($CDCl_3$; 100.6 MHz) −1.98, 24.48, 29.10, 83.51, 106.73, 127.96, 129.70, 134.50 and 135.28 (Found: C, 62.0; H, 5.3; Br, 24.35; M^+, 328.0260. $C_{17}H_{17}BrSi$ requires C, 62.00; H, 5.20; Br, 24.26%; $C_{17}H_{17}{}^{79}BrSi$ requires *M*, 328.0283).

1,9-*Bis*(*Methyldiphenylsilyl*)*nona*-1,8-*diyn*-5-*ol* **13b**.—The procedure for the preparation of alcohol **12b** was followed, using bromide **13a** (7.22 g, 21.94 mmol) in THF (20 cm^3), magnesium turnings (0.64 g, 26.34 mmol), and ethyl formate (0.89 g, 12.07 mmol) in THF (5 cm^3). Flash chromatography of the crude product over silica gel (4 × 18 cm) with 10% ethyl acetate–hexane gave *alcohol* **13b** as a homogeneous [^1H NMR (300 MHz)] oil: ν_{max}($CDCl_3$ cast)/cm^{-1} (FT) 3200–3640, 2800–3080, 2173 and 1428; δ_H($CDCl_3$; 300 MHz) 0.58 (s, 6 H), 0.97–1.18 (m, 4 H), 1.49 (d, *J* 4.7, 1 H), 1.79 (td, *J* 7.0, 3.0, 4 H), 3.14–3.26 (m, 1 H), 6.61–6.76 (m, 12 H) and 6.90–7.02 (m, 8 H); δ_C($CDCl_3$; 100.614 MHz) −1.88 (q′), 14.92 (t′), 40.13 (t′), 72.05 (d′), 81.50 (s′), 110.87 (s′), 127.91 (d′), 129.58 (d′), 134.45 (d′) and 135.58 (s′) (Found: M^+, 528.2288. $C_{35}H_{36}OSi_2$ requires *M*, 528.2305).

1,9-*Bis*(*Methyldiphenylsilyl*)*nona*-1,8-*diyn*-5-*one* **13c**.—The procedure for the preparation of ketone **12c** was followed, using alcohol **13b** (3.83 g, 7.25 mmol) in acetone (10 cm^3). Flash chromatography of the crude product over silica gel (3 × 18 cm) with 10% ethyl acetate–hexane gave *ketone* **13c** (3.40 g, 89%) as a homogeneous [^1H NMR (400 MHz)] white powder: m.p. 92–95 °C; ν_{max}($CDCl_3$ cast)/cm^{-1} (FT) 2176, 1720, 1428 and 1114; δ_H($CDCl_3$; 400 MHz) 0.65 (s, 6 H), 2.55 (br t, *J* 6.8, 4 H), 2.64 (br t, *J* 6.8, 4 H), 7.26–7.41 (m, 12 H) and 7.53–7.69 (m, 8 H); δ_C($CDCl_3$; 75.469 MHz) −1.91 (q′), 14.65 (t′), 41.55 (t′), 81.74 (s′), 109.04 (s′), 127.92 (d′), 129.61 (d′), 134.45 (d′), 135.55 (s′) and 206.07 (s′) [Found: C, 79.5; H, 6.55; (M^+ + 18) (CI) 544. $C_{35}H_{34}OSi_2$ requires C, 79.80; H, 6.51%; *M*, 526].

5-(*Dichloromethyl*)-1,9-*bis*(*methyldiphenylsilyl*)*nona*-1,8-*diyn*-5-*ol* **13d**.—The procedure for the preparation of dichloromethyl alcohol **12d** was followed, using ketone **13c** (187 mg, 0.355 mmol) in dichloromethane (5 cm^3), and dicyclohexylamine (0.14 cm^3, 0.70 mmol) and butyllithium (1.6 mol dm^{-3} in hexanes; 0.42 cm^3, 0.67 mmol) in THF (5 cm^3). Flash chromatography of the crude product over alumina (2 × 18 cm) with 10% ethyl acetate–hexane gave *dichloromethyl alcohol* **13d** (165 mg, 76%) as a homogeneous [^1H NMR; 200 MHz) clear oil: ν_{max}($CHCl_3$ cast)/cm^{-1} (FT) 3440–3600, 2840–3360, 2175 and 1429; δ_H($CDCl_3$; 200 MHz) 0.72 (s, 6 H), 2.02–2.28 (m, 4 H), 2.53 (t, *J* 7.5, 4 H), 2.65 (s, 1 H), 5.99 (s, 1 H), 7.33–7.50 (m, 12 H) and 7.61–7.74 (m, 8 H); δ_C($CDCl_3$; 75.469 MHz) −1.93 (q′), 14.30 (t′), 33.25 (t′), 77.13 (s′), 78.57 (d′), 82.44 (s′), 109.63 (s′), 127.98 (d′), 129.69 (d′), 134.50 (d′) and 135.39 (s′) [Found: C, 70.05; H, 6.15; Cl, 11.75; M^+ (EI) 610. $C_{36}H_{36}Cl_2OSi_2$ requires C, 70.68; H, 5.93; Cl, 11.59%; *M*, 610].

cis-*Octahydro*-1,6-*bis*[(*methyldiphenylsilyl*)*methylene*]*pentalen*-3a-*ol* **13e**.—The procedure for the preparation of pentalenol **12e** was followed, using dichloromethyl alcohol **13d** (92.5 mg, 0.152 mmol) in refluxing benzene (20 cm^3), tributyltin hydride (132 mg, 0.453 mmol) in benzene (5 cm^3), and AIBN (5.0 mg, 0.030 mmol) in benzene (5 cm^3). Flash chromatography of the crude product over silica gel (2 × 18 cm) with 10% ethyl acetate–hexane gave *pentalenol* **13e** (65.5 mg, 80%) as a mixture of two isomers [^1H NMR 200 MHz] which were partially separated during the flash chromatography. The *E,E* isomer had: ν_{max}($CDCl_3$ cast)/cm^{-1} (FT) 3200–3520, 2800–3080, 1626 and 1427; δ_H($CDCl_3$; 200 MHz) 0.67 (s, 6 H), 1.58 (br s, 1 H), 1.74 (t, *J* 7.7, 4 H), 2.07–2.47 (m, 4 H), 3.20 (br s, 1 H), 5.93 (q, *J* 2.0, 2 H), 7.23–7.43 (m, 12 H) and 7.47–7.67 (m, 8 H); δ_C($CDCl_3$; 50.323 MHz) −2.40, 32.00, 37.62, 68.75, 88.37, 117.92, 127.90, 129.12, 134.63, 134.68, 137.45, 137.56 and 164.98 (Found: M^+, 542.2451. $C_{36}H_{38}OSi_2$ requires *M*, 542.2461).

Irradiation of the signal at δ 3.20 in the ^1H NMR spectrum produced an enhancement of 16% in the signal at δ 5.93.

The *Z,E* isomer had: ν_{max}($CDCl_3$ cast)/cm^{-1} (FT) 3160–3600, 2800–3080, 1630 and 1427; δ_H($CDCl_3$; 400 MHz) 0.50 (s, 3 H), 0.67 (s, 3 H), 1.55 (br s, 1 H), 1.70–1.85 (m, 4 H), 2.05–2.27 (m, 2 H), 2.58–2.65 (m, 2 H), 3.02 (br s, 1 H), 5.67 (q, *J* 2.3, 1 H), 5.94 (q, *J* 1.0, 1 H), 7.22–7.46 (m, 16 H) and 7.50–7.60 (m, 4 H); δ_C($CDCl_3$; 50.323 MHz) −2.43, −2.02, 31.60, 35.66, 37.06, 64.93, 89.30, 117.97, 119.37, 127.85, 129.13, 129.55, 134.66, 134.98, 137.36, 137.96, 163.21 and 164.05 (Found: M^+, 542.2453. $C_{36}H_{38}OSi_2$ requires *M*, 542.2461).

3-(2,2,2-*Tribromo*-1-*chloroethoxy*)-1-*phenylprop*-1-*yne* **14b**.—Bromal[21] (2.0 g, 7.12 mmol), phenylprop-2-ynyl alcohol (0.94 g, 7.12 mmol), thionyl chloride (0.35 cm^3, 0.57 g, 4.80 mmol), and dry pyridine (0.88 cm^3, 10.88 mmol) were dissolved in diethyl ether (6 cm^3) and the mixture was stirred at room temperature for 3 h. The ether layer was decanted, washed with water (1 × 10 cm^3), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica (3.5 × 18 cm) with 2% ethyl acetate–hexane gave *chloro ether* **14b** (1.72 g, 56%) as a homogeneous [^1H NMR (400 MHz)] oil: ν_{max}($CHCl_3$ cast)/cm^{-1} (FT) 2090–2335, 1490 and 1109; δ_H($CDCl_3$; 400 MHz) 4.81 (dd, *J* 22.4, 16, 2 H), 6.10 (s, 1 H) and 7.29–7.51 (m, 5 H); δ_C($CDCl_3$; 100.6 MHz) 42.91, 58.88, 81.20, 89.62, 99.06, 121.66, 128.50, 129.21 and 131.94 [Found: C, 30.45; H, 1.9; (M^+ + 18) (CI) 450. $C_{11}H_8Br_3ClO$ requires C, 30.43; H, 1.85%; $C_{11}H_8{}^{81}Br_2{}^{79}Br^{35}ClO$ requires *M*, 432].

3-(2,2-*Dibromoethenyloxy*)-1-*phenylprop*-1-*yne* **14c**.—Zinc dust (0.31 g, 4.74 mmol) was added to a solution of chloro ether **14b** (1.72 g, 3.99 mmol) in methanol (4 cm^3), and the suspension was stirred at 50–60 °C for 4 h. The mixture was cooled to room temperature and filtered through a pad (1 × 2 cm) of Celite. Evaporation of the filtrate and flash chromatography of the residue over silica (2.2 × 18 cm) with 5% ethyl acetate–hexane gave *vinyl ether* **14c** (0.95 g, 75%) as a homogeneous [^1H NMR (400 MHz)] oil: ν_{max}(CH_2Cl_2 cast)/cm^{-1} (FT) 2400–3600 and

1736; $\delta_H(CDCl_3$; 400 MHz) 4.71 (s, 2 H), 7.04 (s, 1 H), 7.26–7.37 (m, 3 H) and 7.41–7.47 (m, 2 H); $\delta_C(CDCl_3$; 100.6 MHz) 60.55, 72.99, 82.52, 88.62, 121.62, 128.36, 129.04, 131.87 and 146.24 [Found: C, 41.4; H, 2.65; (M^+ + 18) (CI) 334. $C_{11}H_8Br_2O$ requires C, 41.81; H, 2.5%; $C_{11}H_8{}^{81}Br^{79}BrO$ requires *M*, 318].

1,1-*Dibromo*-2,2-*bis*(3-*phenylprop*-2-*ynyloxy*)*ethane* **14d**.—Vinyl ether **14c** (1.006 g, 3.19 mmol), phenylprop-2-ynyl alcohol (1.0 g, 7.58 mmol), and concentrated hydrochloric acid (3 drops) were mixed and stirred at 110 °C for 4 h. The mixture was cooled, and flash chromatography of the material over grade III neutral alumina (3.5 × 18 cm) with 5% ethyl acetate–hexane gave *dibromomethyl ketal* **14d** (728 mg, 51%) as a homogeneous [^{1}H NMR (400 MHz)] clear oil: $\nu_{max}(CHCl_3$ cast)/cm^{-1} (FT) 2318, 1490, 1103, 1069 and 1045; $\delta_H(CDCl_3$; 400 MHz) 4.68 (d, *J* 16, 2 H), 4.75 (d, *J* 16, 2 H), 5.22 (d, *J* 4, 1 H), 5.74 (d, *J* 4, 1 H) and 7.24–7.47 (m, 10 H); $\delta_C(CDCl_3$; 100.6 MHz) 44.10, 57.11, 83.68, 87.73, 100.61, 122.07, 128.34, 128.77 and 131.86 [Found: (M^+ + 18) (CI) 466. $C_{20}H_{16}{}^{81}Br^{79}BrO_2$ requires *M*, 448].

cis-3,4-*Bis*(*phenylmethylene*)*hexahydrofuro*[2,3-b]*furan* **14e**.—The procedure for the preparation of pentalenol **12e** was followed, using dibromomethyl ketal **14d** (223 mg, 0.50 mmol) in benzene (40 cm^3), tributyltin hydride (320 mg, 1.10 mmol) in benzene (5 cm^3), and AIBN (16.4 mg, 0.10 mmol) in benzene (5 cm^3). Flash chromatography of the crude product over silica gel (2 × 18 cm) with 10% ethyl acetate–hexane gave compound **14e** as a mixture of two *isomers* [^{1}H NMR 200 MHz] (77.07 mg, 53%). The compounds were separated by HPLC (UV detector; 20% diethyl ether–hexane at a flow rate of 4.5 cm^3 min^{-1}). The *Z,Z* isomer had: $\nu_{max}(CDCl_3$ cast)/cm^{-1} (FT) 2820–3300, 1495, 1450 and 1025; $\delta_H(CDCl_3$; 400 MHz) 3.95–4.00 (m, 1 H), 4.77 (dd, *J* 13.8, 2.2, 1 H), 4.86 (dt, *J* 13.8, 2.2, 4 H), 5.90 (d, *J* 4.5, 1 H), 6.60 (q, *J* 2.0, 2 H), 7.12–7.18 (m, 4 H), 7.22–7.30 (m, 2 H) and 7.33–7.40 (m, 4 H); $\delta_C(CDCl_3$; 100.614 MHz) 18.07, 69.55, 106.77, 123.38, 127.25, 128.28, 128.64 and 141.35 (Found: M^+, 290.1314. $C_{20}H_{18}O_2$ requires *M*, 290.1307).

Irradiation of the signal at δ 4.0 in the ^{1}H NMR spectrum produced enhancements of 21 and 27% in the signals at δ 6.60 and 5.90, respectively.

The *Z,E* isomer had $\nu_{max}(CDCl_3$ cast)/cm^{-1} (FT) 2820–3080 and 1026; $\delta_H(CDCl_3$; 400 MHz) 4.45 [dd, *J* 12.0, 1.5 (including br s at δ 4.44) 2 H], 4.69 (dt, *J* 12.0, 1.5, 1 H), 4.90 (q, *J* 1.4, 2 H), 5.85 (d, *J* 4.5, 1 H), 6.38 (q, *J* 2.3, 1 H), 6.50 (d, *J* 1.0, 1 H) and 7.02–7.52 (m, 10 H); $\delta_C(CDCl_3$; 100.614 MHz) 18.07, 50.99, 70.78, 72.03, 108.71, 122.84, 124.08, 127.27, 127.61, 128.32, 128.57, 128.89, 139.59 and 140.04 (Found: M^+, 290.1316. $C_{20}H_{18}O_2$ requires *M*, 290.1307).

Irradiation of the signal at δ 4.45 in the ^{1}H NMR spectrum produced an enhancement of 12% in the aromatic hydrogen signal at δ 7.5, and an enhancement of 15% in the signal at δ 5.85.

1-*Bromo*-2-(*phenylethynyl*)*benzene*[22] *and* 2-(*Phenylethynyl*)-*benzaldehyde* **15a**.[9]—Copper(I) phenylacetylide (1.29 g, 7.84 mmol) was stirred in dry pyridine (50 cm^3) for 20 min (argon atmosphere). 1-Bromo-2-iodobenzene (1.85 g, 6.55 mmol) was added, and the mixture was refluxed for 10 h, cooled and poured into diethyl ether (100 cm^3). The solution was washed with 10% aqueous hydrochloric acid (2 × 20 cm^3), saturated aqueous cupric sulphate (2 × 20 cm^3), and water (1 × 20 cm^3), and the organic phase was dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 × 18 cm) with 2% ethyl acetate–hexane gave 1-bromo-2-(phenylethynyl)benzene (1.41 g, 84%) as a homogeneous [^{1}H NMR (200 MHz)] clear oil: b.p. 160–165 °C (0.22 mmHg) [lit.,[22] 155–160 °C (0.7 mmHg)]; $\delta_H(CDCl_3$; 200 MHz) 7.04–7.63 (m); $\delta_C(CDCl_3$; 100.614 MHz) 88.07 (s'), 93.97 (s'), 122.94 (s'), 125.43 (s'), 125.66 (s'), 127.03 (d'), 128.39 (d'), 128.65 (d'), 131.71 (d'), 132.46 (d') and 133.23 (d'). The compound was converted by the literature method[9] into 2-(phenylethynyl)benzaldehyde **15a**.

1-[(2-*Phenylethynyl*)*phenyl*]-2,2-*bis*(*phenylseleno*)*ethanol* **15b**.—Bis(phenylseleno)methane[23] (529.7 mg, 1.69 mmol) in THF (2 cm^3) was added over 10 min to a stirred and cooled (−78 °C) solution of potassium diisopropylamide [prepared by addition of butyllithium (1.6 mol dm^{-3} in hexanes; 1.05 cm^3, 1.69 mmol) to a stirred and cooled (−78 °C) solution of potassium *tert*-butoxide (218 mg, 1.95 mmol) and diisopropylamine (0.272 cm^3, 1.95 mmol) in THF (5 cm^3)]. Stirring at −78 °C was continued for a further 10 min, and aldehyde **15a**[9] (263 mg, 1.28 mmol) in THF (3 cm^3) was added over 2 min. After 2 h at −78 °C the mixture was quenched with saturated aqueous ammonium chloride (10 cm^3) and the cooling bath was removed. The mixture was extracted with diethyl ether (2 × 20 cm^3), and the combined ether extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (4 × 18 cm) with 10% ethyl acetate–hexane gave *alcohol* **15b** (550 mg, 81%) as a homogeneous [^{1}H NMR (400 MHz)] pale yellow oil: $\nu_{max}(CH_2Cl_2$ cast)/cm^{-1} (FT) 3440, 3057, 1577, 1492, 1475 and 1437; $\delta_H(CDCl_3$; 400 MHz) 3.37 (d, *J* 4.2, 1 H), 5.23 (d, *J* 3.8, 1 H), 5.50 (t, *J* 3.7, 1 H), 6.93–7.38 (m, 16 H), 7.45–7.52 (m, 2 H) and 7.66–7.73 (m, 1 H); $\delta_C(CDCl_3$; 100.614 MHz) 53.29 (d'), 73.22 (d'), 86.86 (s'), 94.85 (s'), 122.70 (s'), 127.03 (d'), 127.42 (d'), 127.58 (d'), 128.10 (d'), 128.23 (d'), 128.41 (d'), 128.48 (d'), 128.69 (d'), 128.94 (d'), 129.73 (s'), 129.80 (s'), 131.56 (d'), 132.17 (d'), 134.14 (d'), 134.96 (d'), 136.90 (d') and 142.20 (s') (Found: C, 62.95; H, 4.5; M^+, 534.0007. $C_{28}H_{22}OSe_2$ requires C, 63.17; H, 4.16%; *M*, 534.0001).

1-{1-[2-(*Phenylethynyl*)*phenyl*]-2,2-*bis*(*phenylseleno*)*ethoxy*}-3-*phenylprop*-2-*yne* **15c**.—Sodium hydride (60% dispersion in oil; 66 mg, 1.65 mmol) was added to a stirred solution of alcohol **15b** (615 mg, 1.16 mmol) and phenylprop-2-ynyl bromide (676 mg, 3.48 mmol) in THF (20 cm^3). The mixture was refluxed for 1 h, cooled to room temperature, quenched with saturated aqueous ammonium chloride (20 cm^3), and extracted with diethyl ether (2 × 20 cm^3). The combined ether extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (3 × 18 cm) with 5% ethyl acetate–hexane gave *bis*(*phenylseleno*) *ketal* **15c** (569 mg, 76%) as a homogeneous [^{1}H NMR (400 MHz)] clear oil: $\nu_{max}(CH_2Cl_2$ cast)/cm^{-1} (FT) 3175–3010, 1488, 1478 and 1440; $\delta_H(CDCl_3$; 400 MHz) 4.30 (d, *J* 16.0, 1 H), 4.57 (d, *J* 16.0, 1 H), 4.96 (d, *J* 3.5, 1 H), 5.99 (d, *J* 3.5, 1 H), 6.91 (d, *J* 4.4, 4 H), 6.94–7.48 (m, 19 H) and 7.72 (d, *J* 8, 1 H); $\delta_C(CDCl_3$; 100.6 MHz) 51.97 (d'), 57.40 (t'), 80.96 (d'), 84.84 (s'), 86.76 (s'), 87.32 (s'), 95.30 (s'), 122.22 (s'), 122.59 (s'), 122.75 (s'), 127.17 (d'), 127.66 (d'), 127.71 (d'), 127.79 (d'), 128.12 (d'), 128.16 (d'), 128.27 (d'), 128.42 (d'), 128.71 (d'), 130.51 (s'), 131.07 (s'), 131.68 (d'), 131.74 (d'), 132.00 (d'), 134.20 (d'), 134.91 (d') and 140.60 (s') (Found: M^+, 648.0464. $C_{27}H_{28}OSe_2$ requires *M*, 648.0471).

cis-3,4-*Bis*(*phenylmethylene*)-3,3a,4,8b-*tetrahydro*-2H-*indeno*-[1,2-b]*furan* **15d**.—Tributyltin hydride (496 mg, 1.70 mmol) and triethylborane (1.0 mol dm^{-3} solution in hexane; 1.7 cm^3, 1.70 mmol) were added to a solution of bis(phenylseleno) ketal **15c** (501 mg, 0.775 mmol) in hexane (40 cm^3) and benzene (10 cm^3). The mixture was stirred for 10 h with protection from the atmosphere by a drying tube packed with Drierite, and the solvent was then evaporated. Flash chromatography of the residue over silica gel (2 × 18 cm) with 10% ethyl acetate–hexane gave compound **15d**. The material was obtained as two fractions. The first (less polar) was a mixture of two isomers **A**

and **B** (64 mg, 20.8%) and the second contained only a third isomer **C** (45 mg, 17%). Isomers **A** and **B** were partially separated by HPLC (UV detector; 10% ethyl acetate–hexane at a flow rate of 4.0 cm^3 min^{-1}). Isomer **A** (less polar; *Z,Z* geometry, containing 28% of isomer **B**) had: $\nu_{max}(CDCl_3$ cast)/cm^{-1} (FT) 2800–3120, 1492 and 1061; $\delta_H(CDCl_3$; 400 MHz) 4.14 (dd, *J* 7.4, 1.5, 1 H), 4.43 (dt, *J* 13.5, 2.2, 1 H), 4.77 (dd, *J* 13.5, 2.0, 1 H), 5.67 (d, *J* 6.6, 1 H), 6.71 (q, *J* 2.0, 1 H), 6.86 (s, 1 H) and 7.02–7.70 (m, 14 H); $\delta_C(CDCl_3$; 100.614 MHz) 56.00, 69.20, 83.09, 122.65, 124.52, 125.82, 126.87, 127.25, 128.52, 128.55, 128.58, 129.08, 137.35, 137.70, 138.34, 142.66, 144.00 and 145.50 (Found: M^+, 336.1512. $C_{25}H_{20}O$ requires *M*, 336.1514).

Irradiation of the signal at δ 4.14 in the ^1H NMR spectrum produced enhancements of 6, 12 and 24% in the signals at δ 6.71, 6.86 and 5.67, respectively.

Isomer **B** (geometry not determined) had: $\nu_{max}(CDCl_3$ cast)/cm^{-1} (FT) 2800–3120, 1493 and 1063; $\delta_H(CDCl_3$; 400 MHz) 4.51 (dt, *J* 13.6, 2.1, 1 H), 4.79 (d, *J* 6.8, 1 H), 4.90 (dq, *J* 13.6, 1.0, 1 H), 5.73 (d, *J* 6.8, 1 H), 6.41 (q, *J* 2.3, 1 H), 6.96 (d, *J* 7.2, 1 H) and 7.10–7.70 (m, 14 H); $\delta_C(CDCl_3$; 100.614 MHz) 51.87, 70.02, 84.56, 120.61, 121.75, 123.30, 125.62, 126.83, 127.35, 128.29, 128.33, 128.39, 128.93, 137.03, 137.19, 141.29, 141.43, 141.94 and 142.91 (Found: M^+, 336.1512. $C_{25}H_{20}O$ requires *M*, 336.1514).

Isomer **C** (geometry not determined) had: $\nu_{max}(CDCl_3$ cast)/cm^{-1} (FT) 3100–2800, 1475 and 1060; $\delta_H(CDCl_3$; 400 MHz) 3.71 (dq, *J* 6.6, 1.8, 1 H), 4.28 (dd, *J* 13.6, 1.8, 1 H), 4.83 (dd, *J* 13.6, 1.2, 1 H), 5.80 (d, *J* 6.6, 1 H) and 7.00–7.68 (m, 16 H); $\delta_C(CDCl_3$; 50.323 MHz) 49.10, 72.56, 86.13, 119.07, 121.21, 125.55, 126.20, 126.27, 127.17, 128.24, 129.22, 129.58, 130.28, 131.54, 136.88, 139.65, 140.65, 140.75, 142.00 and 145.01 (Found: M^+, 336.1499. $C_{25}H_{20}O$ requires *M*, 336.1514).

(E)-1-{1-[2-(*Phenylethynyl*)*phenyl*]-2,2-*bis*(*phenylseleno*)*ethoxy*}-3-*phenylprop*-2-*ene* **16a**.—Sodium hydride (60% dispersion in oil; 63 mg, 1.58 mmol) was added to a stirred solution of alcohol **15b** (844 mg, 1.58 mmol) and cinnamyl bromide (320 mg, 1.58 mmol) in THF (20 cm^3). The mixture was refluxed for 2 h, cooled to room temperature, quenched with saturated aqueous ammonium chloride (10 cm^3), and extracted with diethyl ether (2 × 20 cm^3). The combined ether extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (4 × 18 cm) with 5% ethyl acetate–hexane gave compound **16a** (682 mg, 66%) as a homogeneous [^1H NMR (400 MHz)] clear oil: $\nu_{max}(CDCl_3$ cast)/cm^{-1} (FT) 3080–3000, 1494, 1475 and 1440; $\delta_H(CDCl_3$; 400 MHz) 4.03 (ddd, *J* 12.8, 6.9, 1.4, 1 H), 4.31 (ddd, *J* 12.8, 6.9, 1.4, 1 H), 4.94 (d, *J* 3.5, 1 H), 5.62 (d, *J* 3.5, 1 H), 6.35 (ddd, *J* 16.0, 6.8, 5.6, 1 H), 6.60 (d, *J* 16.0, 1 H), 6.90–7.44 (m, 23 H) and 7.73 (d, *J* 7.5, 1 H); $\delta_C(CDCl_3$; 100.6 MHz) 52.34 (d′), 70.33 (t′), 81.83 (d′), 87.02 (s′), 95.40 (s′), 122.27 (s′), 123.02 (s′), 125.91 (d′), 126.91 (d′), 127.49 (d′), 127.93 (d′), 127.98 (d′), 128.51 (d′), 128.60 (d′), 129.03 (d′), 130.92 (s′), 131.34 (s′), 131.94 (d′), 132.34 (d′), 133.23 (d′), 134.42 (d′), 136.99 (s′) and 141.54 (s′) (Found: M^+, 650.0596. $C_{37}H_{30}OSe_2$ requires *M*, 650.0627).

3α,3aα,8bα- *and* 3α,3aβ,8bβ-3-(*Phenylmethyl*)-4-(*phenylmethylene*)-3,3a,4,8b-*tetrahydro*-2H-*indeno*[1,2-b]*furan* **16b**.—The procedure for the preparation of compound **15d** was followed, using compound **16a** (670 mg, 1.03 mmol) in hexane (40 cm^3) and benzene (10 cm^3), triethylborane (1 mol dm^{-3} in hexane; 2.3 cm^3, 2.27 mmol), and tributyltin hydride (0.61 cm^3, 2.27 mmol). Flash chromatography of the crude product over silica gel (3 × 18 cm) with 5% ethyl acetate–hexane gave compound **16b** (167 mg, 47%) as a mixture of two isomers* which were separated by HPLC (UV detector; 7% ethyl acetate–hexane at a flow rate of 4.0 cm^3 min^{-1}). The less polar isomer [tentatively assigned 3α,3aα,8bα stereochemistry] had: ν_{max}-($CHCl_3$ cast)/cm^{-1} (FT) 3140–2830, 1494; $\delta_H(CDCl_3$; 400 MHz) 2.32 (d t, *J* 11.0, 4.2, 1 H), 2.71 (dd, *J* 13.0, 11.0, 1 H), 2.92 (dd, *J* 13.0, *J* 4.0, 1 H), 3.13 (ddd, *J* 9.0; 4,4, 1.2, 1 H), 3.50 (d, *J* 9.0, 1 H), 3.84 (br d, *J* 6.5, 1 H), 5.70 (d, *J* 6.9, 1 H) and 6.97–7.60 (m, 15 H); $\delta_C(CDCl_3$; 50.32 MHz) 40.13, 47.63, 52.04, 68.19, 84.04, 119.53, 121.01, 126.19, 126.37, 127.01, 128.43, 128.61, 128.79, 129.17, 137.22, 140.47, 142.54, 142.96 and 143.92 (Found: M^+, 338.1669. $C_{25}H_{22}O$ requires *M*, 338.1670).

Irradiation of the signal at δ 3.84 in the ^1H NMR spectrum produced enhancements of 18 and 20% in the signals at δ 7.54 and 5.70, respectively.

The more polar isomer [tentatively assigned 3α,3aβ,8bβ stereochemistry] had: $\nu_{max}(CDCl_3$ cast)/cm^{-1} (FT) 3120–2810, 1494; $\delta_H(CDCl_3$; 200 MHz) 2.05 (t, *J* 13.0, 1 H), 2.71–3.00 (m, 2 H), 3.47 (dd, *J* 8.8, 5.5, 1 H), 3.85 (dd, *J* 9.0, 6.0, 1 H), 4.21 (ddd, *J* 11.6, 7.0, 2.0, 1 H), 5.65 (d, *J* 7.0, 1 H) and 6.86–7.70 (m, 15 H); $\delta_C(CDCl_3$; 50.32 MHz) 35.12, 44.64, 49.94, 73.01, 86.36, 119.80, 122.30, 125.54, 125.94, 127.19, 128.37, 128.70, 128.84, 129.03, 129.10, 137.45, 140.46, 142.96 and 143.26 (Found: M^+, 338.1667. $C_{25}H_{22}O$ requires *M*, 338.1670).

Irradiation of the signal at δ 4.20 in the ^1H NMR spectrum produced enhancements of 18, 25 and 18% in the signals at δ 7.64, 5.65 and 2.9, respectively.

Bis-O-[(Z)-4-*phenylbut*-3-*enyl*] *Thiocarbonate* **17**.—A solution of (*Z*)-4-phenylbut-3-en-1-ol[24] (0.448 g, 3.03 mmol) and 1,1′-thiocarbonyldiimidazole (0.270 g, 1.51 mmol) in 1,2-dichloroethane (5 cm^3) was refluxed for 2 h. The solvent was evaporated, and flash chromatograhy of the residue over silica gel (2 × 18 cm) with 5% ethyl acetate–hexane gave *thiocarbonate* **17** (182 mg, 35%) as a homogeneous [^1H NMR, 400 MHz] pale yellow oil: $\nu_{max}(CDCl_3$ cast)/cm^{-1} (FT) 1307, 1286 and 1298; $\delta_H(CDCl_3$; 400 MHz) 2.75 (qd, *J* 7.0, 1.8, 4 H), 4.58 (t, *J* 6.7, 4 H), 5.64 (dt, *J* 11.5; 7.2, 1 H), 6.54 (d, *J* 11.5, 1 H) and 7.17–7.36 (m, 10 H); $\delta_C(CDCl_3$; 100.614 MHz) 27.80 (t′), 72.37 (t′), 126.59 (d′), 127.00 (d′), 128.32 (d′), 128.71 (d′), 131.88 (d′), 137.01 (s′) and 195.53 (s′) (Found: C, 74.25; H, 6.7; S, 9.2; M^+, 338.1324. $C_{21}H_{22}O_2S$ requires C, 74.52; H, 6.55; S, 9.47%; *M*, 338.1342).

1,1-*Bis*(*phenylseleno*)*hex*-5-*ene*.[25]—Tris(phenylseleno)borane[26] (0.683 g, 1.43 mmol) and trifluoroacetic acid (0.017 cm^3, 0.22 mmol) were added to a solution of hex-5-enal (210 mg, 2.14 mmol) in chloroform (2 cm^3). The mixture was stirred at room temperature for 8 h, then washed with saturated aqueous sodium hydrogen carbonate (2 cm^3) and water (2 cm^3), dried ($MgSO_4$), and evaporated. Flash chromatography of the residue over silica gel (2 × 18 cm), using first hexane and then 1% ethyl acetate–hexane, gave 1,1-bis(phenylseleno)hex-5-ene (350 mg, 42%) as a homogeneous [^1H NMR 200 MHz] yellow oil: $\nu_{max}(CH_2Cl_2$ cast)/cm^{-1} 3070, 2990, 1578, 1475 and 1438; $\delta_H(CDCl_3$; 200.132 MHz) 1.58–1.74 (m, 2 H), 1.86–2.06 (m, 4 H), 4,48 (t, *J* 6.5, 1 H), 4.85–5.00 (m, 2 H), 5.70 (ddt, *J* 17.0, 10.2, 6.5, 1 H), 7.19–7.34 (m, 6 H) and 7.50–7.63 (m, 4 H); $\delta_C(CDCl_3$; 100.614 MHz) 27.57, 32.93, 36.61, 114.90, 127.97, 129.02, 130.41, 134.72 and 138.11 (Found: M^+, 395. 9819. Calc. for $C_{18}H_{20}Se_2$: *M*, 395.9895).

1-[2-(*Phenylethynyl*)*phenyl*]-2,2-*bis*(*phenylseleno*)*hept*-6-*en*-1-*ol* **18**.—1,1-Bis(phenylseleno)hex-5-ene (250 mg, 0.634 mmol) in THF (2 cm^3) was added to a stirred and cooled (−78 °C) solution of potassium diisopropylamide, generated as described for the preparation of alcohol **15b**, using butyllithium (1.6 mol dm^{-3} in hexanes; 0.43 cm^3, 0.688 mmol), and potassium *tert*-butoxide (89 mg, 0.792 mmol) and diisopropylamine (0.11 cm^3,

* A minor (*ca.* 2%) isomer (^1H NMR) was also isolated by HPLC.

0.792 mmol) in THF (5 cm^3). The mixture was stirred for 10 min at −78 °C, and aldehyde **15a** (109 mg, 0.528 mmol) in THF (4 cm^3) was added over 1 min. Stirring was continued for 1 h, and the mixture was then quenched with water (5 cm^3), allowed to attain room temperature, and extracted with diethyl ether (2 × 10 cm^3). The combined ether extracts were dried ($MgSO_4$) and evaporated. Flash chromatography of the residue over silica gel (2 × 18) with 10% ethyl acetate–hexane gave the *bis(phenylseleno) ketal* **18** (137 mg, 43%) as a homogeneous [^{1}H NMR 200 MHz] clear oil: ν_{max}(CH_2Cl_2 cast)/cm^{-1} (FT) 3459, 3057, 2940, 1492, 1475 and 1436; δ_H($CDCl_3$; 200 MHz) 1.48–2.16 (m, 6 H), 3.80 (d, *J* 1.6, 1 H), 4.66–4.83 (m, 2 H), 5.30 (d, *J* 1.6, 1 H), 5.51 (ddt, *J* 17.0, 10.0, 3.2, 1 H), 6.95–7.63 (m, 18 H) and 8.19 (br d, *J* 8, 1 H); δ_C($CDCl_3$; 100.614 MHz) 26.66, 33.56, 36.02, 70.62, 74.87, 87.81, 93.89, 114.60, 122.86, 123.59, 126.93, 127.88, 128.05, 128.18, 128.612, 128.96, 129.04, 129.22, 130.08, 131.48, 132.27, 137.22, 137.98, 138.18 and 139.92 [Found: (M^+ − PhSe), 445.1073. $C_{27}H_{25}OSe$ (M^+ − PhSe) requires *M*, 445.1071].

Diethyl 2,2-Di(prop-2-enyl)propanedioate **20** *and Diethyl 2-(prop-2-enyl)propanedioate* **21**.—A solution of AIBN (10.2 mg, 0.062 mmol) in benzene (6 cm^3) was added over 8 h to a refluxing solution of diethyl dibromomalonate (192 mg, 0.623 mmol) and allyltributyltin (2.05 g, 6.23 mmol) in benzene (1.7 cm^3). The solution was refluxed for an additonal 4 h, cooled, and evaporated. Flash chromatography of the residue over silica gel (2 × 18 cm) with 1:5:44 ethyl acetate–dichloromethane–hexane gave the double **20**[27] and single **21**[28] addition products in 49 and 27% yield, respectively, as homogeneous [^{1}H NMR 300 MHz] oils. *Compound* **20** had: ν_{max}($CDCl_3$ cast)/cm^{-1} (FT) 2981, 1734 and 1195; δ_H($CDCl_3$; 300 MHz) 1.20 (t, *J* 6.6, 6 H), 2.58 (br d, *J* 14.8, 4 H), 4.12 (q, *J* 7.0, 4 H), 5.00–5.10 (m, 4 H) and 5.51–5.68 (m, 2 H); δ_C($CDCl_3$; 75.469 MHz) 14.03 (q′), 36.70 (t′), 57.17 (s′), 61.10 (t′), 118.99 (t′), 132.30 (d′) and 170.62 (s′) (Found: C, 65.1; H, 8.4; M^+, 240.1360. $C_{13}H_{20}O_4$ requires C, 64.98; H, 8.39%; *M*, 240.1361).

Compound **21** had: ν_{max}($CDCl_3$ cast)/cm^{-1} (FT) 2970, 1750 and 1734; δ_H($CDCl_3$; 300 MHz) 1.27 (t, *J* 7.1, 6 H), 2.65 (tt, *J* 7.1, 1.3, 2 H), 3.42 (t, *J* 7.5, 1 H), 4.20 (qd, *J* 7.1, 0.6, 4 H), 5.03–5.17 (m, 2 H), and 5.78 (ddt, *J* 17.0, 10.0, 6.6, 1 H); δ_C($CDCl_3$); 75.469 MHz) 14.08 (q′), 32.82 (t′), 51.68 (d′), 61.38 (t′), 117.49 (t′), 134.11 (d′) and 168.92 (s′) (Found: C, 60.45; H, 8.2; M^+, 200.1048. $C_{10}H_{16}O_4$ requires C, 59.98; H, 8.05%; *M*, 200.1649).

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