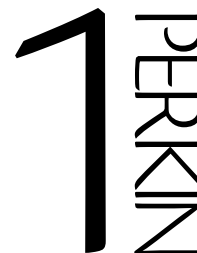# Proposed tennis ball and basket- and -lid routes to C_{60}: two relevant C_{45} compounds †

Robert J. Ferrier,*‡ Steven G. Holden and Olga Gladkikh

School of Chemical and Physical Sciences, Victoria University of Wellington, P.O. Box 600, Wellington, New Zealand

Two formal synthetic routes to C_{60}, both heavily symmetry dependent and based on the use of the $C_{15}H_{18}$ hydrocarbon "trindane" (**1**) which is a repeating unit within the spherical structure, are proposed. One relies on Diels–Alder coupling of the two C_{30} derivatives **5** and **6** of the readily prepared "trindanone" dimer **3** to give the T-shaped molecule **7** which on dehydration and dehydrogenation could afford the spherical target by a "tennis ball" approach. The other is based on the C_{45} bowl-like trindane trimer **17** which could be capped by a C_{15} lid to afford **18** prior to dehydrogenation. Progress along these routes is reported and the two relevant but "off-route" C_{45} compounds **19** and **24** are described, their structures being determined by X-ray crystallographic methods.

Introduction

While the discovery[1] and isolation[2] of C_{60} have led to Nobel Prizes[3] and to considerable advances in the understanding of its organic chemistry,[4] the formal synthesis remains a major challenge despite the apparent simplicity conferred by the symmetry of its spherical structure and the considerable effort expended.[5] First attempts were made in the 1980s by O. L. Chapman's group even before this allotrope of carbon had been identified.[5] In the decade during which C_{60} has been known, synthetic progress toward the goal has been limited to the production of hydrocarbons representing sizeable parts of the target and to C_{60} hydrocarbons with appropriate C–C connectivity to allow generation of the sphere by complete and specific dehydrogenation. It might fairly be concluded that few if any of these approaches suggest practicable methods that might compare with the production procedures dependent on energising graphite[6] or sooting simple hydrocarbons.[7]

We are persuaded that the solution to the problem of a formal synthesis lies in finding feasible means of exploiting the symmetry, and we doubt that a useful solution will result from complex multi-step procedures which do not depend extensively on this feature. Furthermore, we see it as highly desirable that the requisite 12 five-membered rings be established at a very early point and predict that when a good synthetic route is discovered it will also rely on this feature, and we here suggest relevant approaches in this context. In the meantime, the strained spherical geometry of C_{60} represents a particular challenge to synthesisers, with the obvious incentive remaining, however, that it can be made to form spontaneously just by energising various carbon sources under appropriate conditions.[6,7]

Semi-buckminsterfullerenes,[8] and C_{36}[9] and C_{48}[10] hydrocarbons representing 50, 60 and 80% respectively of the surface of C_{60} have been reported, but they were often not designed to lead on to the final goal. The same does not apply, however, to a $C_{60}H_{18}$ poly-yne,[11] and other projected C_{60} poly-ynes,[12] a tricyclic cage-like $C_{60}H_{60}$ containing 7 benzenoid rings linked by 9 C_2 bridges[13] and another compound ($C_{60}H_{36}$) with 3-fold symmetry which is effectively planar and built of 13 benzene rings.[14] Each of these has C–C connectivities to permit C_{60} formation, but none have yet been induced to yield the elusive product on dehydrogenative treatment.[5]

Considerations of the hydrocarbons which have carbon structures representative of components of C_{60}, and which could serve as potential starting-materials for synthesis, have often, but not always,[7a] disregarded the one candidate that meets a key criterion as a synthetic precursor, *i.e.* of having a structure which is a repeating unit within the target. Being "semi-semi-buckminsterfullerene", the $C_{15}H_{18}$ hydrocarbon "trindane" (**1**) not only meets the criterion, but as a "tetramer" would provide the 12 cyclopentane rings required. Furthermore, four trindane structures placed uniformly on the surface of C_{60} as a spherical template leave 16 hexagonal spaces, each of which must become a benzenoid ring for the formation of the target. From this perspective the production of C_{60} requires methods which result in the abstraction of 36 molecules of hydrogen for each set of four trindane molecules. To add to its attractiveness as a basic building-block, trindane is available as a stable crystalline compound by one-step trimerisation of cyclopentanone,[15] and is eminently selectively functionalisable.

Our early attempts to dehydrogenate trindane by pyrolysis,[16] by exposure to high temperatures and pressures[17] or flash vacuum pyrolysis conditions[18] did not yield detectable quantities of C_{60}, although other workers have reported "trace amounts" in the pyrolysates of this hydrocarbon and several others that did not represent constitutional parts of the target structure.[7a] Attention therefore turned to a trindane-based rational synthetic route.

In 1989 French workers prepared "trindanone" (**2**) from the hydrocarbon and converted it to its aldol dimer (**3a**) during which process an insoluble trimer was also formed. On the basis of its mass-spectrometrically-determined molecular weight the trimer was assigned the structure **4**, which represents 75% of the carbon network of C_{60}.[19] It is here suggested that the isomeric enones **3a** and **3b**, both of which are formed in dimerisations of trindanone (**2**), could be key intermediaries for a rational C_{60} synthesis because from them diene **5** and the ene **6** should be derivable, and these, when coupled orthogonally (in one of two possible ways *cf.* Scheme 5; **16**, **19**) by Diels–Alder

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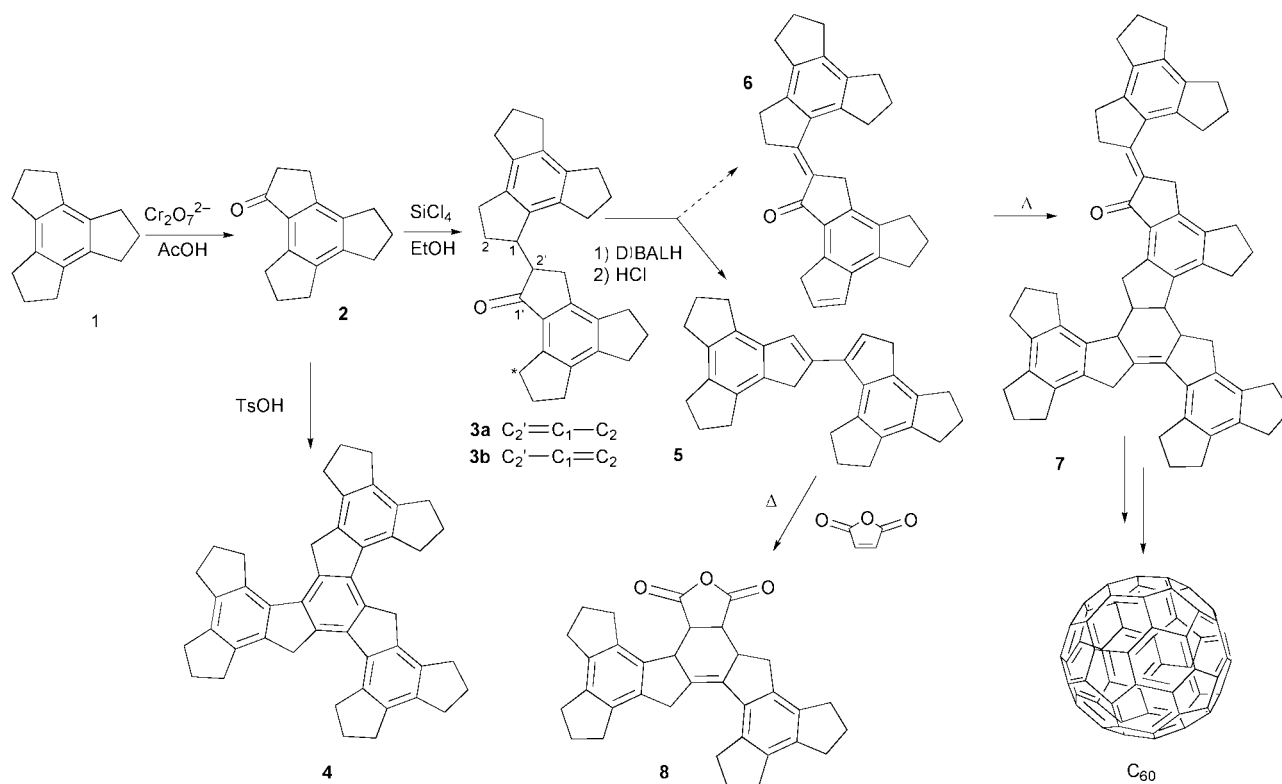
Scheme 1

cycloaddition, would give the "T-shaped" $C_{60}H_{58}O$ ketone **7** (Scheme 1) which has the correct carbon framework for step-by-step dehydration–dehydrogenation to give the target (Scheme 2).

In Scheme 2 the diagrams represent energy-minimised structures,[20] it being envisaged that under dehydration–dehydrogenation conditions initial loss of two molecules of hydrogen from **7** would result in aromatisation of the newly formed "central" cyclohexene ring (H's identified) and that subsequent loss is likely to occur between adjacent pairs of carbon atoms. In the Scheme new C–C double bonds are formed between the closest pairs of relevant methylene groups, each diagram having two more six-membered rings than its precursor. For each step of the process the 8 hydrogen atoms removed are indicated, and each cyclisation involves the molecular unit **9** (Scheme 3).§ Since ethylbenzene can be dehydrogenated to give stryene at high temperatures over a

catalyst in an industrial synthesis,[21] and particularly since indane likewise affords indene,[22] it is envisaged that unit **9** would lose hydrogen to give **10** which would further dehydrogenate as shown (or conjugatively) to **11**, the new ring being subject to aromatisation to give **12**.

This is thus a "tennis ball" design for the "black pentagon soccer ball",[3b] and although this approach to making co-valently bonded spherical molecules seems to have few if any precedents, it does have one in the work of Rebek and colleagues[23] who have used it to produce spherical cage-like complexes made from pairs of complementary orthogonally-oriented self-assembling molecules bound by reciprocating non-covalent forces.
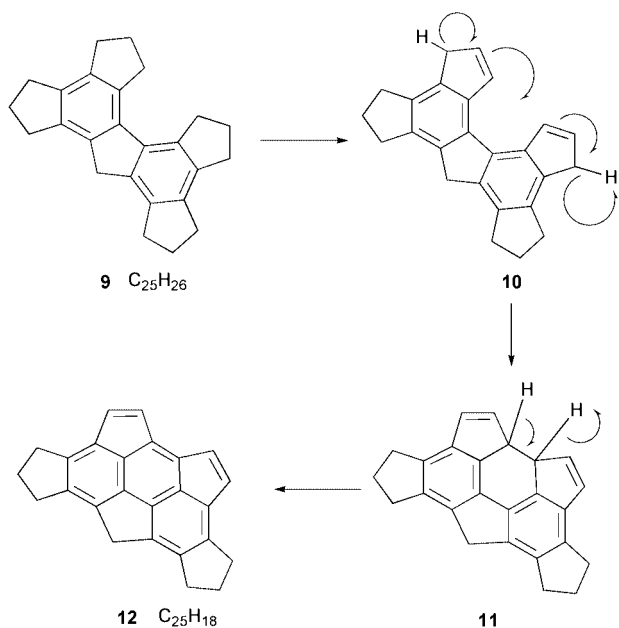
Results and discussion

While we were successful in making the diene **5** from dimer **3a** by reduction of the carbonyl group and acid-promoted dehydration (Scheme 1), we were unable to obtain the enone **6**

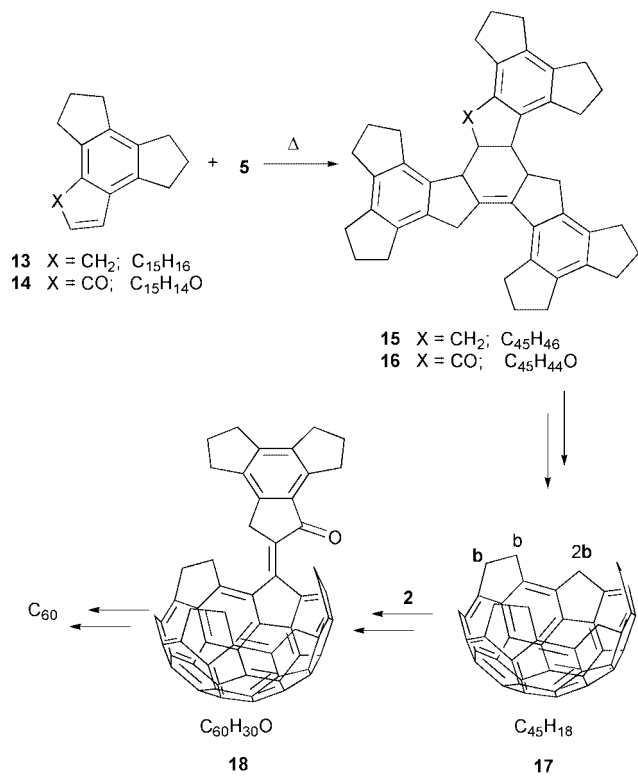§ We are indebted to a reviewer for calling our attention to this matter.

Scheme 2

9 $C_{25}H_{26}$

10

12 $C_{25}H_{18}$

11
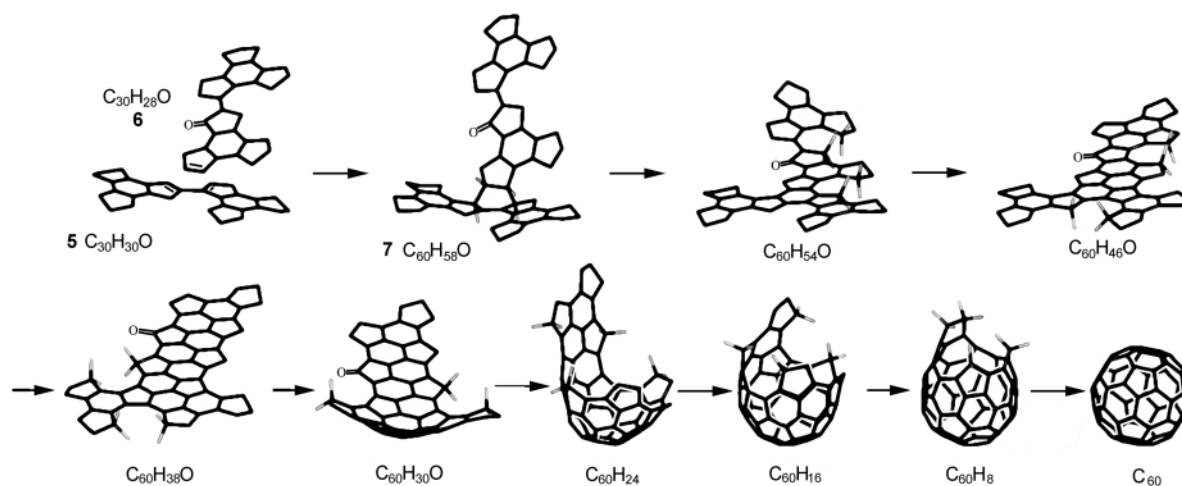
Scheme 3

despite efforts to utilise the carbonyl group of the dihydro derivative of dimers **3a** and **3b** to functionalise the required methylene group (asterisked in **3**) by use of "remote" intra-molecular procedures,[24] including photolysis of a nitrite ester (Barton reaction)[24,25] and the hypoiodite reaction.[24,26]

Attention was therefore turned to a possible alternative route to C_{60} which depends on the cycloaddition reaction of diene **5** with "trindene" (**13**) or "trindenone" (**14**) which would give the C_{45} compounds **15** and **16** (and isomers *e.g.* **19**), and hence, on partial dehydrogenation or loss of water followed by dehydrogenation, the bowl-like $C_{45}H_{18}$ (**17**) (Scheme 4). With a

13 X = CH₂; $C_{15}H_{16}$
14 X = CO; $C_{15}H_{14}O$

+ **5** →

15 X = CH₂; $C_{45}H_{46}$
16 X = CO; $C_{45}H_{44}O$

C_{60} ←

$C_{60}H_{30}O$
18

2

b b 2b

2

$C_{45}H_{18}$
17

Scheme 4

C_3 axis of symmetry (and belonging to the C_{3v} point group) compound **17** has two types of methylene groups on its "rim" labelled "b" and "2b" to signify their benzylic and doubly benzylic character respectively. Selective functionalisation of

one of the latter groups and the formation of a ketone, should open the way for aldol coupling between this centre and the α-methylene group of trindanone to give the C_{60} "bowl and lid" compound **18** which has the correct connectivity for dehydration and dehydrogenation for formation of the sphere (Scheme 4).

To test the Diels–Alder reactivity of diene **5** it was treated with maleic anhydride and gave the cycloadduct **8** (Scheme 1) as expected. Trindenone (**14**) was derived from trindanone by α-phenylselenation—a process which resulted in some α,α-diselenation and α-selenoenone formation as well as production of the required compound (40%). Precedents exist for the formation of such by-products in related α-selenations.[27,28] Elimination from the α-phenylselenotrindanone was induced by hydrogen peroxide treatment,[27] and the trindenone formed was heated with diene **5** under reflux in chlorobenzene to afford the C_{45}-based isomers **19** and **16** (37%) in the ratio 3∶1 (Scheme 5), the former being characterised by X-ray diffraction

14 + **5**

Δ

16 + **19**
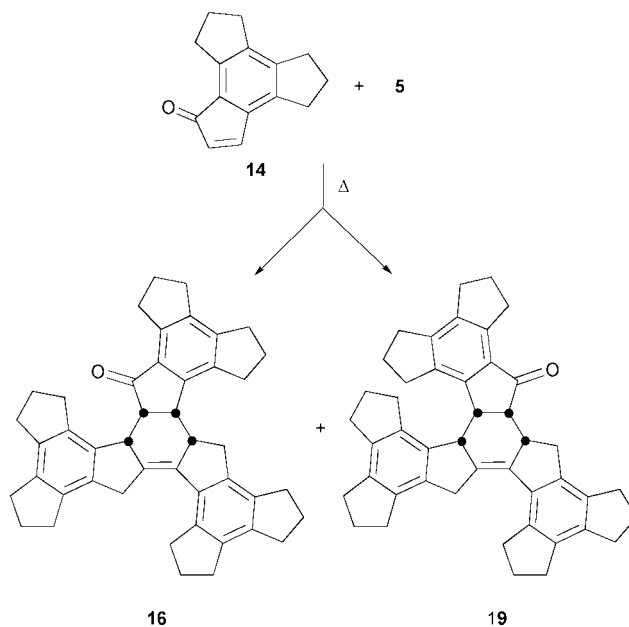
Scheme 5

analysis (Fig. 1). However, it was the minor product **16** that was required as the potential precursor of the basket-like **17**, this isomer having a very much simpler ^{13}C NMR spectrum than does **19**, which is consistent with its pseudo C_3 symmetry.

In an effort to direct the formation of isomer **16** at the expense of **19** the silyl dienol ether **20**, made from dimer **3b** and which would be expected to express its nucleophilicity at the γ-position,[29] was treated with trindenone under Lewis acid Mukaiyama conditions,[30,31] but the sensitivity of the ketone (*cf.* that of indenone[32]) prevented progress along these lines. Likewise, although indenone takes part in Diels–Alder reactions,[33] trindenone did not yield a product on heating with compound **20**—conceivably because the silyloxy group inhibits reaction.

A further effort was made to favour a C_{45} compound with the framework of compound **16** by desilylating **20** with fluoride in the presence of trindanone, but the desired process did not occur, which is consistent with the report that ketones do not react as carbanion acceptors in reactions of this type.[34] The product isolated was the spiro-pyranoid compound **24** formed, apparently, following desilylation of **20** and proton transfer from trindanone to give **3a** and the stabilised anion **21** which reacted in Michael fashion to give the adduct **22**. Cyclisation then led to the hydroxy intermediate **23** which spontaneously lost water to afford the isolated spiro-pyran **24** (Scheme 6) the structure of which was determined by X-ray diffraction analysis (Fig. 2). This type of synthesis of 4*H*-pyrans is not novel.[35]
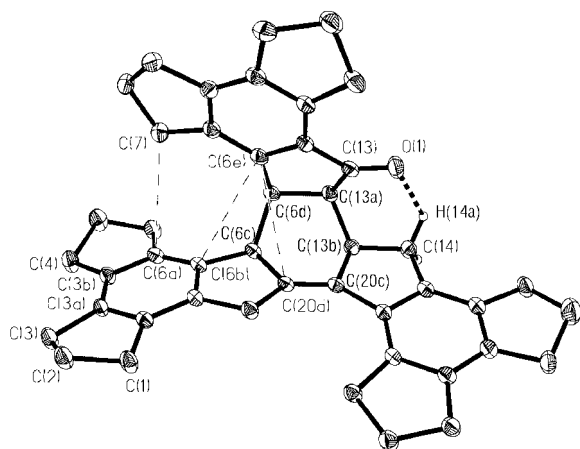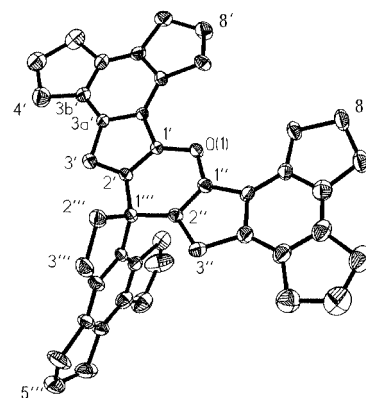
Fig. 1 ORTEP view of **19** with ellipsoids for non-hydrogen atoms drawn at 30% probability and majority of hydrogen atoms omitted for clarity.

Compound **24** gave a ^{13}C NMR solution spectrum consistent with its having a mirror plane of symmetry.

The crystal of compound **19** has monoclinic symmetry with the space group $C2/c$, there being two symmetrically independent molecules in each unit cell. The three "trindane" moieties are found on the same face of the central cyclohexene ring, which adopts a boat conformation with carbon atoms 20c, 20d, 13a, 6d having mean deviation of 0.1 Å from the basal plane and atoms 13b and 6c 0.6 Å from this plane (Fig. 1). The angle between the slope planes 20d, 6c, 6d and 13a, 13b, 20c is 125°, and the double bond 20c=20d keeps two of the trindane units in approximately the same plane. The third, carrying the carbonyl group, is orientated at 71° (averaged value) to the other pair, thus bringing this trindane system into close proximity with one of the others and causing an intramolecular H-bond to be established between the carbonyl oxygen atom and H(14a). Also present within the molecule are van der Waals' contacts, which are indicated in Fig. 1 and are within the range of 3.22–3.32 Å.

The crystal of compound **24** is of space group $P\bar{1}$ with two symmetrically independent molecules in each unit cell. The molecule consists of a central $4H$-pyran core having two trindanes fused in an essentially coplanar manner (mean

Fig. 2 ORTEP view of **24** with ellipsoids for non-hydrogen atoms drawn at 50% probability and hydrogen atoms omitted for clarity.

absolute deviation from the plane is 0.08 ± 0.01 Å) with most deviation, due to the pronounced "envelope" conformations of the 5-membered rings, exhibited in opposite directions by C8′ and C8″. The third (spiro-attached) trindane unit is also essentially planar (mean absolute deviation 0.10 ± 0.01 Å) and lies perpendicular to the rest of the molecule (Fig. 2). Similarly, the only significant deviations are due to envelope conformations, with C2‴ and C5‴ directed out of the plane in the same direction. In the solid state compound **24** therefore does not possess the mirror plane of symmetry it appears to have in solution.

Conclusion

The proposed potential paths to C$_{60}$, the tennis-ball route (Schemes 1, 2) and the basket- and -lid approach (Scheme 4), offer rational possibilities but require further development. In particular, good routes to compounds **6** and **16** must be found, and those to the unwanted **19** and **24** circumvented.

Experimental

General methods

Melting points were determined using a Reichert hot stage melting point apparatus and are uncorrected. NMR spectra

3a, 3b ⟶ **20** + **2** $\xrightarrow{F^-}$ **3a** ⟶ **21**

22 ⟶ **23** ⟶ **24**
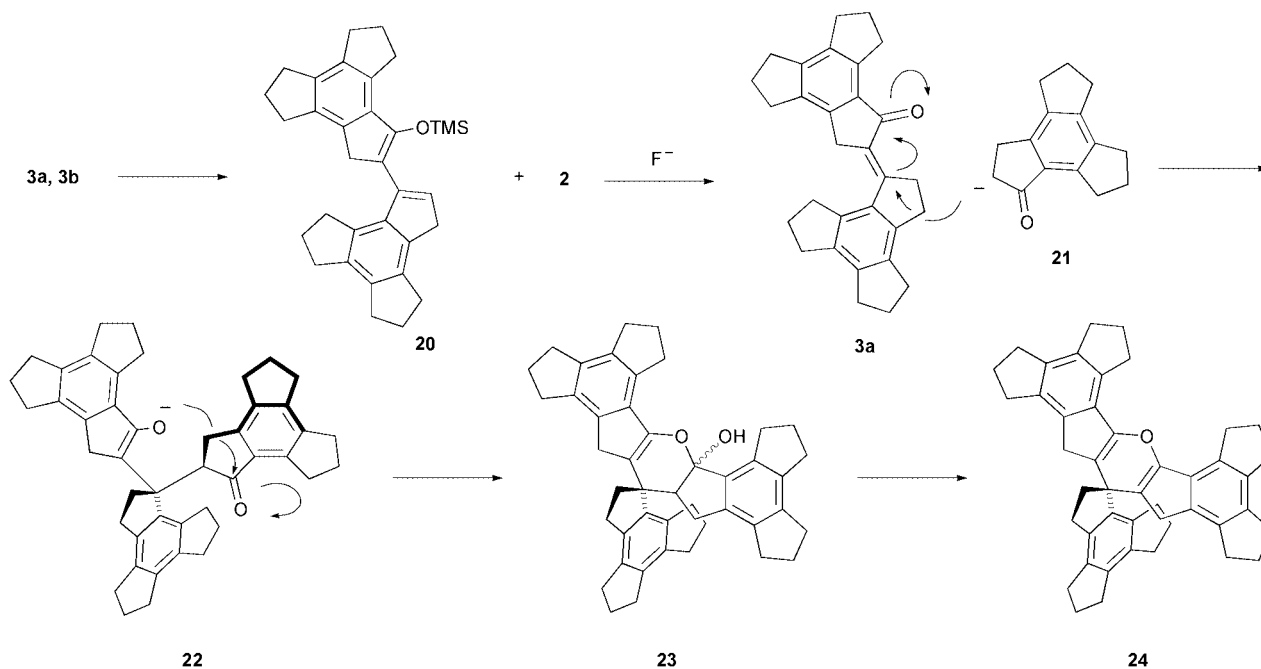
Scheme 6

were recorded on either Varian FT80A, Bruker AC300 or Varian Unity Inova 300 instruments and measured in CDCl$_3$ with Me$_4$Si as internal standard; for compounds containing trimethylsilyl groups, traces of CHCl$_3$ in the sample were used as the reference compound. The numbers of hydrogen atoms bonded to carbons were determined by DEPT experiments; such specific assignments as possible were made by COSY methods, methylene resonances were assigned benzylic or non-benzylic from their chemical shifts. Reactions were followed by thin layer chromatography (TLC) performed on aluminium plates pre-coated with silica gel (Merck Kieselgel 60 F$_{254}$). The components were detected under 254 nm and 315 nm light and by use of a "molybdate dip" [H$_2$SO$_4$, 5 mL, conc.; (NH$_4$)$_2$MoO$_4$, 5 g; Ce(SO$_4$)$_2$, 0.2 g; water, 95 mL] followed by heating with hot air. Column chromatography was effected with Merck Kieselgel 60 (230–400 mesh ASTM) and radial chromatography was performed using plates made with Merck Keiselgel P254. GLC analysis of products of molecular weights <≈300 amu were carried out on a Hewlett Packard 5890 series II instrument, with a DB1 30 m, 25 μ column. The typical temperature profile was 60 °C for 3 min; to 300 °C at 10 °C min^{-1}; 300 °C for 8 min. Low-resolution MS and GCMS analyses were carried out on a Hewlett Packard 5995C instrument (EI 70 eV) using a 12 m HP1 column with an injection temperature of 250 °C and an oven temperature ramp of 50–250 °C over 32 min. High-resolution mass spectra were produced at the University of Canterbury, Christchurch, New Zealand with a Kratos MS 80 instrument (EI 70 eV) run with a source temperature of 200 °C. Elemental analyses were performed at the University of Otago, Dunedin, New Zealand.

Solvents were dried and purified by standard methods.[36] Dry THF was freshly distilled from molten potassium under dried nitrogen with benzophenone added as an indicator of dryness. The petroleum ether employed was of boiling range 60–80 °C. Reactions involving the use of air sensitive materials were performed in sealed reaction vessels under dried nitrogen, with liquid reagents introduced with a syringe through a rubber septum.

2,3,4,5,6,7,8,9-Octahydro-1*H*-trinden-1-one ("trindanone", 2)[19]

2,3,4,5,6,7,8,9-Octahydro-1*H*-trindene (**1**) ("trindane", made by use of SiCl$_4$ in EtOH,[15a] 2.00 g) was dissolved in glacial acetic acid (20 mL) and the stirred solution was maintained at 70 °C while sodium dichromate dihydrate (3.70 g, 1.2 mol equiv.) in glacial acetic acid (15 mL), also at 70 °C, was added. The temperature of the mixture rose to about 80 °C and slowly fell. After 30 min water (10 mL) and ice (10 g) were added and the precipitate which formed was separated, washed with water (2 × 5 mL) and EtOH (3 × 3 mL) and dried under vacuum (1.38 g). GLC analysis indicated the presence of trindane (retention time 21.1 min, 15%) and trindanone (**2**) (24.2 min, 85%).

The washings and filtrate were extracted with diethyl ether (3 × 80 mL), the extracts were combined and washed with NaOH (2 M aq., 2 × 100 mL) and distilled water (100 mL). The ethereal solution was dried (Na$_2$SO$_4$), filtered and concentrated under vacuum to give further crystalline trindanone (**2**) (0.65 g). The combined crude trindanone (2.03 g) was taken up in CH$_2$Cl$_2$ (2 mL) and purified by flash chromatography (diethyl ether–petroleum ether 1:2) on a column of silica gel (R_F 0.59). The product (1.28 g, 59%), mp 113–116 °C was recrystallised (MeOH) to give white crystalline trindanone (**2**) (0.85 g, 43%): mp 115–116 °C (lit.[19] 104 °C); UV (CH$_2$Cl$_2$) λ_{max}/nm (log ε) 268(6.2), 310(5.5); δ_H (CDCl$_3$, 300 MHz, *J*/Hz) 2.14 (2H, quintet, *J* 7.4, ArCH$_2$C*H*$_2$), 2.17 (2H, quintet, *J* 7.4, ArCH$_2$-C*H*$_2$), 2.65 (2H, t, *J* 5.6, ArCOCH$_2$C*H*$_2$), 2.79 (2H, t, *J* 7.4, ArC*H*$_2$CH$_2$), 2.88 (4H, t, *J* 7.4, ArC*H*$_2$CH$_2$), 2.97 (2H, t, *J* 5.6, ArCOC*H*$_2$CH$_2$), 3.21 (2H, t, *J* 7.4, ArC*H*$_2$CH$_2$); δ_C (CDCl$_3$, 20 MHz) 24.6, 25.2, 25.5, all ArCH$_2$*C*H$_2$; 30.0, 30.4, 31.0, 32.0,

36.9, all Ar*C*H$_2$CH$_2$; 131.5, 139.2, 140.0, 141.4, 147.0, 149.5, Ar; 207.6, CO (Found: C, 84.43; H, 7.83. C$_{15}$H$_{16}$O requires C, 84.86; H, 7.55%).

2,3,4,5,6,7,8,9,2′,3′,4′,5′,6′,7′,8′,9′-Hexadecahydro-1*H*,1′*H*-[1,2′-bitrindenyliden]-1′-one (3a)

Trindanone (**2**) (200 mg, 0.94 mmol) was dissolved in aqueous EtOH (95%, 13 mL) and to the stirred solution SiCl$_4$ (0.50 mL, 4.0 mmol) was added dropwise. On standing at 20 °C the solution developed a yellow colour and a pale yellow solid precipitated. Upon isolation after 48 h the solid was washed with absolute EtOH (3 × 3 mL) and dried *in vacuo* to give the title compound as a yellow powder [homogeneous by TLC R_F 0.47 (CH$_2$Cl$_2$–light petroleum 2:1)] (140 mg, 65%, lit.[19] 9%): mp 204–206 °C (lit.[19] 210 °C); UV (CH$_2$Cl$_2$) λ_{max}/nm (log ε) 348(6.1); δ_H (CDCl$_3$, 300 MHz, *J*/Hz) 2.08–2.22 (8H, m, ArCH$_2$C*H*$_2$), 2.78–2.90 (14H, m, ArC*H*$_2$CH$_2$), 3.16 (2H, t, *J* 7.1, ArC*H*$_2$CH$_2$), 3.32 (2H, t, *J* 7.4, ArC*H*$_2$CH$_2$), 3.59 (2H, t, *J* 6.0, ArC(=C)C*H*$_2$), 3.71 (2H, s, ArC*H*$_2$C(CO)=C); δ_C (CDCl$_3$, 75 MHz) 25.2, 25.6, 26.8, 29.9, 30.0, 30.4, 30.8, 30.93, 30.98, 31.1, 31.9, 32.0, 33.5, 33.8, 36.1, all ArCH$_2$*C*H$_2$ and ArCH$_2$-*C*H$_2$; 128.2, vinylic C; 134.1, 136.0, 138.1, 138.3, 138.4, 139.8, 139.9, 141.1, 142.9, 143.2, 143.8, 146.0, Ar; 155.7, vinylic C; 196.4, CO; MS *m/z* 408 (5.5%), 407 (33.6), 406 (100, M$^+$), 378 (8.7), 362 (37.9), 211 (17.4), 194 (50.0), 143 (34.7); *m/z* found 406.2292 (M$^+$); C$_{30}$H$_{30}$O requires 406.2296.

2*RS*-4,5,6,7,8,9,2′,3′,4′,5′,6′,7′,8′,9′-Tetradecahydro-1′*H*,3*H*-[1,2′-bitrindenyl]-1′-one (3b)

Trindanone (**2**) (200 mg, 0.94 mmol) was dissolved in absolute EtOH (11 mL) and to the stirred solution SiCl$_4$ (0.45 mL, 4.0 mmol) was added dropwise. After 24 h the brown suspension was filtered and the white residue was washed with absolute EtOH (3 × 3 mL), dried *in vacuo* and recrystallised (CH$_2$Cl$_2$–EtOH) to give the title compound as a white microcrystalline solid [homogeneous by TLC, R_F 0.55 (CH$_2$Cl$_2$–light petroleum 2:1)] (170 mg, 85%; lit.[19] 24%): mp 214–216 °C (lit.[19] 210 °C); UV (CH$_2$Cl$_2$) λ_{max}/nm (log ε) 266(6.4); δ_H (CDCl$_3$, 300 MHz, *J*/Hz) 2.08–2.22 (8H, m, ArCH$_2$C*H*$_2$), 2.79–2.91 (14H, m, ArC*H*$_2$CH$_2$), 3.00 (1H, dd, J_1 17.0, J_2 < 2, ArCH-*H*′CHR$_2$), 3.17 (2H, d, *J* 8, ArC*H*$_2$CH=R), 3.26 (2H, t, *J* 7.4, ArC*H*$_2$CH$_2$), 3.47 (1H, dd, J_1 17.0, J_2 8.1, ArC*H*(H′)CHR), 4.12 (1H, dd, J_1 8, J_2 < 2, ArCOC*H*R), 6.16 (1H, d, *J* < 2, ArCH$_2$C*H*=C); δ_C (CDCl$_3$, 75 MHz) 25.2, 25.5, 25.6, 25.9, all ArCH$_2$*C*H$_2$; 30.0, 30.5, 30.8, 30.9, 31.1, 31.4, 31.5, 32.0, 34.3, all ArCH$_2$*C*H$_2$; 36.4, ArCH$_2$CH=R; 48.2, ArCOCHR; 127.7, Ar*C*R=CHCH$_2$; 131.1, 133.9, 137.1, 137.3, 138.2, 138.7, 138.9, 139.2, 140.3, 141.9, 144.3, 147.4, 147.4, Ar and Ar*C*R=CHR; 206.6, CO; MS *m/z* 408 (2.9%), 407 (18.5), 406 (53.8, M$^+$), 211 (10.6), 194 (100.0); *m/z* found 406.2295 (M$^+$); C$_{30}$H$_{30}$O requires 406.2296.

4,5,6,7,8,9,4′,5′,6′,7′,8′,9′-Dodecahydro-3*H*,1′*H*-1,2′-bitrindenyl (5)

Diisobutylaluminium hydride (DIBALH) (0.3 mL, 1 M in CH$_2$Cl$_2$, 0.3 mmol) was added dropwise under dry nitrogen to an ice-cold solution of dimer (**3a**) (100 mg, 0.22 mmol) in CH$_2$Cl$_2$ (6 mL) and the mixture held at 0 °C for 3 days. The reaction was quenched with MeOH (3 mL) and the aluminum salts were removed by filtration. Radial chromatography (light petroleum–CH$_2$Cl$_2$ 5:1) of the dried residue (101 mg) yielded the diene (**5**) (13.6 mg, 14%) and a mixture of the diastereomeric alcohols (30.0 mg, 30%, 3:1) corresponding to the products of reduction of the carbonyl group of enone **3b**. A portion of the major alcohol was crystallised from CH$_2$Cl$_2$ to give colourless needles: mp 230–233 °C; UV (CH$_2$Cl$_2$) λ_{max}/nm (log ε) 268(5.9), 304(5.4), 348(5.5); δ_H (CDCl$_3$, 300 MHz, *J*/Hz) 2.0–2.2 (8H, m, ArCH$_2$C*H*$_2$), 2.80–2.95 (12H, m, ArC*H*$_2$CH$_2$),

2.95–3.1 (4H, m, ArCH_2CH_2, OH and ArCH(H′)CHR$_2$), 3.22 (3H, m, CH_2 and ArCH(H′)CHR$_2$), 3.31 (2H, d, J < 2, ArCH_2CH=C), 4.01 (1H, dd, J_1 8, J_2 13, ArCH$_2$CHR$_2$), 5.17 (1H, d, J 5.4, ArCHOH), 6.49 (1H, t, J < 2, ArCH$_2$CH=C); δ_C (CDCl$_3$, 75 MHz) 25.4, 25.4, 25.6, 25.8, all ArCH$_2$$CH_2$; 30.5, 30.7, 30.9, 31.1, 31.2, 31.4, 31.4, 31.7, all ArCH$_2$CH$_2$; 34.4, ArCH$_2$CHR$_2$; 36.6, ArCH$_2$CH=C; 46.0, ArCH$_2$$CHR_2$; 74.4, Ar$C$HOH; 130.7, Ar$CH_2$CH=C; 134.3, 137.1, 137.3, 137.3, 137.5, 137.5, 137.8, 138.3, 139.0, 139.1, 139.3, 140.4, 143.4, Ar; MS m/z 410(1.5%), 409(9), 408(27, M$^+$), 391(37), 390(100), 213(30), 197(24), 196(6), 195(36); m/z found 408.2444 (M$^+$); C$_{30}$H$_{32}$O requires 408.2453.

Addition of aqueous HCl (0.5 mL, 2 M) to the mixed alcohols above (20 mg in CH$_2$Cl$_2$, 2 mL) produced a two-phase magenta solution containing the crude dehydrated title diene (**5**) (10 mg, 52%, mp 170–175 °C), which was isolated by radial chromatography following washing with Na$_2$CO$_3$ (5 mL, 2 M aq.), distilled water (2 × 5 mL) and drying. Recrystallisation (CH$_2$Cl$_2$–pentane) gave colourless needles that discoloured on contact with air: mp 174–176 °C; UV (CH$_2$Cl$_2$) λ_{max}/nm (log ε) 276 (6.3), 308 (shoulder, 6.1); δ_H (CDCl$_3$, 300 MHz, J/Hz) 2.01 (2H, t, J 7.3, ArCH$_2$CH_2), 2.20–2.05 (6H, m, ArCH$_2$CH_2), 2.94–2.78 (12H, m, ArCH_2CH$_2$), 3.00 (2H, t, J 7.1, ArCH_2CH$_2$), 3.02 (2H, t, J 7.1, ArCH_2CH$_2$), 3.33 (2H, d, J < 2, ArCH_2CH=C), 3.60 (2H, s, ArCH_2CR=C), 6.41 (1H, t, J 2.2, ArCH$_2$CH=C), 6.91 (1H, s, ArCH=C); δ_C (CDCl$_3$, 75 MHz) 25.5, 25.6, 25.7, 26.3, all ArCH$_2$$CH_2$; 29.7, 30.9, 31.3, 31.4, 31.9, 31.0, 31.0, 33.1, all ArCH$_2$CH$_2$; 36.8, ArCH$_2$CH=C; 41.4, ArCH$_2$CR=C; 128.1, ArCH=C; 130.9, ArCH$_2$$C$H=C; 134.5, 134.9, 135.7, 136.4, 136.9, 137.1, 137.4, 138.1, 138.4, 139.2, 139.2, 139.4, 142.4, 143.0, vinylic and Ar; MS m/z 392(4.4%), 391(29), 390(88, M$^+$), 196(28), 195(66), 44(100); m/z found 390.2345 (M$^+$); C$_{30}$H$_{30}$ requires 390.2347.

4aRS,4bRS,7aSR,7bRS-1,2,3,4,4a,4b,7a,7b,8,9,10,11,12,13,14,15,16,17-octadecahydro-6-oxabis(*as*-indaceno)[4,5-*a*:4′,5′-*f*]-trindene-5,7-dione (8)

Diene (**5**) (2.7 mg, 0.0069 mmol) and maleic anhydride (2.2 mg, 0.022 mmol, 3.3 mol equiv.) in toluene (1.2 mL) were heated under reflux under nitrogen and the reaction was monitored by TLC (CH$_2$Cl$_2$). After 4.5 h, chromatography on silica gel (CH$_2$Cl$_2$) afforded the cycloaddition adduct **8** as a white solid (2.5 mg, 74%) which upon recrystallisation (CH$_2$Cl$_2$–toluene) gave colourless needles (0.9 mg, 27%): mp 285–295 °C; δ_H (CDCl$_3$, 300 MHz, J/Hz) 2.0–2.2 (8H, m, ArCH$_2$CH_2), 2.75–2.95 (14H, m, ArCH_2CH$_2$), 3.0–3.2 (2H, m, CH$_2$), 3.35–3.5 (2H, m), 3.60–3.66 (3H, m), 3.93 (1H, dt, J_1 9.2, J_2 9.0, ArCH$_2$CHRCHR$_2$), 4.02 (1H, br d, J 9, ArCHRCHR$_2$), 4.09 (1H, br d, J 9, ArCHRCHR$_2$); δ_C (CDCl$_3$, 75 MHz) 25.1, 25.3, 25.3, 25.6, ArCH$_2$$CH_2$; 29.7, 30.6, 31.0, 31.0, 31.2, 31.4, 31.5, 31.6, ArCH$_2$CH$_2$; 34.7, 37.2, ArCH$_2$; 41.7, 42.8, 44.0, 48.9, CH; 130.8, 132.7, 136.1, 138.0, 138.2, 138.7, 139.7, 139.8, 139.3, 141.1, 141.3, 144.5, 145.0, 148.1, vinylic and Ar; 170.0, 172.0, CO; MS 490 (1.2%), 489 (6.6), 488 (17.4, M$^+$), 460 (23.0), 390 (100), 195 (46.9); m/z found 488.2353 (M$^+$); C$_{34}$H$_{32}$O$_3$ requires 488.2352.

(2RS)-2,3,4,5,6,7,8,9-Octahydro-2-phenylselenyl-1*H*-trinden-1-one

A solution of lithium diisopropylamide (LDA) was freshly prepared by the dropwise addition of *n*-BuLi (1.10 mL, 2.5 M in hexanes, 2.75 mmol) to a stirred solution of diisopropylamine (0.42 mL, 2.72 mmol) in dried THF (3 mL) under nitrogen at −70 °C. The LDA (1.2 mol equiv.) was transferred dropwise through a cannula to a continuously stirred solution of trindanone **2** (502 mg, 2.37 mmol) in dried THF (51 mL) also at −70 °C. After 30 min a solution of benzeneselenenyl chloride (0.68 g, 1.5 mol equiv. in THF, 6 mL) was rapidly added and the reaction mixture was allowed to warm to room temperature

over 1 h and partitioned between aqueous HCl (0.5 M, 50 mL) and ether–pentane 1 : 1 (40 mL). The organic layer was washed with water (20 mL), NaHCO$_3$ (aq., sat., 2 × 20 mL), NaCl (aq., sat., 2 × 20 mL), and dried (Na$_2$SO$_4$). Removal of the solvent and column chromatography [light petroleum–CH$_2$Cl$_2$ (4 : 1)→ CH$_2$Cl$_2$ (100%)] afforded the title compound as an orange solid (349 mg, 40%) which, when recrystallised (pentane–CH$_2$Cl$_2$ 3 : 1, −25 °C), gave pink microcrystals: mp 105–107 °C; UV (CH$_2$Cl$_2$) λ_{max}/nm (log ε) 270(6.91), 308(6.35); δ_H (CDCl$_3$, 300 MHz, J/Hz) 2.13 (2H, quintet, J 7.4, ArCH$_2$CH_2), 2.13 (2H, quintet, J 7.5, ArCH$_2$CH_2), 2.77 (4H, br t, J 7.5, ArCH_2CH$_2$), 3.19 (2H, br t, J 7.3, ArCH_2CH$_2$), 2.84 (2H, t, J 7.6, ArCH_2-CH$_2$), 3.00 [1H, dd, J_1 2.6, J_2 17.9, ArCH(H′)CHSePh], 3.47 [1H, dd, J_1 7.6, J_2 17.8, ArCH(H′)CHSePh], 4.21 (1H, dd, J_1 2.8, J_2 7.7, ArCOCHSePh), 7.27–7.19 (3H, m, Ph), 7.62–7.57 (2H, m, Ph); δ_C (CDCl$_3$, 75 MHz) 25.0, 25.4, all ArCH$_2$$CH_2$; 29.8, 30.4, 30.9, 31.9, all ArCH$_2$CH$_2$; 34.0, ArCH(H′)CHSePh; 44.4, ArCOCHSePh; 127.9, Ph; 128.5, Ar; 128.9, Ph; 129.7, C; 134.7, Ph; 136.8, 138.7, 140.4, 142.0, 146.3, 147.7, Ar; 203.6, CO; MS m/z 369(11%), 368(32, M$^+$), 367(21), 287(25), 212(18), 211(100), 210(39) (Found: C 68.49; H 5.73. C$_{21}$H$_{20}$OSe requires C, 68.66; H, 5.44%). A later fraction gave 2,3,4,5,6,7,8,9-octahydro-2,2-bis(phenylselenyl)-1*H*-trinden-1-one as an orange oil (187 mg, 15%): δ_H (CDCl$_3$, 300 MHz, J/Hz) 2.00 (2H, quintet, J 7.3, ArCH$_2$CH_2), 2.11 (2H, quintet, J 7.3, ArCH$_2$CH_2), 2.50 (2H, t, J 7.3, ArCH_2CH$_2$), 2.73 (4H, br t, J 7, ArCH_2CH$_2$), 3.15 (2H, t, J 7.3, ArCH_2CH$_2$), 3.23 [2H, s, ArCH_2C(SePh)$_2$], 7.20–7.29 (6H, m, Ph), 7.59 (4H, m, Ph); δ_C (CDCl$_3$, 75 MHz) 25.1, 25.4, all ArCH$_2$$CH_2$; 29.6, 30.4, 30.9, 31.9, all ArCH$_2$CH$_2$; 41.5, ArCH$_2$$C$(SePh)$_2$; 55.1, ArCO$C$(SePh)$_2$; 127.9, Ar; 128.6, Ph; 128.9, Ar; 129.0, Ph; 134.6, Ar; 136.8, Ph; 138.1, 140.5, 142.5, 143.5, Ar; 199.9, CO; MS m/z 522(2%), 368(9), 367(39): 366(30), 286(26), 279(15), 210(100). Also isolated was the phenylselenyl-substituted "trindenone" 4,5,6,7,8,9-hexahydro-2-phenylselenyl-1*H*-trinden-1-one as an orange oil (26 mg, 3%): δ_H 2.0–2.3 (4H, m, ArCH$_2$CH_2), 2.67 (2H, m), 2.7–2.9 (4H, m), 2.99 (1H, t, J 7), 3.0–3.4 (2H, m), 7.23 (2H, m, Ph), 7.30 (1H, m, Ph), 7.58 (2H, m, Ph); δ_C 25.3, 25.5, ArCH$_2$$CH_2$; 29.4, 30.2, 30.3, 31.4, ArCH$_2$CH$_2$; 128.1, 129.4, 130.9, Ar; 134.4, 134.4, CH; 138.0, 141.1, 144.5, Ar; 144.5, CH; MS m/z 366(11%, M$^+$), 279(22), 212(21), 211(56), 210(100). A small amount of "trindenone" (**14**) was also isolated from the reaction products.

4,5,6,7,8,9-Hexahydro-1*H*-trinden-1-one (14)

(2*RS*)-2,3,4,5,6,7,8,9-Octahydro-2-phenylselenyl-1*H*-trinden-1-one (49.0 mg, 0.133 mmol) was dissolved in CH$_2$Cl$_2$–Et$_3$N (2 mL, 19 : 1) and H$_2$O$_2$ (1 mL, 27% aq.) was added slowly with vigorous stirring until reaction was complete (5 min). The organic layer was washed with water (2 mL) and dried (Na$_2$SO$_4$). Radial chromatography gave "trindenone" (**14**) (8.8 mg, 31%) as orange prisms: mp 87–88 °C (decomp.); UV (CH$_2$Cl$_2$) λ_{max}/nm (log ε) 248(sh., 4.4), 252(4.5), 354(3.6); δ_H (CDCl$_3$, 300 MHz, J/Hz) 2.12 (2H, quintet, J 7.3, ArCH$_2$-CH_2), 2.12 (2H, quintet, J 7.3, ArCH$_2$CH_2), 2.68–2.86 (6H, m, ArCH_2CH$_2$), 3.04 (2H, t, J 7.4, ArCH_2CH$_2$), 5.75 (1H, d, J 6.1, ArCOCH=CHAr or ArCOCH=CHAr), 7.52 (1H, d, J 6.1, ArCOCH=CHAr or ArCOCH=CHAr); δ_C (CDCl$_3$, 75 MHz) 25.4, 25.5, all ArCH$_2$$CH_2$; 29.4, 30.17, 30.22, 31.4, all ArCH$_2$-CH$_2$; 123.4, Ar; 126.1, ArCOCH=CHAr or ArCOCH=CHAr; 137.0, 137.8, 141.8, 142.2, 145.9, Ar; 147.7, ArCOCH=CHAr or ArCOCH=CHAr; 199.9, CO; MS m/z 211(17%), 210(100, M$^+$), 209(33), 195(9), 182(29), 165(26), 153(21), 152(23) (Found: C, 85.21; H, 6.99. C$_{15}$H$_{14}$O requires C, 85.68; H, 6.66%).

(6cSR,6dRS,13aSR,13bRS)-1,2,3,4,5,6,6c,6d,7,8,9,10,11,12,13a,13b,14,15,16,17,18,19,20,21-Tetracosahydrotris(*as*-indaceno)[4,5-*a*:4′,5′-*f*:4″,5″-*l*]trinden-13-one (19)

A solution of diene **5** (16.3 mg, 0.042 mmol) and "trindenone" (**14**) (9.8 mg, 0.047 mmol) in PhCl (3 mL) was heated under

Table 1 Crystallographic properties and data collection statistics for compounds **19** and **24**

	19	24
Formula	$C_{45}H_{44}O$	$C_{45}H_{44}O$
Formula weight	600.33922 amu	600.33922 amu
Crystal system	Monoclinic, B	Triclinic
Space group	$C2/c$	$P\bar{1}$
Unit cell parameters		
a	30.5643(6) Å	11.7970(3) Å
b	11.0494(2) Å	13.9116(1) Å
c	21.8027(3) Å	20.5335(5) Å
α	90.00°	86.534(1)°
β	115.389(1)°	78.640(1)°
γ	90.00°	89.716(1)°
Unit cell volume	6652.0(2) Å³	3297.7(1) Å³
Temperature of data collection	149(2) K	150(2) K
R_{int}	0.069	0.031
Z	8	4
R	0.065(5)	0.1183
R_w (all data)	0.214	0.386
Experimental absorption coefficient (T)	0.069 mm⁻¹	0.070 mm⁻¹
Wavelength of radiation	0.71073 Å	0.68870 Å
Number of data	19936	6997
Number of independent data	14379	5965
Cut-off [$I > 2\sigma(I)$]	5557	1032

reflux under dry nitrogen for 1 h and the solvent was removed *in vacuo*. Radial chromatography of the crude residue (light petroleum–CH_2Cl_2 3:1) achieved partial separation of two compounds of like mobility. The bulk of the partitioned product mixture (9.3 mg, 37%) contained a majority (3:1) of the chromatographically slower title product, a sample of which was obtained by fractional crystallisation (toluene–pentane) as colourless needles (7.0 mg, 28%): mp >250 °C (decomp.); δ_H (CDCl₃, 300 MHz, *J*/Hz) 1.50–1.75 (2H, m, ArCH₂C*H₂*), 1.95–2.35 (10H, m, ArCH₂C*H₂*), 2.5–2.6 (2H, t, *J* 8, ArC*H₂*-CH₂), 2.64 (2H, t, *J* 7.7, ArCH₂C*H₂*), 2.7–3.0 (16H, m, ArCH₂C*H₂*), 3.00–3.05 (2H, dd, J_1 7, J_2 14), 3.09 (2H, t, *J* 7), 3.15–3.25 (3H, m), 3.40 (1H, d, *J* 21.8), 3.92 (1H, d, *J* 21.8), 3.99 (1H, d, *J* 6), 4.09 (1H, dd, J_1 3.7, J_2 16.9), 4.28 (1H, t, *J* 6); δ_C (CDCl₃, 75 MHz) 25.10, 25.15, 25.20, 25.5, 25.7, 26.0, all ArCH₂C*H₂*; 30.1, 30.4, 30.9, 30.9, 31.0, 31.0, 31.18, 31.26, 31.31, 31.6, 31.7, 31.7, 34.5, 36.8, all ArC*H₂*CH₂; 42.5, 44.3, 49.5, 53.6, CH; 130.6, 133.6, 134.8, 135.4, 136.8, 137.8, 138.0, 138.1, 138.2, 138.4, 138.5, 138.9, 139.2, 139.5, 140.0, 140.6, 140.6, 142.7, 146.9, 148.5, vinylic C and Ar; 207.4, CO; MS *m/z* 600(0.17%, M⁺), 391(28), 390(100), 210(9), 195(45). See Fig. 1 for X-ray crystallographic analysis. A second fraction was a near pure compound deemed to be the isomer (4a*SR*, 4b*SR*,18a*RS*,18b*SR*)-1,2,3,4a,4b,5,6,7,8,9,10,11,12,13,14,15, 16,17,18,18a,18b,19,20,21-tetracosahydrotris(*as*-indaceno)[4,5-*a*:4′,5′-*f*:4″,5″-*k*]trinden-4-one (**16**) (1.1 mg, 4%): δ_C (CDCl₃, 75 MHz) 34.4, 38.5, 41.6, 41.8, 46.6, 50.0, 51.4, 91.2, 123.4, 125.8, 134.8, 135.4, 136.6, 137.3, 138.1, 141.6, 146.6, 148.9, 208.0; MS *m/z* 601(0.03%), 600(0.16, M⁺), 391(35), 390(100), 210(22), 196(10), 195(41).

Spiro[2,3,4,5,6,7,8,9,10,11,12,13,14,15-tetradecahydro-1*H*-bis-(trindeno)[1,2-*b*:2′,1′-*e*]pyran-8,1′-(2′,3′,4′,5′,6′,7′,8′,9′-octa-hydro-1*H*-trindene)] (24)

A solution of LDA (6.6 mL, 0.10 M in THF, 0.66 mmol) at −78 °C was added *via* cannula, over 10 min, to dimer **3a** (200 mg, 0.49 mmol) in THF (13 mL) also at −78 °C. The dark solution was stirred for a further 1 h at −78 °C, TMSCl (0.20 mL, 2 mmol) was added over 5 min and the mixture was allowed to reach ambient temperature over 3 h. Lithium salts were removed from the crude reaction products by filtering through Florisil™ and the required trimethylsilyl compound 3′-trimethylsilyloxy-4,5,6,7,8,9,4′,5′,6′,7′,8′,9′-dodecahydro-

3*H*,1′*H*-1,2′-bitrindenyl (**20**) was obtained by column chromatography (light petroleum–CH_2Cl_2 20:1) as a colourless glass (100 mg, 42%), which discolours rapidly on exposure to air: mp 95–105 °C; δ_H (CDCl₃, 300 MHz, *J*/Hz) 0.01 (3H, s, OSiC*H₃*), 0.11 (3H, s, OSiC*H₃*), 0.18 (3H, s, OSiC*H₃*), 1.95 (2H, quintet, *J* 7.4, ArCH₂C*H₂*), 2.1–2.2 (6H, m, ArCH₂C*H₂*), 2.7–2.9 (14H, m, ArC*H₂*CH₂); 3.17 (2H, br t, *J* 7.2, C*H₂*), 3.29 (2H, d, *J* < 2, ArC*H₂*CH=C), 3.40 (2H, s, ArC*H₂*CR=C), 6.33 (1H, t, *J* < 2, ArCH₂C*H*=C); δ_C (CDCl₃, 75 MHz) 0.7, OSi(CH₃)₃; 25.4, 25.4, 26.0, 26.2, all ArCH₂C*H₂*; 30.3, 30.5, 30.7, 30.8, 30.9, 31.1, 31.28, 31.32, 31.6, all ArC*H₂*CH₂; 36.7, Ar*C*H₂CH=C; 38.3, ArC*H₂*CR=C; 117.6, vinylic C; 131.6, vinylic CH; 133.6, 134.9, 135.2, 136.3, 136.7, 136.9, 136.9, 137.1, 137.5, 138.7, 139.0, 139.6, 141.2, 149.9, vinylic C and Ar; MS *m/z* 479(6%), 478(13, M⁺), 420(32), 406(32), 283(17), 212(38), 211(55), 210(47), 196(41), 195(37), 194(100).

Trimethylsilyldiene (**20**) (21 mg, 0.044 mmol) was dissolved with "trindanone" (**2**) (84 mg, 0.40 mmol) in THF (24 mL). Tetrabutylammonium fluoride (0.2 mL, 1 M in THF) was added to the stirred solution and the reaction mixture was kept for 24 h at 20 °C. Radial chromatography (light petroleum) of the residue obtained on removal of solvent gave the title compound as a chromatographically highly mobile white solid (3.8 mg, 12%) which decomposed around 200 °C. Recrystallisation (pentane–toluene) furnished a small number of colourless platelets: δ_H 1.8 (2H, quintet, *J* 7.3, ArCH₂C*H₂*), 2.09 (6H, quintet, *J* 8.4, ArCH₂C*H₂*), 2.21 (4H, quintet, *J* 8.4, ArCH₂-C*H₂*), 2.44 (2H, t, *J* 6.7, ArC*H₂*CH₂), 2.48 (2H, t, *J* 7.4, ArC*H₂*CH₂), 2.62 (2H, t, *J* 7.3, ArC*H₂*CH₂), 2.76–2.95 (18H, m, ArC*H₂*CH₂), 2.98 (2H, t, *J* 7.3, ArC*H₂*CH₂), 3.18 (2H, d, *J* 21.8, ArC*H*(H′)CR=C), 3.34 (4H, t, *J* 6.6, ArC*H₂*CH₂); δ_C (CDCl₃, 75 MHz) 25.2, 25.3, 25.4, 25.9, ArCH₂C*H₂*; 29.1, 29.8, 30.4, 30.8, 30.9, 31.0, 31.2, 31.2, 31.5, 31.8, all ArC*H₂*CH₂ and CR₂*C*H₂; 41.2, (C=C)₂*C*R₂; 118.3, 131.9, 133.1, 134.5, 135.8, 137.1, 138.8, 149.0 vinylic C and Ar; MS *m/z* 602(3.5%), 601(37), 600(100, M⁺), 599(10), 453(2.5), 430(5.3), 300(28, M²⁺), 286(14), 279(13), 272(10), 265(12); *m/z* found 600.3396 (M⁺); $C_{45}H_{44}O$ requires 600.3392. See Fig. 2 for synchrotron X-ray diffraction analysis.

Crystallographic data collection and refinement of the structures

Details of the data collection are listed in Table 1; both structures were solved by conventional methods (SHELXS, SHELXL).[37] All non-hydrogen atoms were refined with anisotropic thermal parameters.

For compound **19** a conventional X-ray source was used. Hydrogen atoms were refined with fixed thermal isotropic parameters, starting from calculated positions.

Data for a crystal of **24** (approximately 0.42 × 0.12 × 0.06 mm) were collected using synchrotron radiation at the Daresbury Laboratory, Warrington. The positions of hydrogen atoms were calculated geometrically, and refined with a common isotropic thermal parameter U of 0.08 Å². Hydrogen atoms of solvent molecules (water) were found from the last Fourier map and refined with an isotropic thermal parameter of 0.05 Å².

CCDC reference number 207/471. See http://www.rsc.org/suppdata/p1/b0/b004272m/ for crystallographic files in .cif format.

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