# 3aH-Indenes. Part 3.[1] Base Induced Dimerisation of 3,7a-Dihydro-4,7a-dimethyl-5H-inden-5-one. X-Ray Structure Determination of the Hexacyclic Dimer System

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When the enolate anion (3) of the bicyclic ketone (8) is treated with methyl fluorosulphonate and dienophiles, the normal sequence of O-methylation and cycloaddition is not observed; instead, addition of the anion (3) to the trienone (8) occurs to give, in the presence of 4-phenyltriazole-3,5-dione, the hexacyclic adducts (10) and (11). Structure (10) was determined by X-ray diffraction (Figure 1). When water is used to quench the enolate anion solution, the dimer (16) is formed. Thus three new carbon–carbon bonds are formed regio- and stereo-selectively, for which a sequence of three stereoelectronically favoured Michael additions is proposed (Scheme 2). The new hexacyclic system is highly concave with a self-filling cavity (Figure 2) having near-parallel sides with a separation of less than 3.4 Å. The initial red solution of the anion (3) rapidly changes to a persistent blue colour; it is suggested that this could be caused by intramolecular charge transfer across the molecular cavity, from the enolate anion donor to the dienone acceptor, in the hexacyclic anion (15).

We have recently described the synthesis of some 3aH-indenes as simple, but previously unknown, examples of bicyclic conjugated polyenes in which the peripheral unsaturation is interrupted by only one tetrahedral carbon atom at a ring junction.[1,2] These strained, reactive and sometimes transient species are of interest because of the rearrangement reactions and the extended cycloaddition reactions which they readily undergo. Such tetraenes, for example (1) and (2), were prepared by converting bicyclic trienones into their enolate anions with potassium hydride and 18-crown-6, followed by O-methylation of the anion with methyl fluorosulphonate.[1,2] The resulting 3aH-indenes, (1) and (2), were then intercepted, for example with 4-phenyltriazole-3,5-dione (PTAD), in [8 + 2]cycloaddition reactions across the termini of the π-system.

(1)   (2)   (3)
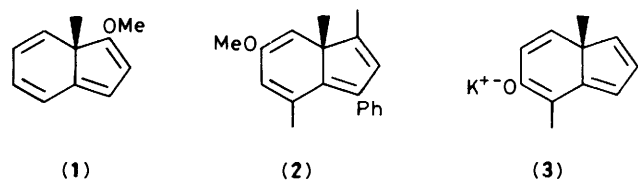
We now describe the generation of a similar enolate anion (3) of a 3a-methyl-3aH-indene, but with the oxygen function at position 6, and show that O-methylation and cycloaddition are completely suppressed in favour of an unexpectedly facile reaction between the anion (3) and its precursor trienone (8) in which three new carbon–carbon bonds are formed regio- and stereo-selectively.

The bicyclic trienone (8) was prepared as shown in Scheme 1. The enedione (4) is readily available by condensation of 2-methylcyclopentane-1,3-dione and 1-chloropentan-3-one;[3] by addition of hydrochloric acid as catalyst and scaling up the reaction fivefold, the yield of (4) was increased to 90%. Compound (4) was reduced to the alcohol (5a) with sodium borohydride in ethanol, the literature[4] yield again being slightly improved, to 87%, by careful control of the reaction temperature; the alcohol was then converted into its crystalline toluene-4-sulphonate (5b). This was dehydrogenated to the dienone (6) in only poor yield (maximum 28%) with 2,3-dichloro-5,6-dicyanobenzoquinone under various conditions, but in better yield (61%) by the phenylselenation–oxidation procedure. However the best yields (76—94%) of (6) were
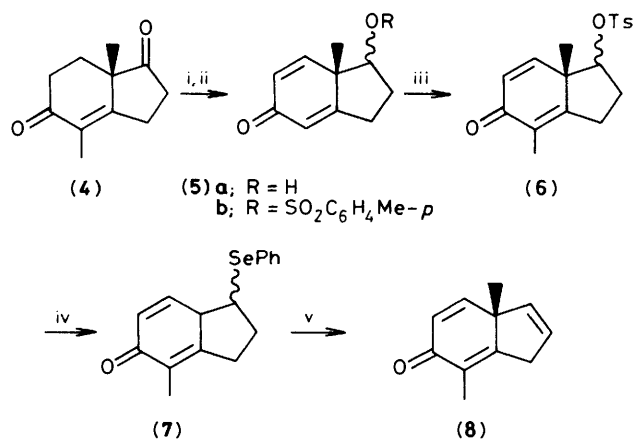
Scheme 1. *Reagents:* i, NaBH₄; ii, tosyl chloride, pyridine; iii, (PhSeO)₂O; iv, PhSeBH₃Na; v, H₂O₂, THF, pyridine.

obtained by direct oxidation of (5b) with benzeneseleninic anhydride in chlorobenzene at 90 °C if care was taken to avoid over-reaction.[5] Attempts to eliminate the toluene-4-sulphonate group in (6) to give the trienone (8) directly were unsuccessful but this transformation was effected by displacement of the sulphonate with diphenyl diselenide–sodium borohydride to give (7) (61%) followed by oxidation of this with hydrogen peroxide in tetrahydrofuran containing pyridine, and elimination of phenylseleninic acid (85%).

Our plan was to convert the trienone (8) into the 3a-methyl-3aH-indene (9) by forming the enolate anion followed by O-methylation with methyl fluorosulphonate which worked well

(8)   (9)
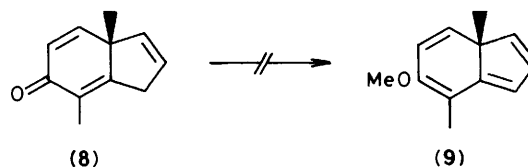
in the formation of 3aH-indenes (1) and (2).[1,2] However, compound (9) could not be isolated, detected, nor intercepted by cycloaddition with PTAD or dimethyl acetylenedicarboxyl-

ate, under a range of experimental conditions using the previously most successful reagents (KH, 18-crown-6,1,2-dimethoxyethane). The trienone (8) in dimethoxyethane was added slowly to the base, to encourage complete conversion into the enolate, at different rates of addition and at temperatures from $-78\,^{\circ}C$ to $-10\,^{\circ}C$. The colour of the reaction solutions ranged from crimson to deep blue and the products were complex. They appeared to be dimeric, with and without molecules of the dienophiles incorporated, but in this series of experiments none of the many products were obtained pure and in sufficient quantity for full characterisation.

However, if all the trienone (8) was added to the potassium hydride mixture at $-20\,^{\circ}C$ over 1 min the reaction was much cleaner. A crimson anion was formed instantaneously and this changed within a few seconds to give a persistent, deep blue solution. Methyl fluorosulphonate was added, followed after 5 min by PTAD, with further stirring whilst warming to room temperature. In this way two colourless crystalline products, m.p. 220—221 $^{\circ}C$ and 193—195 $^{\circ}C$, were isolated, each in ca. 20% yield. Both had molecular weights of 509, suggesting incorporation of two molecules of trienone (8) and one molecule of PTAD, the whole being monomethylated, to give $C_{31}H_{31}N_3O_4$. In agreement with this the ^1H n.m.r. spectra of the adducts each included four C-methyl signals between δ 1.3 and 1.7, one at δ 3.95 and 3.16 respectively from the methylation reaction, and five-proton multiplets at δ 7.3—7.5 for the phenyl group of PTAD; the ^{13}C n.m.r. spectra substantiated the total count of carbon atoms. The structure of the higher melting adduct was solved by X-ray diffraction analysis; this was found to be (10) (see Figure 1) in which, unexpectedly, it is the PTAD unit, rather than the enolate, which has become methylated. The ^1H and ^{13}C n.m.r. spectra of the two adducts were very similar, though the O-methyl group signals of (10) (^1H, δ 3.95; ^{13}C δ 48) were replaced by similar signals at δ 3.16 and δ 38, respectively, which were assigned to an N-methyl group. This, together with an alternative synthesis (see below) led to the assignment of the closely related structure (11), with the PTAD unit methylated

(10) R = (triazole structure with NPh and OMe)

(11) R = (triazole structure with NPh and MeN, O)
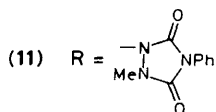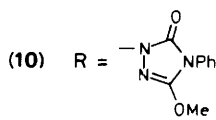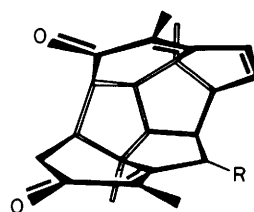
on nitrogen instead of oxygen, for the lower melting adduct. Thus two molecules of starting trienone (8), with their ring system and carbonyl groups intact and without being methylated, have become united by three bonds to form a hexacyclic concave structure with the bridgehead methyl groups on the outside of the molecular cavity. A molecule of PTAD is attached to the periphery of this structure and is methylated on oxygen and on nitrogen, respectively.

The phenyl ring of the molecule (Figure 1) is rotated by 56° from the plane of the triazole ring. The triazole ring and both its oxygen and methoxy substituents are coplanar. The ring plane

nearly bisects the C(2)–C(1)–C(14) angle of the hexacyclic system with C(2)–C(1)–N(23)–N(27) and C(14)–C(1)–N(23)–C(24) torsion angles of 66 and $-55°$ respectively.
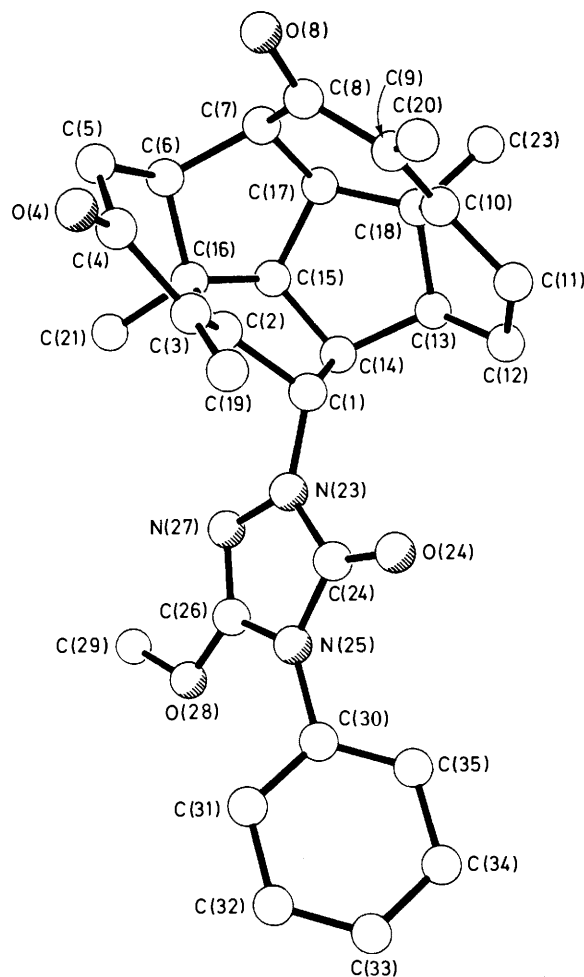

Figure 1. The molecular structure of (10) together with the atom numbering scheme.

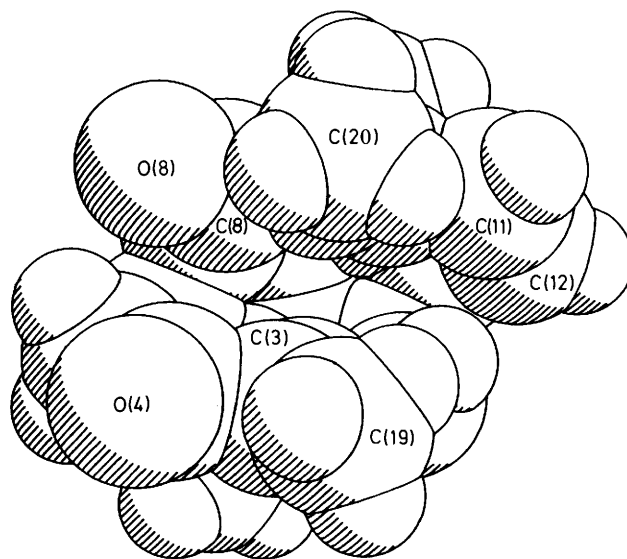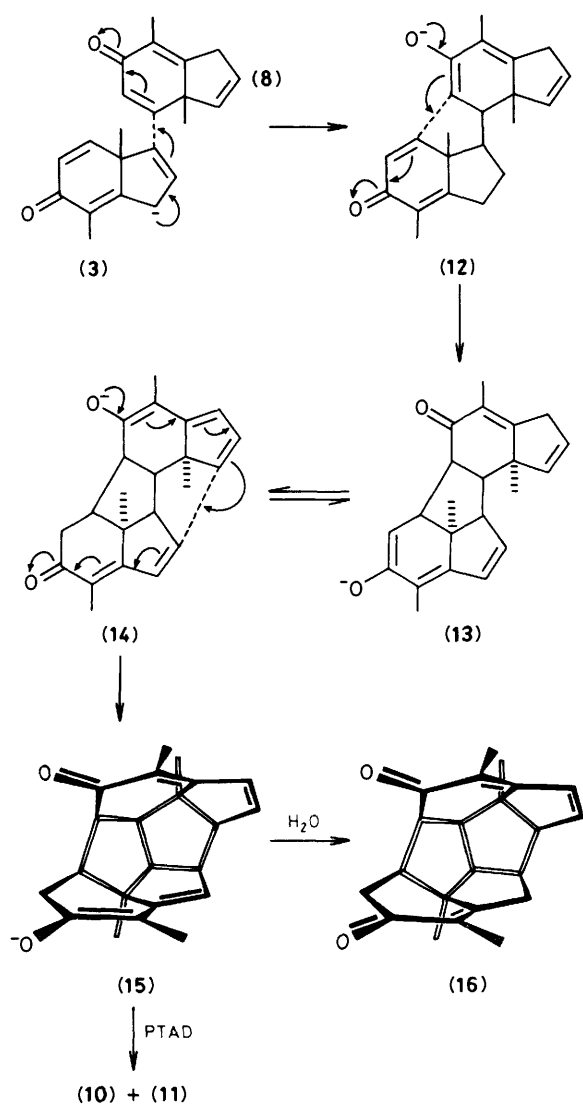Figure 2. Space-filling representation of the hexacyclic portion of (10) with selected atoms identified.

(3)   (12)

(14)   (13)

(15)   (16)

PTAD

(10) + (11)

Scheme 2.

Despite an apparently strained conformation, departures from planar geometries at the peripheral double bonds in the hexacyclic portion of the molecule are small. There are torsional twists of 7, 10, and 2° about the C(2)–C(3), C(9)–C(10) and C(11)–C(12) bonds respectively.

The folded conformation of the hexacyclic system creates a U-shaped cavity with near-parallel sides. Inspection of a space-filling representation of this part of the molecule (Figure 2) shows this potential cavity to be self-filled. There are, however, notable juxtapositions of some of the atoms and bonds in opposite faces. Of particular interest is a near overlap of the C(2)–C(3) and C(9)–C(10) double bonds. These bonds and their substituents lie in two near-parallel planes with the bonds inclined by *ca.* 30° to each other. The closest approaches are between C(2) and the mid-point of C(9)–C(10) and between C(9) and the mid-point of C(2)–C(3), both of 3.40 Å. Another trans-cavity contact is between the C(4) and C(8) carbonyl groups; C(4) is 3.22 Å from C(8) and 3.17 Å from the mid-point of the C(8)–O(8) bond.

Mechanism of Formation of Adducts (**10**) *and* (**11**).—It was originally expected that the delocalised anion (**3**) formed from the trienone (**8**) would be methylated on oxygen by methyl

fluorosulphonate to give 3a*H*-indene (**9**), but when reaction conditions favoured rapid and complete conversion of (**8**) into (**3**) the product mixture was complex. Adducts (**10**) and (**11**) were isolated when the anion (**3**) was slowly formed in the presence of the trienone (**8**), and we propose that the first step in their formation is Michael addition of (**3**) to (**8**) to give the dimeric anion (**12**), as shown in Scheme 2. This new anion is then well disposed for a second, intramolecular, Michael addition in the reverse direction, to give the pentacyclic ion (**13**) which would equilibrate with the more delocalised ion (**14**). This, in its turn, is also well disposed for a third Michael addition, as shown, to give the hexacyclic anion (**15**) which adds to PTAD to form a heterocyclic anion which is finally methylated to give (**10**) and (**11**). However it does seem puzzling that we observe no products of *O*-methylation of the anions (**3**) and (**15**) or even of the other, intermediate, anions. The striking difference between the reactions reported here and those which are initiated by *O*-methylation of the 3a*H*-indene enolates reported earlier[1,2] is attributed to the favourable sequence of conjugate additions, shown in Scheme 2, which are available to the trienone (**8**) and its anion with their precise arrangement of the double bonds and with the oxo group at position 6. Furthermore, this sequence of carbon–carbon bond-forming steps appears to proceed regio-and stereo-selectively since (**10**) and (**11**) are the only isomers that we could isolate or detect.

Since the structure of the *O*-methyl compound (**10**) was established by *X*-ray diffraction, it was desirable to confirm the structure of the *N*-methyl isomer (**11**) by preparing it from (**10**) in an *O*- to *N*-methyl rearrangement, for example in an iodomethane-catalysed process. This rearrangement was very slow in boiling toluene or xylene, but on heating in neat iodomethane at 100 °C compound (**10**) was converted into (**11**) over several hours. The slowness of this catalysed isomerisation argues strongly against the formation of the *N*-methyl isomer in this way in the trienone (**8**) reaction, and suggests that the two derivatives were formed independently in competitive methylation reactions. Since methyl fluorosulphonate usually favours *O*-methylation over *N*-methylation,[6] it is possible that the actual methylating species here is the *O*-methyl derivative of the solvent, 1,2-dimethoxyethane, or of 18-crown-6, formed by their reaction with the methylating agent.

To provide support for the mechanism proposed in Scheme 2, the reaction was repeated without the addition of methyl fluorosulphonate and PTAD but with water to quench the final anion. This should result in the formation of the protonated form of the hexacyclic anion (**15**), without the heterocyclic appendage. The trienone (**8**) was treated as before with potassium hydride and 18-crown-6 in dimethoxyethane at −20 °C; (**8**) was added rapidly and again the initial red solution turned blue almost immediately. On addition of water the blue colour faded rather slowly (5 min), to give one crystalline product, m.p. 192—194 °C in 64% yield. This had the molecular formula, $C_{22}H_{24}O_2$, equivalent to a dimer of the starting material, and structure (**16**) was assigned to it on the basis of extensive ^1H and ^{13}C n.m.r., decoupling, and n.O.e. experiments and comparison with the analogous results for the adducts (**10**) and (**11**).[7] The relatively long time required for the protonation of the anion (**15**) to give (**16**) suggests that it is stable enough to survive to react with PTAD in the earlier experiment.

The formation of a persistent blue solution in these experiments is intriguing since neither anion (**15**), nor any of the others would be expected to be blue. The near overlap and 3.4 Å separation of the C(2)–C(3) and C(9)–C(10) double bonds across the molecular cavity in the structure (**16**) were described earlier. This suggests the possibility of an intramolecular charge-transfer interaction, across the cavity of the anion (**15**), from the electron-rich dienolate anion to the electron-poor dienone, especially if even better overlap can be achieved through

conformational flexing. Separations of this order are consistent with such a charge-transfer interaction.[8]

Experimental

For general points see ref. 1. 1,2-Dimethoxyethane and tetrahydrofuran used for enolisation reactions were dried over sodium wire, distilled onto potassium metal under nitrogen, redistilled from potassium, and stored over calcium hydride under nitrogen. They were used for up to two weeks before being re-dried. Enolisation reactions were carried out in flame-dried glassware, cooled under dry nitrogen with exclusion of oxygen. Solutions and liquids were transferred with dry syringes and needles.

7,7a-Dihydro-4,7a-*dimethyl*-1-*hydroxyindan*-5(6H)-*one* **(5a)**.—7,7a-Dihydro-4,7a-dimethyl-1H-indan-1,5-dione[3] **(4)** (6.0 g, 33.9 mmol) was dissolved in dry ethanol (30 ml) and cooled to $-10\,^{\circ}$C. Sodium borohydride (340 mg, 8.7 mmol) in dry ethanol (20 ml) was added dropwise to the stirred solution. The reaction mixture was maintained below $-5\,^{\circ}$C throughout the addition and at $-5\,^{\circ}$C for a further 0.5 h. The reaction mixture was cooled to $-10\,^{\circ}$C and the pH of the solution adjusted, with 2M-hydrochloric acid, to 6. The solvent was removed under reduced pressure and the yellow semisolid partitioned between ethyl acetate and water. The organic phase was retained, dried (Na_2SO_4), and the solvent removed under reduced pressure to leave an oil which was distilled (b.p. 141—143 °C, 0.02 mmHg) to give 7,7a-dihydro-4,7a-dimethyl-1-hydroxyindan-5(6H)-one **(5a)** (5.2 g, 87%), m.p. 60—62 °C (lit.,[4] m.p. 63 °C).

7,7a-Dihydro-4,7a-*dimethyl*-1-(p-*tolylsulphonyloxy*)*indan*-5-(6H)-*one* **(5b)**.—7,7a-Dihydro-4,7a-dimethyl-1-hydroxyindan-5 (6H)-one **(5a)** (20.4 g, 0.12 mol) was dissolved in redistilled pyridine (50 ml) and stirred, whilst recrystallised toluene-*p*-sulphonyl chloride (23.0 g, 0.12 mol) was added at room temperature. After 5 h a further quantity of recrystallised toluene-*p*-sulphonyl chloride (11.43 g, 60.0 mmol) was added and the mixture stirred for a further 15 h. The mixture was poured into water (200 ml) and extracted with ether (4 × 100 ml). The ether layer was washed with 2M-hydrochloric acid (3 × 50 ml), saturated aqueous sodium hydrogen carbonate (3 × 50 ml), and water (3 × 50 ml) and then dried (Na_2SO_4). The solvent was removed under reduced pressure to leave a pale yellow oil which solidified on trituration (petroleum) to give *7,7a-dihydro*-4,7a-*dimethyl*-1-(p-*tolylsulphonyloxy*)*indan*-5 (6H)-*one* **(5b)** (34.4 g, 87%), m.p. 85.5—86.5 °C (from ether–petroleum) (Found: C, 64.8; H, 6.7; S, 9.6. $C_{18}H_{22}O_4S$ requires C, 64.7; H, 6.6; S, 9.5%); $\nu_{max.}$(KBr) 1 640s, 1 380s, 1 357s, 1 343s, 1 185s, 1 172s, 978s, 880s, 840s, and 663s cm^{-1}; δ_H (250 MHz; CDCl$_3$) 1.15 (3 H, s), 1.5—1.6 (1 H, m), 1.62 (3 H, s), 1.85—2.15 (3 H, m), 2.3—2.7 (5 H, m), 7.36 (2 H, d, *J* 11 Hz), and 7.81 (2 H, d, *J* 11 Hz); δ_C(CDCl$_3$) 11.2, 20.6, 21.8, 24.9, 28.1, 48.2, 82.0, 128.0, 128.8, 130.2, 131.3, 134.0, 145.0, 149.0, 160.4, and 186.2; *m/z* 334 (*M*$^+$), 179, 162, 161, 155, 151, 147, 137, 135, 134, 133, 119, and 91.

4,7a-*Dimethyl*-1-(p-*tolylsulphonyloxy*)-1,2,3,7a-*tetrahydro*-*inden*-5-*one* **(6)**.—(*a*) *With* 2,3-*dichloro*-5,6-*dicyano*-1,4-*benzoquinone*. 7,7a-Dihydro-4,7a-dimethyl-1-(p-tolylsulphonyloxy)-indan-5(6H)-one **(5b)** (5 g, 15 mmol) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (5 g, 22.0 mmol) were dissolved in dry benzene (150 ml) and glacial acetic acid (7.5 ml) and heated under reflux for 36 h. The brown solid was filtered off and washed with benzene. The filtrate and washings were combined and washed with sodium dithionite solution (1M; 3 × 30 ml), saturated aqueous sodium hydrogen carbonate (3 × 25 ml),

and water (3 × 25 ml). The solution was dried (Na_2SO_4) and the solvent removed under reduced pressure to give a yellow liquid. Column chromatography (silica, chloroform–ethyl acetate 10:1) gave 4,7a-*dimethyl*-1-(p-*tolylsulphonyloxy*)-1,2,3,7a-*tetrahydro*-5H-*inden*-5-*one* **(6)** (1.4 g, 28%), m.p. 127.5—129 °C (from ether–dichloromethane) (Found: C, 65.0; H, 6.0. $C_{18}H_{20}O_4S$ requires C, 65.1; H, 6.0); $\nu_{max.}$(KBr) 1 665s, 1 592s, 1 380s, 1 360s, 1 325s, 1 190s, 1 170s, 970s, 890s, and 765 cm^{-1}; δ_H (250 MHz; CDCl$_3$) 1.21 (3 H, s), 2.1—2.2 (2 H, m), 2.4—2.55 (4 H, m), 2.6—2.75 (1 H, m), 4.45—4.52 (1 H, m), 6.15 (1 H, d, $J_{6,7}$ 11 Hz), 6.85 (1 H, d, $J_{7,6}$ 11 Hz), 7.37 (2 H, d, J_A 9 Hz), and 7.82 (2 H, d, J_B 9 Hz); *m/z* 332 (*M*$^+$), 314, 177, 160, 159, 155, 149, 135, and 91.

(*b*) *By phenylselenation–oxidation*. The toluenesulphonate **(5b)** (2.0 g, 6 mmol) was dissolved in tetrahydrofuran (15 ml) and cooled to $-78\,^{\circ}$C. Lithium di-isopropylamide [from n-butyl-lithium (1.6M; 5 ml, 8.0 mmol) and di-isopropylamine (1.05 ml, 8.0 mmol)] in tetrahydrofuran (10 ml) was added and the resulting solution stirred for 0.25 h after which phenyl-seleninyl bromide [from diphenyl diselenide (1.13 g, 3.6 mmol) and bromine (200 µl, 3.6 mmol)] in tetrahydrofuran (5 ml) was added. The solution was allowed to warm to room temperature and after 0.5 h hydrogen peroxide (30%; 7 ml, 62 mmol) was added with stirring over 0.5 h. After being stirred for 3 h the mixture was poured into water (50 ml) and extracted with chloroform (2 × 75 ml); the organic phase was washed with saturated aqueous sodium hydrogen carbonate (3 × 25 ml) and water (3 × 25 ml) and dried (Na_2SO_4). The solvent was removed under reduced pressure and the oil subjected to column chromatography (silica, dichloromethane–ether) to give the dienone **(6)** (1.22 g, 61%), m.p. 127.5—129 °C.

(*c*) *With benzeneseleninic anhydride*. To stirred chlorobenzene (10 ml) at 90 °C was added the toluenesulphonate **(5b)** (186 mg, 0.56 mmol) and benzeneseleninic anhydride (200 mg, 0.56 mmol); the stirring and heating were continued for 1.5 h. The reaction mixture was poured into saturated aqueous sodium hydrogen carbonate (100 ml) and extracted with dichloro-methane (3 × 50 ml). The organic phase was washed with water (2 × 50 ml), dried (Na_2SO_4), and the solvent removed under reduced pressure to give a yellow solid. Column chromatography (silica, petroleum–dichloromethane–ether) gave the dienone **(6)** (174 mg, 94%), m.p. 127—129 °C (from petroleum–ether).

4,7a-*Dimethyl*-1-*phenylseleno*-1,2,3,7a-*tetrahydro*-5H-*inden*-5-*one* **(7)**.—Diphenyl diselenide (1.58 g, 5.1 mmol) was dissolved in hot ethanol (20 ml) and the solution cooled. Sodium borohydride (0.41 g, 10.8 mmol) was added to the yellow solution, with stirring, and acetone (3 ml) was added when the solution had decolourised. The toluenesulphonate **(5b)** (1.69 g, 5.0 mmol) was added to the solution and the mixture heated under reflux for 3 h. The reaction mixture was filtered and the precipitate washed with chloroform. The extracts were combined, concentrated under reduced pressure and the residual oil partitioned between chloroform (150 ml) and water (50 ml). The organic phase was retained, washed with water (2 × 50 ml), and dried (Na_2SO_4). The solvent was removed under reduced pressure and the mixture subjected to column chromatography (silica, petroleum–dichloromethane), to give 4,7a-*dimethyl*-1-*phenylseleno*-1,2,3,7a-*tetrahydro*-5H-*inden*-5-*one* **(7)** (991 mg, 61%) as a crystalline solid, m.p. 117—117.5 °C (from ether–petroleum) (Found: C, 64.1; H, 5.6. $C_{17}H_{18}OSe$ requires C, 64.3; H, 5.7%); $\nu_{max.}$(KBr) 1 660s, 1 455s, 1 330s, 1 038s, 838s, 752s, 749s, 741s, and 694s cm^{-1}; δ_H (250 MHz; CDCl$_3$) 1.32 (3 H, s), 1.82 (3 H, s), 2.1—2.2 (1 H, m), 2.52—2.62 (1 H, m), 2.75 (1 H, m), 3.75—3.80 (1 H, m), 6.22 (1 H, d, $J_{6,7}$ 11 Hz), 7.03 (1 H, d, $J_{7,6}$ 11 Hz), 7.27—7.30 (2 H, m), and 7.47—7.52 (3 H, m); *m/z* 318 (*M*$^+$), 316, 303, 219, 161, 145, 118, 117, 105, and 91.

3,7a-*Dihydro*-4,7a-*dimethyl*-5H-*inden*-5-*one* (8).—The selenide (7) (900 mg, 2.84 mmol) was dissolved in tetrahydrofuran (5 ml) and cooled in an ice-bath. The solution was stirred whilst hydrogen peroxide (30%; 3.4 ml, 30 mmol) was added dropwise over 1 h. The temperature was maintaned at 0 °C for a further 0.5 h and the mixture then allowed to warm to room temperature and stirred for a further 5 h. The reaction mixture was poured into water and extracted with ether (3 × 50 ml). The organic layer was washed with saturated aqueous sodium hydrogen carbonate (2 × 25 ml) and water (2 × 25 ml) and dried (Na_2SO_4). The solvent was removed under reduced pressure to give a pale yellow oil which was subjected to bulb to bulb distillation to give 3,7a-*dihydro*-4,7a-*dimethyl*-5H-*inden*-5-*one* (8) (0.38 g, 85%) as a colourless oil (b.p. 85—86 °C, 0.08 mmHg) (Found: C, 82.3; H, 7.7. $C_{11}H_{12}O$ requires C, 82.5; H, 7.6%); $\nu_{max.}$(KBr) 1 680s, 1 660s, 1 640s, 1 610s, 1 310s, 825s, and 725s cm^{-1}; δ_H (250 MHz; $CDCl_3$) 1.3 (3 H, s), 1.85 (3 H, s), 3.27 (2 H, m), 5.85—5.95 (2 H, m), 6.17 (1 H, J 11 Hz), and 7.16 (1 H, J 11 Hz); m/z 160 (M^+), 145, 117, 115, and 91.

Formation of the Adducts (10) *and* (11).—Potassium hydride (20% in oil; 520 mg, 2.6 mmol) was de-oiled with petroleum (b.p. 60—80 °C) and suspended in 1,2-dimethoxyethane (10 ml) in a flame-dried flask under nitrogen. 18-Crown-6 (343 mg, 1.3 mmol) in dimethoxyethane (10 ml) was added and the suspension was cooled to −20 °C in a carbon tetrachloride bath and to it the trienone (8) (206 mg, 1.29 mmol) in dimethoxyethane (5 ml) was added over 1 min to give a crimson solution which rapidly changed to blue. After 0.5 h methyl fluorosulphonate (CAUTION: HIGHLY TOXIC) (*ca.* 160 μl, 2 mmol) was added and after the mixture had been stirred for a further 5 min 4-phenyltriazole-3,5-dione (300 mg) was added. The reaction mixture was allowed to warm to room temperature, stirred for a further 0.5 h, and then poured into water (100 ml) and extracted with dichloromethane (3 × 50 ml). The organic phase was washed with water (2 × 50 ml), dried (Na_2SO_4), and the solvent removed under reduced pressure. The resulting brown oil was subjected to column chromatography (silica, petroleum–ether) to give the *adduct* (10) (139 mg, 21%), m.p. 220—221 °C, and the *adduct* (11) (126 mg, 19%), m.p. 193.5—195 °C, as crystalline solids.

Adduct (10): (Found: C, 73.4; H, 6.1; N, 8.3. $C_{31}H_{31}N_3O_4$ requires C, 73.1; H, 6.1; N, 8.3%); $\nu_{max.}$(CHCl$_3$) 3 490 (m, br), 2 970s, 1 770s, 1 690s, 1 640s, 1 610s, 1 435s, 1 400s, 1 340s, 1 320s, 1 310s, 1 130m, 980s, and 670m cm^{-1}; δ (250 MHz; $CDCl_3$) 1.30 (3 H, s), 1.59 (3 H, s), 1.64 (3 H, s), 1.68 (3 H, s), 2.63 (1 H, dd, J_{5H} 6 Hz), 2.83—3.15 (5 H, m), 3.30 (1 H, dd, $J_{11,10}$ 3 Hz, $J_{10.5H}$ 4 Hz), 3.56 (1 H, dd, J_{5H} 8.5 Hz, J_{5H} 5.5 Hz), 3.95 (3 H, s), 5.26 (1 H, d, J_{5H} 5.5 Hz), 6.50 (1 H, dd, $J_{10,11}$ 3.3 Hz, $J_{10,9}$ 5.5 Hz), 6.80 (1 H, d, $J_{9,10}$ 5.5 Hz), and 7.30—7.52 (5 H, m); n.O.e. spectrum ($CDCl_3$), irradiation at: δ 1.3 enhances δ 2.84—3.10 (m), 3.30 (dd) and 6.8 (d, secondary); δ 1.64 enhances δ 2.64 (dd), 3.30—3.12 (m) and 3.48 (dd); δ 1.64 enhances δ 5.25 (d); δ 1.68 enhances δ 6.82 (d); δ_C(CDCl$_3$) 12.1(q), 12.4(q), 25.5(q), 30.2(q), 33.9(t), 38.6(q), 47.4(d), 48.1(d), 49.7(d), 54.0(d), 55.0(d), 56.6(d), 64.3(d), 66.3(d), 66.7(d), 125.3(d), 127.3(s), 128(d), 129.2(d), 131(s), 131.6(d), 136(s), 143.8(d), 154.9(s), 157.3(s), 159.9(s), 164.5(s), 196.2(s), and 198.1(s); m/z 509 (M^+), 494, 368, 360, 349, 334, 319, 213, 191, and 159.

Adduct (11): (Found: C, 73.3; H, 6.1; N, 8.3. $C_{31}H_{31}N_3O_4$ requires C, 73.1; H, 6.1; N, 8.3%); $\nu_{max.}$(CHCl$_3$) 3 480m, br, 2 910s, 1 770s, 1 710s, 1 665s, 1 620s, 1 400s, 1 200br, 1 045m, 1 085m and 870s cm^{-1}; δ_H (250 Mz; $CDCl_3$) 1.28 (3 H, s), 1.55 (3 H, s), 1.66 (3 H, s), 1.72 (3 H, s), 2.65 (1 H, dd, J_{8H} 9.5 Hz, J_{8H} 6 Hz), 2.80—3.22 (8 H, m), 3.30 (1 H, dd, $J_{11,10}$ 3.3 Hz, $J_{11,8H}$ 4 Hz), 3.43 (1 H, dd, J_{8H} 8.8 Hz, J_{8H} 5.5 Hz), 4.78 (1 H, d, J_{8H} 5 Hz), 6.53 (1 H, dd, $J_{10,11}$ 3.3 Hz, $J_{10,9}$ 5.5 Hz), 6.74 (1 H, d, $J_{9,10}$ 5.5 Hz), and 7.38—7.53 (5 H, m); n.O.e. spectrum ($CDCl_3$),

Table 1. Atom co-ordinates (× 104)

Atom	x	y	z
C(1)	3 430(5)	3 426(3)	7 058(3)
C(2)	3 714(5)	3 906(4)	7 854(3)
C(3)	4 982(6)	4 288(4)	7 861(3)
C(4)	4 928(7)	4 977(5)	8 616(3)
O(4)	6 076(5)	5 280(5)	8 655(3)
C(5)	3 405(7)	5 349(5)	9 308(3)
C(6)	1 907(6)	5 201(4)	9 068(3)
C(7)	943(6)	6 138(4)	8 495(3)
C(8)	1 957(6)	6 794(4)	7 941(3)
O(8)	2 434(6)	7 448(4)	8 298(3)
C(9)	2 425(6)	6 614(4)	7 007(3)
C(10)	1 697(5)	6 042(4)	6 624(3)
C(11)	2 217(6)	5 528(4)	5 750(3)
C(12)	1 678(7)	4 616(5)	5 748(4)
C(13)	716(6)	4 492(4)	6 627(4)
C(14)	1 615(5)	3 632(4)	7 227(3)
C(15)	924(5)	4 187(4)	8 137(3)
C(16)	2 277(5)	4 056(4)	8 584(3)
C(17)	130(6)	5 496(4)	8 038(3)
C(18)	260(5)	5 692(4)	7 084(4)
C(19)	6 397(6)	4 122(5)	7 129(4)
C(20)	3 781(7)	7 032(5)	6 558(4)
C(21)	2 574(7)	3 017(4)	9 180(3)
C(22)	−1 287(7)	6 568(5)	6 889(5)
N(23)	4 411(4)	2 247(3)	6 831(2)
C(24)	5 560(5)	1 884(4)	6 088(3)
O(24)	5 986(4)	2 470(3)	5 507(2)
N(25)	6 117(4)	694(3)	6 151(2)
C(26)	5 277(5)	433(4)	6 927(3)
N(27)	4 233(4)	1 321(3)	7 356(2)
O(28)	5 584(4)	−659(3)	7 136(2)
C(29)	4 632(7)	−859(4)	7 935(3)
C(30)	7 308(5)	−72(4)	5 505(3)
C(31)	8 691(6)	−806(4)	5 723(3)
C(32)	9 860(6)	−1 540(4)	5 094(4)
C(33)	9 614(7)	−1 513(5)	4 268(4)
C(34)	8 241(7)	−773(5)	4 059(4)
C(35)	7 081(6)	−28(4)	4 686(3)
C(40) †	7 374(11)	1 368(8)	9 745(6)
C(41) †	8 143(14)	1 907(8)	9 122(8)
C(42) †	9 498(13)	1 191(9)	8 418(7)
C(43) †	9 206(13)	232(10)	8 162(7)
C(44) †	8 312(11)	−355(8)	8 738(8)
C(45) †	7 160(12)	300(11)	9 469(8)

† Estimated occupancy 0.5

irradiation at: δ 1.28 enhances δ 3.30 (dd), 2.90—3.10 (m and s) and 6.85 (d, secondary); δ 1.55 enhances δ 2.66 (dd), 2.96—3.10 (m and s) and 3.42 (dd); δ 1.66 enhances δ 6.72 (s); δ 1.72 enhances δ 3.08 (s) and 4.79 (d); δ_C(CDCl$_3$) 12.1(q), 12.2(q), 24.7(q), 30.2(q), 34.2(t), 48.0 and 48.2(d with q), 50.8(d), 53.9(s), 54.9(s), 56.3 and 56.3(d with d), 60.0(d), 64.2(d), 66.9(d), 125(d), 127.7(s), 127.9(d), 129(d), 131(s), 132(d), 133(s), 143(d), 150.1(s), 150.3(s), 163.9(s), 164.3(s), 196(s), and 198(s); m/z 509 (M^+) 368, 319, 213, 191, and 160.

Conversion of the Adduct (10) *into the Adduct* (11).—The O-methyl adduct (10) (9.4 mg, 0.018 mmol), carefully freed from the N-methyl adduct (11) by chromatography and recrystallisation, was dissolved in methyl iodide (7 ml) and sealed in a glass tube. The tube was slowly heated in an oil-bath to 100 °C over 8 h, held at 100 °C for 5 h and cooled over a further 8 h. The solvent was removed under reduced pressure to give a brown solid, t.l.c. analysis of which showed starting material and the N-methyl dimer (11). Filtration (through silica) gave a colourless solid (8.9 mg) which was examined by n.m.r. (250 MHz); this

Table 2. Bond lengths (Å)

C(1)-C(2)	1.519(7)	C(1)-C(14)	1.522(6)
C(1)-N(23)	1.445(5)	C(2)-C(3)	1.359(8)
C(2)-C(16)	1.500(6)	C(3)-C(4)	1.481(8)
C(3)-C(19)	1.486(6)	C(4)-O(4)	1.211(9)
C(4)-C(5)	1.505(7)	C(5)-C(6)	1.533(9)
C(6)-C(7)	1.584(7)	C(6)-C(16)	1.536(7)
C(7)-C(8)	1.518(8)	C(7)-C(17)	1.523(8)
C(8)-O(8)	1.228(8)	C(8)-C(9)	1.459(7)
C(9)-C(10)	1.336(8)	C(9)-C(20)	1.493(9)
C(10)-C(11)	1.466(7)	C(10)-C(18)	1.512(7)
C(11)-C(12)	1.352(9)	C(12)-C(13)	1.504(8)
C(13)-C(14)	1.540(7)	C(13)-C(18)	1.561(7)
C(14)-C(15)	1.537(7)	C(15)-C(16)	1.493(8)
C(15)-C(17)	1.551(6)	C(16)-C(21)	1.543(7)
C(17)-C(18)	1.511(8)	C(18)-C(22)	1.538(7)
N(23)-C(24)	1.369(5)	N(23)-N(27)	1.410(5)
C(24)-O(24)	1.217(6)	C(24)-N(25)	1.391(6)
N(25)-C(26)	1.380(5)	N(25)-C(30)	1.428(5)
C(26)-N(27)	1.287(5)	C(26)-O(28)	1.321(5)
O(28)-C(29)	1.428(6)	C(30)-C(31)	1.379(6)
C(30)-C(35)	1.356(7)	C(31)-C(32)	1.388(6)
C(32)-C(33)	1.374(9)	C(33)-C(34)	1.369(8)
C(34)-C(35)	1.388(6)	C(40)-C(41)	1.353(15)
C(40)-C(45)	1.481(18)	C(41)-C(42)	1.518(13)
C(42)-C(43)	1.378(18)	C(43)-C(44)	1.411(16)
C(44)-C(45)	1.444(15)		

Table 3. Bond angles (°)

C(2)-C(1)-C(14)	105.5(3)	C(2)-C(1)-N(23)	114.3(3)
C(14)-C(1)-N(23)	114.3(4)	C(1)-C(2)-C(3)	124.3(4)
C(1)-C(2)-C(16)	109.9(4)	C(3)-C(2)-C(16)	125.2(4)
C(2)-C(3)-C(4)	118.9(4)	C(2)-C(3)-C(19)	124.1(5)
C(4)-C(3)-C(19)	116.9(5)	C(3)-C(4)-O(4)	120.1(5)
C(3)-C(4)-C(5)	119.5(6)	O(4)-C(4)-C(5)	120.4(5)
C(4)-C(5)-C(6)	115.0(5)	C(5)-C(6)-C(7)	118.9(5)
C(5)-C(6)-C(16)	112.8(4)	C(7)-C(6)-C(16)	104.2(4)
C(6)-C(7)-C(8)	113.8(4)	C(6)-C(7)-C(17)	104.5(4)
C(8)-C(7)-C(17)	117.5(4)	C(7)-C(8)-O(8)	118.6(5)
C(7)-C(8)-C(9)	120.9(5)	O(8)-C(8)-C(9)	120.4(5)
C(8)-C(9)-C(10)	119.0(5)	C(8)-C(9)-C(20)	116.0(5)
C(10)-C(9)-C(20)	124.9(4)	C(9)-C(10)-C(11)	128.0(5)
C(9)-C(10)-C(18)	123.7(4)	C(11)-C(10)-C(18)	107.9(5)
C(10)-C(11)-C(12)	108.5(5)	C(11)-C(12)-C(13)	110.1(5)
C(12)-C(13)-C(14)	117.0(4)	C(12)-C(13)-C(18)	104.3(4)
C(14)-C(13)-C(18)	104.4(5)	C(1)-C(14)-C(13)	114.9(4)
C(1)-C(14)-C(15)	105.8(4)	C(13)-C(14)-C(15)	105.6(3)
C(14)-C(15)-C(16)	109.4(3)	C(14)-C(15)-C(17)	107.7(4)
C(16)-C(15)-C(17)	106.8(4)	C(2)-C(16)-C(6)	109.2(4)
C(2)-C(16)-C(15)	103.2(4)	C(6)-C(16)-C(15)	107.0(4)
C(2)-C(16)-C(21)	110.5(3)	C(6)-C(16)-C(21)	112.4(4)
C(15)-C(16)-C(21)	114.0(5)	C(7)-C(17)-C(15)	108.2(4)
C(7)-C(17)-C(18)	115.9(4)	C(15)-C(17)-C(18)	106.6(4)
C(10)-C(18)-C(13)	98.8(4)	C(10)-C(18)-C(17)	116.0(5)
C(13)-C(18)-C(17)	107.4(4)	C(10)-C(18)-C(22)	108.5(4)
C(13)-C(18)-C(22)	113.4(5)	C(17)-C(18)-C(22)	112.1(4)
C(1)-N(23)-C(24)	125.3(4)	C(1)-N(23)-N(27)	122.6(3)
C(24)-N(23)-N(27)	112.1(3)	N(23)-C(24)-O(24)	127.9(4)
N(23)-C(24)-N(25)	103.9(4)	O(24)-C(24)-N(25)	128.2(4)
C(24)-N(25)-C(26)	106.9(3)	C(24)-N(25)-C(30)	124.4(4)
C(26)-N(25)-C(30)	128.7(4)	N(25)-C(26)-N(27)	113.6(4)
N(25)-C(26)-O(28)	118.5(3)	N(27)-C(26)-O(28)	127.8(4)
N(23)-N(27)-C(26)	103.5(3)	C(26)-O(28)-C(29)	115.1(3)
N(25)-C(30)-C(31)	119.0(4)	N(25)-C(30)-C(35)	119.2(4)
C(31)-C(30)-C(35)	121.7(4)	C(30)-C(31)-C(32)	119.1(5)
C(31)-C(32)-C(33)	119.1(5)	C(32)-C(33)-C(34)	121.1(5)
C(33)-C(34)-C(35)	119.8(5)	C(30)-C(35)-C(34)	119.1(4)
C(41)-C(40)-C(45)	115.8(9)	C(40)-C(41)-C(42)	119.2(9)
C(41)-C(42)-C(43)	113.0(10)	C(42)-C(43)-C(44)	122.0(10)
C(43)-C(44)-C(45)	117.1(10)	C(40)-C(45)-C(44)	118.3(10)

showed the presence of the O-methyl adduct (**10**) and the N-methyl adduct (**11**) (36%).

Formation of the Dimer (**16**).—Potassium hydride (240 mg, 20% in oil, 1.2 mmol) was de-oiled with petroleum (b.p. 60—80 °C) and suspended in 1,2-dimethoxyethane (5 ml) in a flame-dried flask under nitrogen. 18-Crown-6 (147 mg, 0.56 mmol) in dimethoxyethane (5 ml) was added and the suspension was cooled to -20 °C; the trienone (**8**) (64.3 mg, 0.40 mmol) was then added rapidly to give a red solution which quickly changed to blue. The reaction mixture was sitrred for 0.5 h and water (3 ml) was then added. The mixture was poured into water (100 ml), the solution was saturated with sodium chloride, and extracted with ether (3 × 75 ml). The organic phase was washed with water (2 × 50 ml), dried (Na$_2$SO$_4$), and subjected to column chromatography (silica, petroleum–ether) to give the *dimer* (**16**) (41.3 mg, 64%), as a crystalline solid, m.p. 192—194 °C, (from petroleum–dichloromethane) (Found: C, 82.6; H, 7.4. C$_{22}$H$_{24}$O$_2$ requires C, 82.5; H, 7.5%); ν_{max}.(neat) 2 960m, 2 920m, 1 720s, 1 660s, 1 350m, and 1 330m cm^{-1}; δ_H (250 MHz; CDCl$_3$) 1.20 (3 H, s), 1.22 (3 H, s), 1.55 (3 H, s), 1.62 (3 H, s), 2.26—2.56 (3 H, m), 2.73—3.08 (5 H, m), 3.19 (1 H, dd, $J_{11,10}$ 3.1 Hz, $J_{11,5H}$ 4.4 Hz), 3.31 (1 H, dd, J_{5H} 8.0 Hz, J_{5H} 5.6 Hz), 6.28 (1 H, dd, $J_{10,11}$ 3.3 Hz, $J_{10,9}$ 5.5 Hz), and 6.53 (1 H, d, $J_{9,10}$ 5.5 Hz); m/z 320 (M^+), 305, 161, 160, 159, 145, and 91.

Crystal Data.—C$_{31}$H$_{31}$N$_3$O$_4$·0.5C$_6$H$_{12}$, M_r = 551.7, triclinic, a = 8.927(1), b = 12.265(2), c = 15.897(3) Å, α = 87.57(2), β = 77.49(2), γ = 71.35(1)°, U = 1 609 Å^3, space group P1̄, Z = 2, D_c = 1.14 g cm^{-3}. Refined unit-cell parameters were obtained by centering 18 reflections on a Nicolet R3m diffractometer. 3 307 Independent reflections ($\theta \leqslant 50°$) were measured with Cu-K_α radiation (graphite monochromator) using the omega-scan measuring routine. Of these 2 813 had $|F_o| > 3\sigma$ ($|F_o|$) and were considered to be observed. The data were corrected for Lorentz and polarisation factors; no absorption correction was applied.

The structure was solved by direct methods. An E-map computed using 428 $E'^s > 1.54$ from the phase solution with the highest figure of merit gave the positions of all the non-

hydrogen atoms in the molecule. A ΔF map revealed six weak peaks which were identified as belonging to a trapped cyclohexane molecule. The occupancy of the cyclohexane was estimated as being 0.5.

The non-hydrogen atoms were refined anisotropically. The positions of the C(3) and C(9) methyl hydrogen atoms were obtained from a ΔF map; those of the other methyl groups were placed in ideal staggered positions. All the methyl groups were refined as rigid bodies. The positions of the other hydrogen atoms were idealised (C–H = 0.96 Å), assigned isotropic thermal parameters, $U(H)$ = 1.2 U_{eq}(C), and allowed to ride on their parent carbons. 14 Reflections that had $|F_o| \ll |F_c|$ were suspected of being affected by extinction and were removed. Refinement was by block-cascade full-matrix least-squares to R = 0.086, R_w = 0.099 (w^{-1} = σ^2 (F) + 0.0048 F^2). The principal cause of the rather high final R value is probably the disorder in the trapped cyclohexane molecule. There were eleven peaks in the final ΔF map with heights ranging between 0.28 and 0.63 eÅ^{-3} in the region of the cyclohexane molecule, and a maximum residual electron density of 0.22 eÅ^{-3} in the rest of the structure.

Computations were carried out on an Eclipse S140 computer using the SHELXTL program system.[9] The fractional co-ordinates of the non-hydrogen atoms, the bond lengths, and the valence angles are given in Tables 1, 2 and 3 respectively. The fractional co-ordinates of the hydrogen atoms and their

isotropic thermal parameters, the isotropic and anisotropic thermal parameters of the non-hydrogen atoms. have been deposited as a Supplementary publication Sup. No. 56113 (4 pp.).* Tables of the observed and calculated structure factors are available on request from the editorial office.

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* For details of the Supplementary publications scheme see Instructions for Authors (1985), J. Chem. Soc., Perkin Trans. 1, 1985, issue 1.

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