3a*H*-Indenes. Part 4.[1] Formation and Reactions of Some Dienone Intermediates

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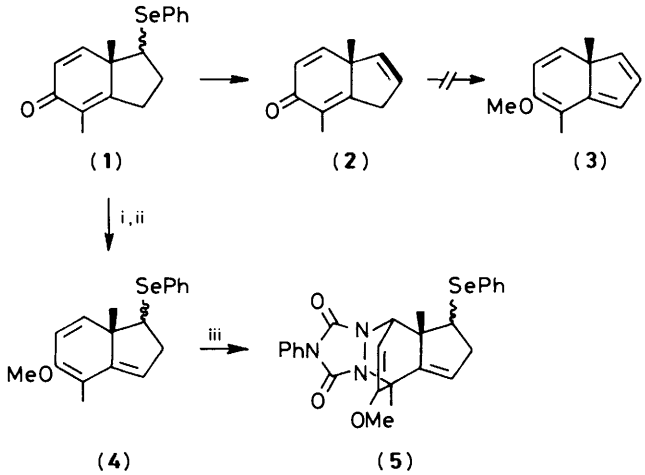
Methylation of the enolate anion of the cyclohexadienone (**1**) with methyl fluorosulphonate gave the unstable trienol ether (**4**) which was converted into the 4-phenyl-1,2,4-triazole-3,5-dione adduct (**5**) and the tricarbonyliron complex (**6**). The phenylseleno group of the triene (**4**) could not be oxidatively eliminated, under various conditions, to give the tetraene (**3**), but it was eliminated from the adduct (**5**) to give the rearranged adduct (**9**). The best reagent for selenide oxidation and elimination was chloramine-T under phase-transfer conditions. This was very effective in the conversion of the selenide (**12**) into the dienone (**13**). The dienone (**15**) was also prepared from the selenide (**14**).

We have shown[1] that the strained 3a-methylindene (**3**) could not be prepared from the trienone (**2**) by our standard enolisation and *O*-methylation sequence as the enolate anion of compound (**2**) is diverted by a rapid reaction with the starting trienone. We hoped that the formation of the enol ether (**4**) before the elimination of the selenium group, thus avoiding the enolate anion intermediate, might prove more successful and the results of this approach are described here.

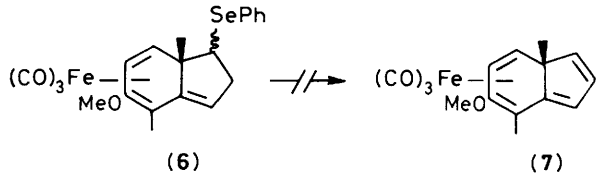
When the dienone (**1**) was treated with potassium hydride and 18-crown-6 in 1,2-dimethoxyethane (DME) at 0 °C followed by methyl fluorosulphonate, the expected trienol ether (**4**) was formed; this ether was somewhat unstable and could not be fully purified and its structure was therefore assigned on the basis of the ^{1}H n.m.r. spectrum. The attempted oxidation and elimination of the selenide group in compound (**4**) were unsuccessful however (see below). Treatment of compound (**4**) with 4-phenyl-1,2,4-triazole-3,5-dione (PTAD) in dichloromethane at room temperature rapidly gave one product, the Diels–Alder adduct (**5**) (52%), whose structure was established by the ^{1}H and ^{13}C n.m.r. spectra. None of the protons was exchangeable with D_2O and no N–H stretching frequency was seen in the spectrum, thus excluding an ene reaction product. The ^{13}C off-resonance decoupled n.m.r. spectrum showed five CH doublets between δ 90 and 160, in agreement with structure (**5**) and excluding the possible [2 + 2] cycloadducts.

The trienol ether (**4**) did not react with *N*-phenylmaleimide in toluene at room temperature, and on heating it decomposed extensively, faster than it gave a cycloadduct. It also decomposed extensively when heated alone in benzene under nitrogen. It could be converted, though in poor yield, into the rather air-sensitive tricarbonyliron derivative (**6**) on treatment in benzene, with stirring at room temperature, with di-iron nonacarbonyl or 4-methoxybenzylideneacetoneiron tricarbonyl. The complex (**6**) was, as expected, more stable to acid than the uncomplexed material and it could be isolated by column chromatography on silica. However, on standing in air it decomposed, reverting to the trienol ether (**4**) and a brown precipitate. Treatment of the complex (**6**) with hydrogen peroxide in the hope of preferential oxidation, and hence elimination, of the phenylseleno group to give (**7**) was unsuccessful. The formation of a dark brown inorganic precipitate suggested that the iron carbonyl group was one site of oxidative attack. There are several examples of organoiron tricarbonyl complexes being oxidised with retention of the $Fe(CO)_3$ group, but none of these has a selenide as part of the ligand.[2]

We then investigated the direct conversion of the trienol ether (**4**) into the 3a*H*-indene (**3**) by oxidation and elimination of the phenylseleno group. This was expected to be difficult because 3a*H*-indenes are highly reactive, and as the double bond is being introduced into a strained five-membered ring the final reaction

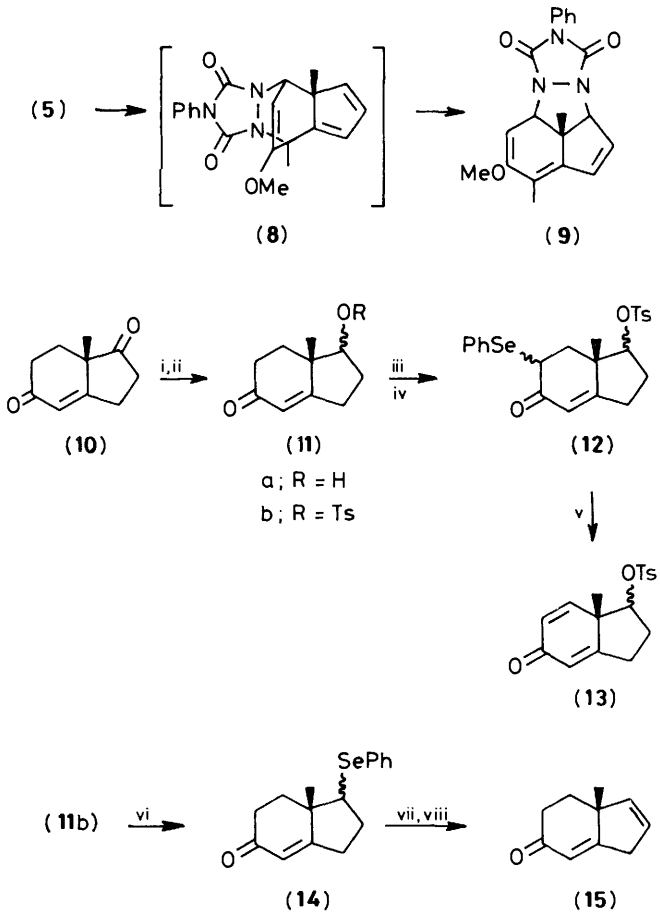


Scheme 1. *Reagents:* i, KH, 18-crown-6, DME 0 °C; ii, $MeOSO_2F$; iii, PTAD



will probably be slow at low temperatures. We therefore decided to oxidise compound (**4**) in a two-phase system in the presence of a dienophile to intercept the 3a*H*-indene. *N*-Phenylmaleimide was chosen as it does not react with the starting material, but does react with 3a*H*-indenes.[3] However, when a solution of the trienol ether (**4**), *N*-phenylmaleimide, and pyridine in dichloromethane was treated with aqueous hydrogen peroxide at 0 °C until all of compound (**4**) had been consumed and then kept at room temperature, only highly polar material, and no pure product, was produced. The same results were obtained if the organic layer was separated from the aqueous hydrogen peroxide after the initial reaction at 0 °C.

To gain more information about this selenide oxidation and elimination route, we studied the same reaction but starting with the PTAD-adduct (**5**). Again a fairly strained fused cyclopentadiene (**8**) should be formed, but one which is presumably less reactive than the 3a*H*-indene (**3**). The adduct (**5**) reacted with hydrogen peroxide in tetrahydrofuran (THF) at 0 °C, but only polymeric material was formed when the mixture was kept at room temperature. When the oxidised



Scheme 2. *Reagents:* i, $NaBH_4$, 4-methylbenzenesulphonyl chloride (TsCl); iii, LDA, THF, −78 °C; iv, PhSeBr; v, H_2O_2 or chloramine-T; vi, $PhSeBH_3Na$; vii, H_2O_2, THF, 0 °C; viii, CCl_4, reflux

product was added to boiling tetrachloromethane in an attempt to accelerate the decomposition of the selenoxide, a very small amount of the elimination product described below was formed. Better results were obtained with the Sharpless procedure, using chloramine-T as the oxidant under phase-transfer conditions.[4] When the adduct (**5**) in dichloromethane was stirred with an aqueous solution of chloramine-T containing benzyltriethylammonium chloride at room temperature, it was all consumed in 4 min. Two products were formed cleanly: 4-methylbenzenesulphonamide and an elimination product which was shown by its ^1H n.m.r spectrum to be the rearranged adduct (**9**) (36%). Thus the phenylseleno group has been eliminated, presumably to form the expected product (**8**), but this has rearranged to give the less strained compound (**9**) which is formally an [8 + 2] cycloadduct of the 3a*H*-indene (**3**). This rearrangement could indeed have proceeded by a retro [4 + 2] followed by an [8 + 2] cycloaddition (*cf.* ref. 3), or by a [1,5] shift of the triazoline ring.

The Sharpless two-phase chloramine-T procedure was then applied to the original trienol ether (**4**), with *N*-phenylmaleimide present to intercept the 3a*H*-indene. Compound (**4**) reacted considerably more slowly than its PTAD-adduct (**5**) however, and gave a complex mixture of highly polar, unidentified products. The reaction was no cleaner at 0 °C.

In spite of this failure, the chloramine-T procedure proved valuable in some closely related work aimed at the synthesis of the same 3a*H*-indene system as that in (**3**), but without the extra C-4 methyl group. The introduction of unsaturation was again much more difficult in the five- than the six-membered ring. The diketone (**10**)[5] was selectively reduced with sodium borohydride in ethanol at −5 °C to the alcohol (**11a**) (86%) which was converted into its 4-methylbenzenesulphonate (**11b**) (87%) (Scheme 2). Treatment of compound (**11b**) with lithium diisopropylamide (LDA) in THF at −78 °C followed by quenching of the anion with phenylselenium bromide gave the phenylselenide (**12**) in 60% yield. This selenide gave the cyclohexadienone (**13**) in good yield (76%) on treatment with hydrogen peroxide; however, with chloramine-T the yield of compound (**13**) was virtually quantitative.

The 4-methylbenzenesulphonate (**11b**) was also converted into the phenylselenide (**14**) with the sodium borohydride complex of diphenyl diselenide; the yield was high (88%) under the precise conditions specified. The dienone (**15**) could then be prepared, in modest yield (37%), from the selenide (**14**) with hydrogen peroxide in THF at 0 °C followed by addition of the reaction mixture to boiling tetrachloromethane.

Experimental

For general points see ref. 1.

2,3-Dihydro-3a,7-dimethyl-6-methoxy-3-phenylseleno-3aH-indene (**4**).—Potassium hydride (300 mg, 20% in oil, 1.5 mmol) was de-oiled and suspended in 1,2-dimethoxyethane (10 ml) containing 18-crown-6 (186 mg, 0.70 mmol) at room temperature, under nitrogen. The reaction mixture was cooled to 0 °C and the dienone (**1**)[1] (164 mg, 0.52 mmol) in 1,2-dimethoxyethane (5 ml) was added dropwise with stirring, to give the yellow enolate anion. After 15 min, methyl fluorosulphonate (**CAUTION: HIGHLY TOXIC**) (41 μl, 0.5 mmol) was added. After a further 10 min the solution was poured into water (100 ml) and sodium chloride was added to form a saturated solution which was extracted with ether (3 × 75 ml). The organic phase was washed with water (2 × 50 ml), dried (Na_2SO_4), and the solvent removed under reduced pressure below room temperature to give crude 2,3-dihydro-3a,7-dimethyl-6-methoxy-3-phenylseleno-3a*H*-indene (**4**), δ($CDCl_3$; 90 MHz), 1.08 (3 H, s), 1.85 (3 H, s), 2.5—3.0 (2 H, m), 3.55 (3 H, s), 4.02 (1 H, dd, *J* 5.6 and 6.2 Hz), 5.64 (1 H, t, *J* 2.5 Hz), 6.0 (1 H, d, *J* 11 Hz), 6.2 (1 H, d, *J* 11 Hz), and 7.15—7.62 (5 H, m).

Reaction of the Trienol Ether (**4**) *with a 4-Phenyltriazole-3,5-dione* (*PTAD*).—The trienol ether (**4**) was made by enolisation of the phenylselenide (**1**) (149 mg, 0.47 mmol) with potassium hydride (300 mg, 20% in oil, 1.5 mmol) in 1,2-dimethoxyethane (15 ml) containing 18-crown-6 (202 mg, 0.76 mmol) and alkylating with methyl fluorosulphonate as in the method used above. The trienol ether (**4**) was dissolved in dichloromethane (25 ml) and titrated with a solution of PTAD (90.4 mg, 0.52 mmol) in dichloromethane (10 ml) with stirring until the pink colour of PTAD remained. The solvent was removed under reduced pressure and the resulting solid was subjected to column chromatography (silica, light petroleum–dichloromethane–ether) to give the cycloadduct 12-*methoxy*-5,8a-*diethyl*-2-*phenyl*-8-*phenylseleno*-7,8,8a,9-*tetrahydro*-5,9-*etheno*-2H,5H-*cyclopenta*[d][1,2,4]*triazolo*[1,2-a]*pyridazine*-1,3-*dione* (**5**) (123.5 mg, 52%) as a crystalline solid, m.p. 160—162 °C (from dichloromethane–hexane fraction) (Found: C, 61.4; H, 4.9; N, 8.2. $C_{26}H_{25}N_3O_4Se$ requires C, 61.7; H, 4.9; N, 8.3%); $\nu_{max.}$ (neat) 1 765m, 1 710s, 1 670s, 1 400s, 1 245s, 1 020m, 765m, 735m, 690s, and 630s cm^{-1}; δ($CDCl_3$) 1.19 (3 H, s), 2.10 (3 H, s), 2.74 (1 H, dd, $J_{2eq,3}$ 4 Hz, $J_{2eq,2ax}$ 17.5 Hz), 3.40 (1 H, ABX, $J_{2ax,2eq}$ 17.5 Hz, $J_{2ax,3}$ 1 Hz, $J_{2ax,1eq}$ 5 Hz), 3.63 (3 H, s), 3.86 (1 H, d, $J_{1ax,2ax}$ 5 Hz), 5.19 (2 H, d), 5.9 (1 H, dd, $J_{3,2ax}$ 1 Hz, $J_{3,2eq}$ 4 Hz), and 7.22—7.63 (10 H, m); δ_C($CDCl_3$) 12.6 (q), 22.8 (q), 43.3 (t), 53.3 (s), 53.5 (s), 55.8 (d), 61.3 (d), 62.5 (s), 92.3 (d), 123.4 (d),

125.6 (d), 127.1 and 128.0 (d and s), 128.9 (s), 129.0 (s), 131.7 (d), 131.8 (s), 133.7 (s), 148.2 (s), and 153.7 (s); *m/z* 507 (M^+, Se isotope pattern), 358 (Se isotope pattern) 347, 314, 234, 173, 157, 119, 115, 91, and 77.

Iron Carbonyl Complexes of the Trienol Ether (**4**).—(*a*) *With* $Fe_2(CO)_9$. The trienol ether (**4**) was prepared by the enolisation of the phenylselenide (**1**) (560 mg, 1.76 mmol) with potassium hydride (809 mg, 20% in oil, 4.0 mmol) in 1,2-dimethoxyethane (25 ml) containing 18-crown-6 (650 mg, 2.5 mmol) and alkylating with methyl fluorosulphonate as in the method used above. The trienol ether (**4**) was dissolved in benzene (20 ml) under nitrogen and $Fe_2(CO)_9$ (1.3 g, 3.6 mmol) was added with stirring. The reaction mixture was stirred for a further 12 h at room temperature and the solvent was removed under reduced pressure whilst the temperature was maintained below 25 °C. The dark brown residue was subjected to column chromatography (silica, ether–light petroleum) to give 2,3-*dihydro*-3a,7-*dimethyl*-6-*methoxy*-3-*phenylseleno*-3a*H*-*indeneiron tricarbonyl* (**6**) (133 mg, 16%) as a light yellow air-sensitive oil; $\nu_{max.}$ (neat) 2 920s, 2 860s, 2 050s, 1 990s, 1 620m, 1 570s, 1 470s, 1 380s, 1 210m, 1 130m, 1 065s, and 910m cm^{-1}; δ($CDCl_3$; 100 MHz) 1.06 (3 H, s), 1.80 (3 H, s), 2.4—2.65 (1 H, m), 2.85—3.35 (2 H, m; with δ 2.94, d, *J* 7 Hz), 3.66 (1 H, d, *J* 5.5 Hz), 3.84 (3 H, s), 5.14 (1 H, d, *J* 7 Hz), 5.19 (1 H, m), and 7.14—7.60 (5 H, m); *m/z* 472 (M^+), 470, 444, 416, 388, 373, 332, 218, 175, 174, 160, 159, 145, 115, and 91.

(*b*) *With 4-methoxybenzylideneacetoneiron tricarbonyl.* The trienol ether (**4**) was prepared by enolisation of the dienone (**1**) (610 mg, 1.9 mmol) with potassium hydride (840 mg, 20% oil, 4.2 mmol) in 1,2-dimethoxyethane (25 ml) containing 18-crown-6 (693 mg, 2.6 mmol) and alkylating the resulting anion with methyl fluorosulphonate as in the method used above. The trienol ether (**4**) was dissolved in benzene (20 ml) containing 4-methoxybenzylideneacetoneiron tricarbonyl[6] (2.4 g, 7.6 mmol) and stirred under nitrogen for 14 h at room temperature. The solvent was removed under reduced pressure and the resulting dark brown solid subjected to column chromatography (silica, light petroleum–ether) to give the iron tricarbonyl complex (**6**) (224 mg. 25%).

Oxidation of the Iron Tricarbonyl Complex (**6**).—The iron tricarbonyl complex (**6**) (119 mg, 0.25 mmol) was dissolved in tetrahydrofuran (10 ml) and passed through a filtration column (Celite) to remove any metallic iron. The solution was cooled to 0 °C under nitrogen and hydrogen peroxide solution (30%, 250 mg, 2.2 mmol) was added dropwise. A rust-brown precipitate formed immediately. The solution was stirred at 0 °C for 0.5 h and filtered to give a pale yellow solution. T.l.c. analysis indicated only highly polar material and a trace of a material corresponding to diphenyl diselenide. Column chromatography (silica, ether–light petroleum) gave only diphenyl diselenide (13 mg).

Reaction of the Cycloadduct (**5**) *with Chloramine-T.*—The triazolinedione adduct (**5**) (200 mg, 0.40 mmol) was dissolved in dichloromethane (25 ml) and added to water (25 ml) containing chloramine-T (223 mg, 0.80 mmol) and triethylbenzylammonium chloride (20 mg). The two-phase mixture was stirred at room temperature until no starting material remained (4 min). The organic layer was run off, washed with water (2 × 25 ml), dried (Na_2SO_4) and the solvent removed under reduced pressure. This gave a pale yellow solid which was chromatographed (silica, dichloromethane–ether) to give the rearranged cycloadduct 4-*methoxy*-3-*methyl*-8-*phenyl*-10a,10b-*dihydro*-5a*H*,8*H*-*indeno*[3′,4′,5′:3,4,5]*pyrazolo*[1,2-a][1,2,4]*triazole*-7,9-*dione* (**9**) as a powder (50.5 mg, 36%), m.p. 157—160 °C; $\nu_{max.}$ (neat, NaCl) 2 960m, 1 700s, 1 660s, 1 590s, 1 405s, 1 360s, 1 250s, 1 230s, 1 120m, 1 065m, 870m, 760s, 730s, and 700s cm^{-1}; δ($CDCl_3$) 1.18 (3 H, s), 1.93 (3 H, s), 3.71 (3 H, s), 4.31 (1 H, d, $J_{7,6}$ 7.7 Hz), 4.64 (1 H, d, $J_{1,2}$ 2.5 Hz), 5.04 (1 H, d, $J_{6,7}$ 7.7 Hz), 6.53 (1 H, dd, $J_{2,1}$ 2.5 Hz, $J_{2,3}$ 5.5 Hz), 6.73 (1 H, d, $J_{2,3}$ 5.5 Hz), and 7.30—7.55 (5 H, m); *m/z* 349 (M^+), 230, 215, 187, 173, 172, 160, 145, 119, and 91.

7,7a-*Dihydro*-1-*hydroxy*-7a-*methylindan*-5(6H)-*one* (**11a**).—The dione (**10**)[5] (7.86 g, 47.9 mmol) was dissolved in dry ethanol (50 ml) and the solution cooled to −10 °C in an ice–sodium chloride bath whilst sodium borohydride (421 mg, 13.2 mmol) in dry ethanol (25 ml) was added, maintaining the temperature below −5 °C throughout the addition. After the addition, the reaction mixture was stirred at −5 °C for a further 0.5 h, then the acidity of the reaction was adjusted to pH 6. The reaction mixture was poured into saturated sodium chloride solution (250 ml), extracted with ethyl acetate (3 × 100 ml), and the organic phase dried (Na_2SO_4). The solvent was removed under reduced pressure to give a yellow oil which was distilled at 150—154 °C/0.02 mmHg to give the required product, 7,7a-dihydro-1-hydroxy-7a-methylindan-5(6H)-one (**11a**) as a pale yellow oil (6.86 g, 86%) which solidified on cooling, m.p. 62—64 °C (lit.,[7] m.p. 63 °C).

7,7a-*Dihydro*-7a-*methyl*-1-(4-*methylphenylsulphonyloxy*)-*indan*-5(6H)-*one* (**11b**).—7,7a-Dihydro-1-hydroxy-7a-methylindan-5(6*H*)-one (**11a**) (6.86 g, 47.2 mmol) was dissolved in dry pyridine (50 ml), recrystallised 4-methylbenzenesulphonyl chloride (16 g, 79.2 mmol) was added and the mixture was stirred for 5 h. A further quantity of 4-methylbenzenesulphonyl chloride (8 g, 39.6 mmol) was added and the mixture was stirred overnight and was then poured into water (500 ml), extracted with ether (3 × 200 ml), and the organic phase washed with 2M-hydrochloric acid (3 × 100 ml), saturated sodium hydrogen carbonate solution (3 × 100 ml), and water (3 × 100 ml), and dried (Na_2SO_4). The solvent was removed under reduced pressure to leave a pale yellow foam which solidified on standing. 7,7a-*Dihydro*-7a-*methyl*-1-(4-*methylphenylsulphonyloxy*)*indan*-5(6H)-*one* (**11b**) (13.8 g, 91%) was obtained as plates, m.p. 119—120 °C (from ether) (Found: C, 64.0; H, 6.3; S, 9.9. $C_{17}H_{20}O_4S$ requires C, 63.8; H, 6.3; S, 10.0%); $\nu_{max.}$ (KBr) 2 990m, 2 970m, 2 960m, 1 660s, 1 595s, 1 350s, 1 190s, 1 170s, 980s, 870s, and 665s cm^{-1}; δ($CDCl_3$) 1.2 (3 H, s), 1.52—1.70 (3 H, m), 1.98—2.55 (9 H, m), 2.65—2.84 (1 H, m), 4.4 (1 H, t, *J* 7.6 Hz), 5.70 (1 H, t), 7.47 (2 H, d, d, J_A 9 Hz), and 7.81 (2 H, d, J_B 9 Hz); *m/z* 320 (M^+), 165, 155, 148, 121, and 91.

7,7a-*Dihydro*-7a-*methyl*-1-(4-*methylphenylsulphonyloxy*)-6-*phenylselenoindan*-5(6H)-*one* (**12**).—The 4-methylbenzenesulphonate (**11b**) (200 mg, 0.625 mmol) was dissolved in dry tetrahydrofuran (15 ml) in a dry flask under nitrogen and cooled to −78 °C, and lithium di-isopropylamide (0.81 mmol) [from n-butyl-lithium (1.6 M; 0.5 ml, 0.81 mmol) and di-isopropylamine (82.06 mg, 113.6 μl, 0.81 mmol)] in tetrahydrofuran (5 ml) was then added. The solution was stirred for a further 0.5 h and phenylselenium bromide (0.34 mmol) [from diphenyl diselenide (107 mg, 0.34 mmol) and bromine (55 mg, 18 μl, 0.34 mmol)] in tetrahydrofuran (5 ml) was added. The solution was then allowed to warm to room temperature during 1 h, poured into 0.5M-hydrochloric acid (50 ml) and extracted with ether (3 × 50 ml). The organic phase was washed with water (2 × 20 ml), dried (Na_2SO_4), and the solvent removed under reduced pressure to give a yellow solid which was chromatographed to give the starting material (**11b**) (39 mg, 19%) and 7,7a-*dihydro*-7a-*methyl*-1-(4-*methylphenylsulphonyloxy*)-6-*phenylselenoindan*-5(6H)-*one* (**12**) (178 mg, 60%) as a crystalline solid, m.p. 148—148.5 °C (from light petroleum–dichloromethane) (Found: C, 57.7; H, 5.0; S, 6.8. $C_{23}H_{24}O_4SSe$ requires C, 58.1; H,

5.0; S, 6.7%); $\nu_{max.}$ (KBr) 1 660s, 1 350s, 1 180s, 980s, 875s, 850s, 810s, 690s, and 670s cm^{-1}; δ($CDCl_3$) 1.15 (3 H, s), 1.78 (1 H, t, *J* 14 Hz), 1.98—2.24 (3 H, m), 2.25—2.53 (4 H, m), 2.62—2.80 (1 H, m), 4.18 (1 H, dd, $J_{6,7}$ 6.8 and 5.5 Hz), 4.28 (1 H, dd, $J_{1,2}$ 7.3 and 5.1 Hz), 5.83 (1 H, t, *J* 1.7 Hz), 7.25—7.4 (5 H, m, aromatics), 7.52 (2 H, d, J_A 8.5 Hz), and 7.73 (2 H, d, J_B 8.5 Hz); *m/z* 476 (M^+), 330, 314, 312, 258, 223, 184, 155, 148, 147, and 121.

7a-*Methyl*-1-(4-*methylphenylsulphonyloxy*)-1,2,3,7a-*tetrahydro*-5H-*inden*-5-*one* (**13**).—(*a*) *With hydrogen peroxide.* The phenylselenide (**12**) (170 mg, 0.36 mmol) was dissolved in tetrahydrofuran (10 ml), the solution was cooled in an ice-bath to 0 °C and pyridine (57 mg, 100 μl, 0.72 mmol) was added. Hydrogen peroxide (15%; 0.81 ml, 3.6 mmol) was added dropwise during 3 min maintaining the temperature below 2 °C. The solution was allowed to warm to 10 °C after 1 h and then to room temperature during 3 h. The reaction mixture was poured into water (150 ml) and extracted with dichloromethane (3 × 50 ml). The organic phase was washed with saturated sodium carbonate (2 × 25 ml), water (2 × 25 ml), and dried (Na_2SO_4). The solvent was removed under reduced pressure to leave a pale yellow oil which was subjected to column chromatography (silica, ether–light petroleum) to give 7a-*methyl*-1-(4-*methylphenylsulphonyloxy*)-1,2,3,7a-*tetrahydro*-5H-*inden*-5-*one* (**13**) (87 mg, 76%) as a crystalline solid, m.p. 67—71 °C (from dichloromethane–light petroleum) (Found: C, 63.9; H, 6.0; S, 9.9. $C_{17}H_{18}O_4S$ requires C, 64.2; H, 5.7; S, 10.0%); $\nu_{max.}$ 2 990m, 2 970m, 1 655s, 1 635s, 1 595s, 1 355s, 1 185s, 1 170s, 1 000s, 980s, 840s, 810s, and 670s cm^{-1}; δ($CDCl_3$) 1.28 (3 H, s), 2.00—2.28 (2 H, m), 2.32—2.52 (4 H, m), 2.78—2.97 (1 H, m), 4.50 (3 H, t, *J* 12 Hz), 6.07 (1 H, m), 6.14 (1 H, d, $J_{6,7}$ 12 Hz), 6.85 (1 H, d, $J_{7,6}$ 12 Hz), 7.39 (2 H, d, J_A 8.5 Hz), and 7.81 (2 H, d, J_B 8.5 Hz); *m/z* 318 (M^+) 300, 163, 155, 146, 145, 135, 121, and 91.

(*b*) *With chloramine-T.* The phenylselenide (**12**) (212 mg, 0.46 mmol) was dissolved in dichloromethane (25 ml) and placed in a flask containing chloramine-T (138 mg, 0.49 mmol) and benzyltriethylammonium chloride (20 mg) dissolved in water (25 ml). The solution was stirred until no starting material could be detected by t.l.c. (*ca.* 15 min). The organic layer was separated, washed with water (25 ml), and dried (Na_2SO_4), and the solvent removed under reduced pressure to give a white solid which was subjected to column chromatography (silica, light petroleum–dichloromethane–ether) to give the dienone (**13**) as a crystalline solid (134 mg, 95%), identical with that described in section (*a*).

7,7a-*Dihydro*-7a-*methyl*-1-*phenylselenoindan*-5(6H)-*one* (**14**).—Diphenyl diselenide (335 mg, 1.1 mmol) was dissolved in dry ethanol (20 ml) and sodium borohydride (70 mg, 2.2 mmol) was added to it slowly, with cooling. The solution was stirred until it decolourised, then acetone (3 ml) was added followed by the 4-methylbenzenesulphonate (**11b**). The solution was stirred while being refluxed for 1 h, cooled, filtered and the precipitate washed with chloroform. The filtrate and washings were combined, the solvent removed under reduced pressure, and the residue partitioned between water (100 ml) and dichloromethane (100 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 oil. Column chromatography (silica, light petroleum–dichloromethane) of this oil gave 7,7a-*dihydro*-7a-*methyl*-1-*phenylselenoindan*-5(6H)-*one* (**14**) (381 mg, 89%) as a pale yellow oil which was further purified by bulb-to-bulb distillation (b.p. 138—145 °C, 0.07 mmHg); $\nu_{max.}$ (film) 2 960s, 2 930s, 1 670s, 1 560s, 1 480s, 1 440s, 1 260s, 1 200s, 1 020m, 865m, 740s, and 690s cm^{-1}; δ($CDCl_3$; 90 MHz) 1.18 (3 H, s), 1.65—2.31 (2 H, m), 2.2—3.85 (6 H, m), 4.05—4.15 (1 H, m), and 7.20—7.60 (5 H, m); *m/z* 306 (M^+ Se pattern) 149, 148, 121, 107, and 91.

7a-*Methyl*-3,6,7,7a-*tetrahydro*-5H-*inden*-5-*one* (**15**).—The phenylseleno derivative (**14**) (200 mg, 0.65 mmol) was dissolved in tetrahydrofuran (5 ml) containing pyridine (0.2 ml, *ca* 2.5 mmol) and cooled to 0 °C in an ice–sodium chloride bath. Hydrogen peroxide (15%, 1 ml, 4.4 mmol) was added to it dropwise, with stirring. Once added, the solution was stirred for 10 min and then added to boiling tetrachloromethane (25 ml) containing pyridine (1 ml). This mixture was refluxed for 10 min, cooled, and washed with saturated sodium hydrogen carbonate solution (2 × 10 ml), water (2 × 10 ml), and dried (Na_2SO_4) and the solvent was removed under reduced pressure. Column chromatography (silica, light petroleum–dichloromethane) of the remaining oil gave 7a-*methyl*-3,6,7,7a-*tetrahydro*-5H-*inden*-5-*one* (**15**) as a pale yellow oil (28.6 mg, 37%); $\nu_{max.}$ (neat) 1 660s, 1 320s, 1 290s, 1 200m, 1 070m, 1 030m, 850s, and 730m cm^{-1}; δ($CDCl_3$; 90 MHz) 1.27 (3 H, s), 1.78—2.21 (2 H, m), 2.38—2.75 (2 H, m), 2.88—3.62 (2 H, m), and 5.76—6.0 (3 H, m); *m/z* 148 (M^+), 134, 133, 121, 106, and 91.

References

1 Part 3, S. J. Foster, C. W. Rees, and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1985, preceding paper.

2 *E.g.* A. J. Pearson and C. W. Ong, *J. Am. Chem. Soc.*, 1981, **103**, 6686; A. J. Birch and K. B. Chamberlain, *Org. Synth.*, 1973, **53**, 1860; A. Pelter, K. J. Gould, and L. A. P. Kane-Maguire, *J. Chem. Soc., Chem. Commun.*, 1974, 1029; G. Evans, B. F. G. Johnson, and J. Lewis, *J. Organomet. Chem.*, 1975, **102**, 507; T. Mitsudo, H. Nakanishi, T. Inubishi, I. Morishima, Y. Watanabe, and Y. Takegami, *J. Chem. Soc., Chem. Commun.*, 1976, 416.

3 R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2399.

4 K. B. Sharpless, K. M. Gordon, R. F. Lauer, D. W. Patrick, S. P. Singer, and M. W. Young, *Chem. Scr.*, 1975, **8A**, 9.

5 Z. G. Hajos and D. R. Parrish, *J. Org. Chem.*, 1974, **39**, 1612, 1615.

6 D. H. R. Barton, A. A. L. Gunatilaka, T. Nakanishi, H. Patin, D. A. Widdowson, and B. R. Worth, *J. Chem. Soc., Perkin Trans. 1*, 1976, 821.

7 Z. G. Hajos, D. R. Parrish, and E. P. Olivetto, *Tetrahedron*, 1968, **24**, 2039.

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