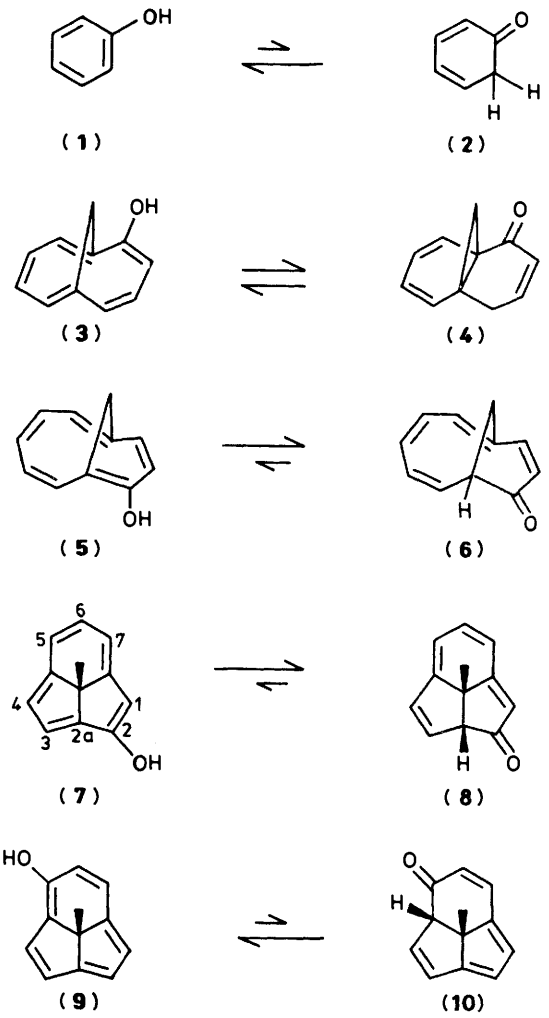
Tricyclic [10]Annulenes. Part 5.[1] Phenol–Keto Tautomerism in the 2- and 5-Hydroxy Derivatives of 7b-Methyl-7b*H*-cyclopent[*cd*]indene

Zev Lidert, Raymond McCague, Christopher J. Moody, and Charles W. Rees*
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

The 2- and 5-hydroxy derivatives of the 10π aromatic system 7b-methyl-7b*H*-cyclopent[*cd*]indene have been synthesised and their properties compared. The 2-hydroxy isomer (**7**) exists entirely in the non-aromatic keto form (**8**) (+1.41)† but its lithium enolate (**13**; M = Li) (−1.45), like its methyl (−1.51) and trimethylsilyl (−1.51) ethers, (**14**) and (**12**), sustains a substantial diamagnetic ring current. The ketone (**8**) is methylated on oxygen and on carbon, at the C-2a position only, the ratio varying with conditions in the expected manner. In contrast, the 5-hydroxy isomer (**9**) exists entirely in the annulenol form (−1.49), as does the 5-hydroxy-diester (**25**) (−1.15) and the 5-hydroxy-dialdehyde (**32**) (−1.00). These three compounds are thus the first [10]annulenols to be isolated.

One consequence of the delocalisation energy of the benzene ring is that phenols, unlike simple enols, are much more stable in the enol (**1**) than the keto form (**2**). Indeed, it is only recently that the keto tautomer of phenol has been observed directly by spectroscopic methods at low temperature.[2] However, in annulenes higher than benzene, the 'phenol' is not necessarily more stable than the keto form, since the aromatic delocalisation energy of the annulenol may not be sufficient to compensate for the loss of carbonyl bond energy in the keto form. Indeed in the 1,6-methano- and 1,5-methano-[10]annulenes the hydroxy derivatives exist predominantly in the keto form. Thus, the n.m.r. spectrum of 1,6-methano[10]annulen-2-ol (**3**) suggests that the keto form (**4**) is favoured in benzene solution, although the 'phenol' (**3**) preponderates in dimethyl sulphoxide (DMSO).[3] Similarly, the 1,5-methano[10]annulen-8-ol (**5**) exists predominantly in the keto form (**6**).[4]

In previous papers we have described the synthesis[5] and properties[6] of 7b-methyl-7b*H*-cyclopent[*cd*]indene, a 10π aromatic system. We now report full details of the preparation and properties of hydroxy derivatives of this tricyclic [10]-annulene.[7,8] These studies show, in agreement with a trend predicted by MNDO SCF-MO calculations,[9] that for the 2-hydroxy derivative (**7**) the tautomeric equilibrium lies far on the side of the keto form (**8**), whereas the 5-hydroxy derivative (**9**) exists entirely in the 'phenol' form.



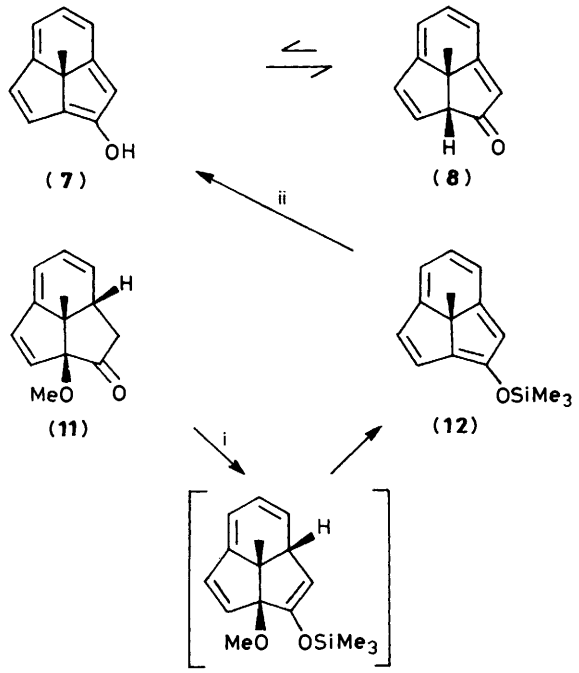
Results and Discussion

The 2-Hydroxy Series.—Cycloaddition of 3-methoxy-3a-methyl-3a*H*-indene to the ketene equivalent 2-chloroacryloyl chloride gave, after treatment of the initial adduct with sodium azide under standard conditions, the tricyclic ketone (**11**).[10] Treatment of (**11**) with an excess of chlorotrimethylsilane and sodium iodide in refluxing acetonitrile in the presence of triethylamine,[11] followed by addition of water at 0 °C gave the tetraenone (**8**) (80%) in a one-pot operation. This sequence of reactions involves initial silylation on oxygen, elimination of methanol to aromatise the system, and final hydrolysis of the trimethylsilyl ether (**12**) (Scheme 1).

The ketone (**8**) is an orange-red oil. There are no signals upfield of tetramethylsilane (TMS) in the n.m.r. spectrum, the central methyl group resonating at δ($CDCl_3$) 1.41, whilst the i.r. spectrum shows a carbonyl stretch at 1 702 cm^{-1} and no hydroxy stretching vibrations. There is no spectral evidence for the presence of any significant amount of the enol tautomer (**7**). Although, in principle, the 2-hydroxyannulene (**7**) can ketonise to tetraenones with the hydrogen on C-1, C-4, C-5, or C-7 it does so exclusively to the tetraenone (**8**) with the hydrogen on C-2a, thereby maximising the relief of ring strain.

The ketone (**8**) forms a mauve 2,4-dinitrophenylhydrazone, and is slightly soluble in water. It does not undergo deuterium exchange when shaken, as a carbon tetrachloride solution, with

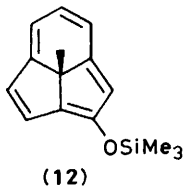
† (The number in brackets is the chemical shift of the central methyl group in the ^1H n.m.r. spectrum).



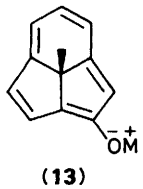
Scheme 1. *Reagents:* i, Me_3SiCl, NaI, Et_3N, MeCN, reflux; ii, H_2O, 0 °C

deuterium oxide, or in the presence of acid even at reflux. However, exchange did occur in this two-phase system in the presence of a catalytic amount of tetra-n-butylammonium hydroxide after 2 h at 40 °C. As expected, the exchange occurred exclusively at C-2a. Deuterium exchange at the C-2a position was also complete after 1 h at 60 °C in DMSO containing a trace of the same catalyst. Since deuterium exchange had taken place, the keto–enol equilibrium must have been established assuming that kinetic protonation (deuteriation) of the 'phenolate' is on oxygen. The absence of any detectable amount of the annulenol (**7**) in a polar solvent which would stabilise the enol form by hydrogen bonding[3] implies that the keto form is much more energetically favoured than the enol form.

The trimethylsilyl ether (**12**), an intermediate in the preparation of the ketone (**8**) (Scheme 1), is readily prepared from (**8**) by treatment with chlorotrimethylsilane–sodium iodide in acetonitrile in the presence of triethylamine. It is a bright yellow oil which shows the expected n.m.r. signal upfield of TMS at $\delta(CDCl_3)$ −1.51 for the central methyl group. It is interesting that the carbon-13 chemical shift of C-2a which is 178.7 in the unsubstituted annulene is shifted to higher field (δ 156.4, 158.8, 159.7, or 160.3—assignment uncertain) in the trimethylsilyl ether (**12**), indicating significant electron release by the oxygen to the C-2a position. Treatment of the ether (**12**) with methyllithium (1 equiv.) in 1,2-dimethoxyethane (DME) afforded a deep yellow solution of the lithium enolate (**13**; M = Li) which gives an n.m.r. signal upfield of TMS at δ(DME) −1.45, indicating that this ion can sustain a diamagnetic ring current. In the same solvent the central methyl group of the trimethylsilyl ether (**12**) resonates at δ −1.62. When this DME solution of the anion (**13**; M = Li) was quenched at −78 °C with an acetate buffer or aqueous acetic acid and immediately examined by n.m.r. spectroscopy, the resulting red solution showed no signals upfield of TMS.

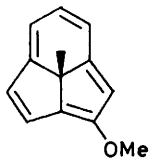


(12)

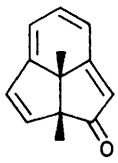


(13)

Methylation of the ketone (**8**) occurred on both oxygen and carbon, the ratio depending on the conditions. Thus treatment of the potassium salt (**13**; M = K), generated from (**8**) with potassium hydride and 18-crown-6 in DME, with methyl fluorosulphonate gave the 2-methoxyannulene (**14**) (67%) as the only isolated product. When the sodium salt (**13**; M = Na), generated from (**8**) and sodium hydride in tetrahydrofuran (THF), was treated with iodomethane, carbon alkylation was the major pathway and the C-2a methyl substituted ketone (**15**) was isolated (40%) together with the 2-methoxyannulene (25%). The highest ratio of carbon to oxygen alkylation was obtained when the lithium enolate (**13**; M = Li), from the sodium enolate and lithium bromide, was treated with iodomethane to give the ketone (**15**) (59%) and the 2-methoxyannulene (**14**) (19%).



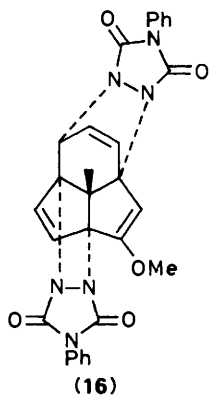
(14)



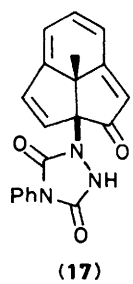
(15)

The methoxyannulene (**14**) is a yellow oil and in its n.m.r. spectrum the central methyl group resonates at $\delta(CDCl_3)$ −1.51. The tetraenone (**15**), on the other hand, is an orange–red oil similar in properties to the unmethylated ketone (**8**), with the central methyl group resonating at $\delta(CDCl_3)$ 1.47.

The 2-methoxy- and 2-trimethylsiloxy-annulenes both react with 4-phenyl-1,2,4-triazole-3,5-dione (PTAD); the 2-methoxy derivative (**14**) reacted at room temperature to give the 1:2 adduct (**16**) in low yield. The structure was assigned by comparison with the 1:2 adduct formed from the unsubstituted annulene and PTAD.[6] Although the 2-trimethylsiloxyannulene (**12**) also reacted with PTAD at room temperature the product was not a 1:2 adduct, but the 1:1 adduct (**17**) (54%). This reaction presumably proceeds by electrophilic addition of PTAD at C-2a, followed either by transfer of the trimethylsilyl group to nitrogen and hydrolysis during work-up, or by direct hydrolysis to the product.



(16)

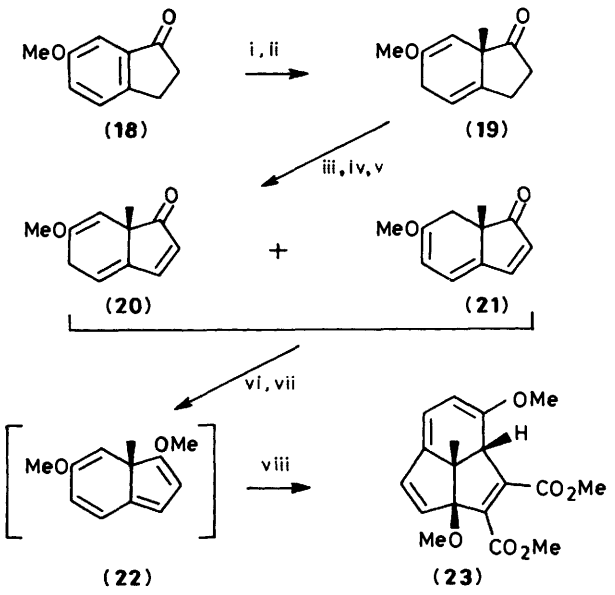


(17)

Thus in the 2-substituted series, the delocalisation energy of the 2-hydroxyannulene (**7**) is insufficient to compensate for the loss of carbonyl bond energy and the greater strain of the phenolic tautomer. This strain is most effectively relieved by sp^3 hybridisation at C-2a, and hence the ketone (**8**) is appreciably more stable than its phenol tautomer.

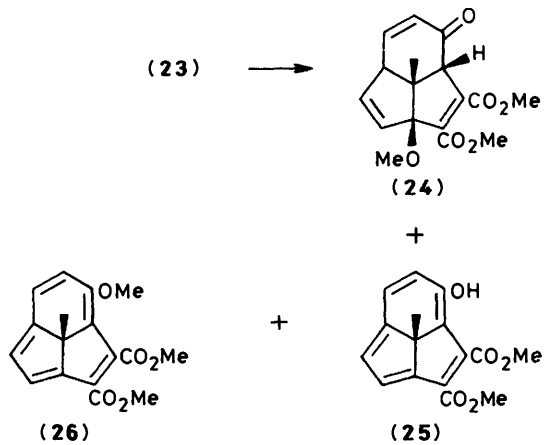
The 5-Hydroxy Series.—The relief of ring strain in the tricyclic [10]annulene system by protonation at C-2a is clearly instrumental in determining the relative stabilities of the 2-hydroxyannulene (**7**) and its keto form (**8**). However, for the 1- and 5-hydroxyannulenes, ring junction protonation can only occur at C-4a and C-7a, and in doing so less strain is relieved than for C-2a protonation. Hence smaller energy differences between these annulenes and their keto tautomers is expected, and this was borne out by MNDO SCF-MO calculations.[9] These expectations were confirmed by the synthesis of (**9**) and its ring substituted derivatives (**25**) and (**32**).

6-Methoxyindan-1-one (**18**)[12] was converted into the tricyclic adduct (**23**) by a similar sequence of reactions (Scheme 2)



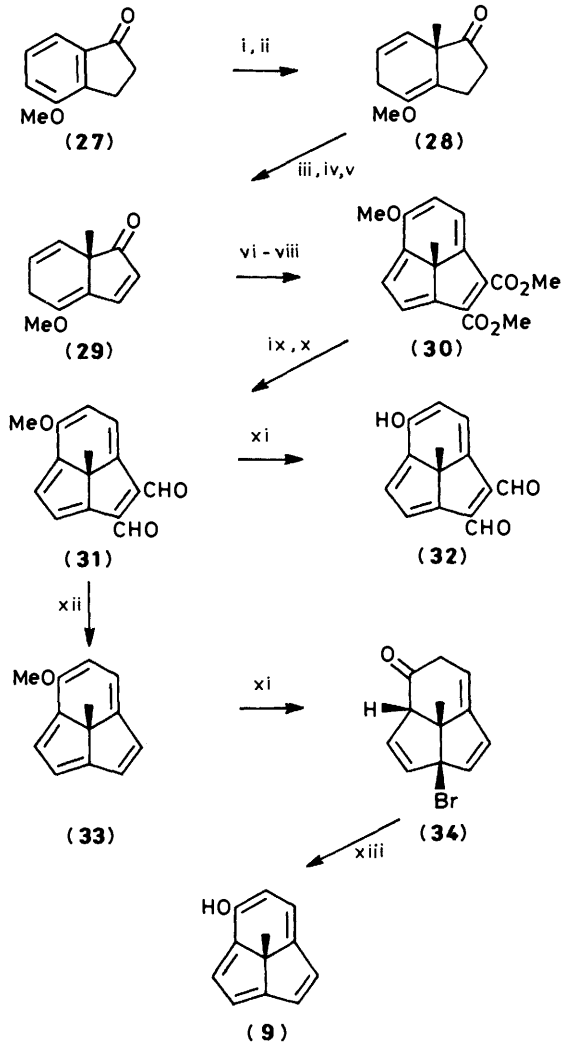
Scheme 2. *Reagents:* i, K, Bu^{t}OH, THF, LiBr, NH_3, −78 °C; ii, MeI, THF, NH_3, −78 °C; iii, $LiNPr^i_2$, THF, −78 °C; iv, PhSeCl, THF, −90 °C; v, H_2O_2, pyridine, 0 °C; vi, KH, 18-crown-6, DME, −20 °C; vii, $MeOSO_2F$; viii, $MeO_2CC{\equiv}CCO_2Me$

to that described previously for indan-1-one.[10] Treatment of the adduct (**23**) with 1:1 concentrated sulphuric acid–methanol at 0 °C gave three compounds which were identified as the ketone (**24**) (40%), the hydroxyannulene (**25**) (15%), and its *O*-methyl ether (**26**) (8%). On prolonged treatment under the same conditions, the ketone (**24**) is slowly converted into the



hydroxyannulene (**25**). The hydroxyannulene (**25**) is a deep orange crystalline solid whose spectral properties are in accord with the aromatic annulenol structure. Thus, the central methyl group resonates upfield of TMS at $\delta(CDCl_3)$ −1.15, and the i.r. spectrum exhibits an absorption at $\nu_{max.}(CHCl_3)$ 3 240 cm^{-1} which is unaltered on dilution.

In order to rule out the possibility that the 'phenol' form was stabilised by the presence of the two ester groups by intramolecular hydrogen bonding to one, and by electron withdrawal by the other, it was necessary to prepare the parent 5-hydroxyannulene before reaching any definite conclusions about the position of the phenol–keto equilibrium in the 5-series. As the yields of the possible precursors (**25**) and (**26**) were low, an alternative route from 4-methoxyindan-1-one (**27**)[13] was developed. Birch reduction, methylation, and introduction of the extra double bond proceeded as before to give the trienone (**29**) (35% overall), which was converted into the annulenediester (**30**) (Scheme 3), characterised as the corres-



Scheme 3. *Reagents:* i—viii as i—viii in Scheme 2; ix, $LiAlH_4$; x, $BaMnO_4$; xi, BBr_3, CH_2Cl_2, −78 °C; xii, $[Rh(PPh_3)_3Cl]$; xiii, DBU

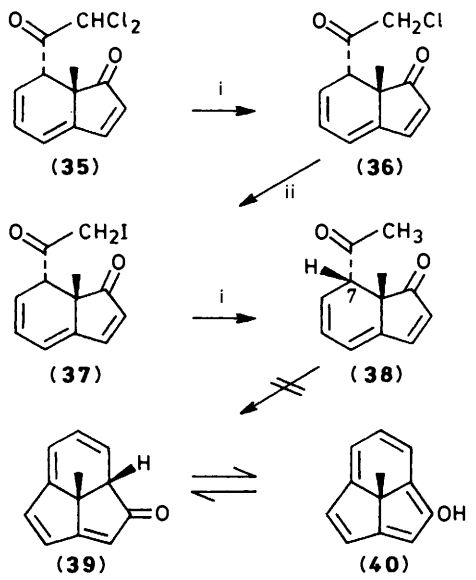
ponding diacid. The diester (**30**) was converted into the dialdehyde (**31**) by reduction to the diol with lithium aluminium hydride followed by oxidation with barium manganate. Demethylation of (**31**) with boron tribromide gave the 5-hydroxyannulenedicarbaldehyde (**32**) as red crystals, the

aromatic annulenol structure being supported by the chemical shift of the central methyl group in the n.m.r. spectrum [$\delta(CDCl_3)$ – 1.00].

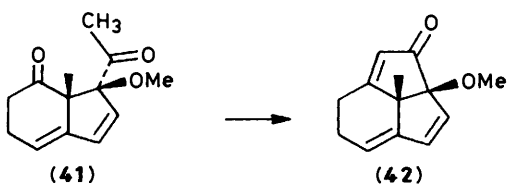
The annulenedialdehyde (**31**) underwent decarbonylation when heated in benzene with tristriphenylphosphinerhodium(I) chloride to give the 5-methoxyannulene (**33**). Attempted cleavage of the ether (**33**) to the 5-hydroxyannulene (**9**) with boron tribromide in dichloromethane at −78 °C gave instead a bromo-ketone, the structure (**34**) being assigned by n.m.r. spectroscopy. However, when this bromo-ketone was stirred with 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU) in dry benzene, it was converted into the required 5-hydroxyannulene (**9**).

The hydroxyannulene (**9**) is a yellow oil which exhibits an OH stretch in its i.r. spectrum at 3 600 cm^{-1}, and the central methyl group of which resonates at $\delta(CDCl_3)$ −1.49 in the n.m.r. spectrum. There was no spectroscopic evidence for a keto tautomer, and no deuterium was incorporated when the annulenol was stored in [$^2H_6$]DMSO/D_2O for one week. Furthermore, no C-methylation could be detected when the annulenol was treated under the exact conditions which favoured C-methylation of the 2-'hydroxy' isomer. The u.v. spectrum of the annulenol (**9**) is very similar to that of its *O*-methyl ether (**33**), and that of the 2-methoxyannulene (**14**).

Attempts to prepare the 1-*Hydroxyannulene*.—An attempt was also made to synthesise the 1-hydroxyannulene (**40**). Thus the dichloromethylketone (**35**), prepared by reaction of 3a-methyl-3-trimethylsiloxy-3a*H*-idene with dichloroketene,[10] was converted into the methyl ketone (**38**) *via* the monochloro and iodomethyl ketones (**36**) and (**37**) (Scheme 4). The preparation of the methyl ketone (**38**) from (**35**) directly was unsuccessful. All attempts to effect ring closure of (**38**) to (**39**) by an intramolecular aldol reaction failed. This is in contrast to the ring closure of (**41**) which gave the tricyclic ketone (**42**) on treatment



Scheme 4. *Reagents:* i, Bu^n_3SnH, $CMe_2(CN)N{=}NCMe_2CN$, C_6H_6, 80 °C; ii, NaI, acetone, 20 °C



with base,[14] and no doubt reflects the fact that in (**38**) the protons of the methyl group are less acidic than 7-H.

Experimental

For general points see references 5 and 10.

2a,7b-*Dihydro*-7b-*methyl*-7H-*cyclopent*[cd]*inden*-2-*one* (**8**)[5].—Chlorotrimethylsilane (14.5 ml, 120 mmol) was added to a solution of sodium iodide (17 g, 120 mmol) in dry acetonitrile at room temperature under nitrogen. A mixture of the ketone (**11**)[10] (4.6 g, 22.7 mmol) and dry triethylamine (16.5 ml, 120 mmol) was then added, and the mixture refluxed for 6 h. The yellow mixture was cooled in ice, and water (140 ml) was added. The mixture immediately became deep red, and the product was extracted into ether (4 × 150 ml). The combined extracts were washed with water, dried ($MgSO_4$), evaporated, and the residue chromatographed on silica gel. Elution with petroleum–ether (7:3) gave the *title compound* (**8**) (3.1 g, 80%) as an orange–red oil, $\nu_{max.}(CCl_4)$ 2 964, 2 924, 1 702, 1 622, 1 192, 890, 864, 842, and 678 cm^{-1}; $\lambda_{max.}$(EtOH) 252 (log ε 4.34), 335sh (3.11), and 446 nm (3.03); δ (250 MHz, $CDCl_3$) 1.41 (3 H, s), 3.01 (1 H, dd, *J* 2.2, 3.4 Hz), 4.97 (1 H, s), 5.71 (1 H, d, *J* 5.2 Hz), 6.21 (1 H, dd, *J* 2.2, 5.4 Hz), 6.25 (1 H, dd, *J* 5.2, 9.4 Hz), 6.39 (1 H, d, *J* 9.4 Hz), and 6.86 (1 H, dd, *J* 3.4, 5.4 Hz); $\delta_C(CDCl_3)$ 22.4, 52.4, 63.4, 113.5, 114.7, 119.6, 132.5, 132.8, 143.8, 163.8, 183.7, and 211.7; *m/z* 170 (M^+), 155, 142, 141 (base), 137, and 115; 2,4-*dinitrophenylhydrazone*, mauve needles, m.p. 180—182 °C (from ethyl acetate) (Found: C, 62.0; H, 4.0; N, 16.0. $C_{18}H_{14}N_4O_4$ requires C, 61.7; H, 4.0; N, 16.0%).

Deuterium Exchange in the Ketone (**8**).—A solution of the ketone (**8**) (100 mg) in carbon tetrachloride (1 ml) was treated with deuterium oxide (99.7 atom %; 1 ml) and tetra-n-butylammonium hydroxide (25% w/v in methanol; *ca.* 0.1 ml), and the mixture warmed at 40 °C for 2 h. The organic layer was separated, washed with deuterium oxide (1 ml), and evaporated to give 2a,7b-*dihydro*-7b-*methyl*-2H-[2a-^{2}H]*cyclopent*[cd]-*inden*-2-*one* as an orange–red oil, δ (250 MHz, $CDCl_3$) 1.42 (3 H, s), 4.96 (1 H, s), 5.71 (1 H, d, *J* 5 Hz), 6.21 (1 H, d, *J* 5 Hz), 6.25 (1 H, dd, *J* 5, 9 Hz), 6.39 (1 H, d, *J* 9 Hz), and 6.84 (1 H, d, *J* 5 Hz).

7b-*Methyl*-2-*trimethylsiloxy*-7bH-*cyclopent*[cd]*indene* (**12**).—Chlorotrimethylsilane (0.12 ml, 0.93 mmol) was added to a stirred solution of sodium iodide (137 mg, 0.93 mmol) in dry acetonitrile (1 ml) under nitrogen at room temperature. A mixture of the ketone (**8**) (127 mg, 0.75 mmol) and triethylamine (0.13 ml, 0.93 mmol) was added. After 10 min at room temperature, the mixture was extracted with petroleum (3 × 2 ml). The combined extracts were concentrated (to 2 ml), filtered, and the filtrate evaporated to give the *title compound* (**12**) (128 mg, 74%) as a yellow oil, δ (250 MHz, $CDCl_3$) −1.51 (3 H, s), 0.42 (9 H, s), 7.25 (1 H, s), 7.36 (1 H, d, *J* 7.0 Hz), 7.50 (1 H, t, *J* 7.0 Hz), 7.60 (1 H, d, *J* 7.0 Hz), 7.63 (1 H, d, *J* 3.1 Hz), and 7.79 (1 H, d, *J* 3.1 Hz); $\delta_C(CDCl_3)$ 0.29, 29.6, 57.3, 112.2, 115.1, 125.0, 128.9, 129.9, 130.7, 156.4, 158.8, 159.7, and 160.3.

Generation of the Lithium Enolate (**13**; M = Li).—A solution of the trimethylsilyl ether (**12**) (57 mg, 0.25 mmol) in dry DME (0.5 ml) in an n.m.r. tube was treated with a solution of methyllithium in ether (1.5M; 2 ml, 0.3 mmol). A deep yellow solution of (**13**; M = Li) resulted, which showed δ (60 MHz, DME) −1.45 (3 H, s), 6.92 (1 H, s), 7.0—7.4 (4 H, m), and 7.77 (1 H, d). The solution was cooled to −78 °C under nitrogen and treated with a neutral sodium acetate–acetic acid buffer. The resulting red solution was immediately examined by n.m.r. which showed no signals upfield of TMS.

In a separate experiment, the anion was quenched by the addition of aqueous acetic acid at −78 °C. Again no signals upfield of TMS were observed in the n.m.r. spectrum.

2-*Methoxy*-7b-*methyl*-7bH-*cyclopent*[cd]*indene* (**14**).—A solution of the ketone (**8**) (29.5 mg, 0.17 mmol) in dry DME (1 ml) was added to a stirred suspension of potassium hydride (from a 25% dispersion in oil; 100 mg, 0.6 mmol) in dry DME (2 ml) containing 18-crown-6 (150 mg, 0.6 mmol) under nitrogen at −23 °C. After 15 min, methyl fluorosulphonate (0.1 ml, 1.2 mmol) was added. Addition of triethylamine (0.5 ml) destroyed the excess of methyl fluorosulphonate. The mixture was filtered, the filtrate evaporated, and the residue chromatographed to give the *title compound* (**14**) (21.3 mg, 67%) as a bright yellow oil (Found: M^+, 184.0887. $C_{13}H_{12}O$ requires M^+, 184.0888); $\nu_{max.}$(CCl_4) 1 464, 1 414, 1 338, 1 168, and 1 042 cm^{-1}; $\lambda_{max.}$(EtOH) 234sh (log ε 3.78), 2.91 (4.70), 326 (3.72), and 459 nm (2.96); δ (250 MHz, $CDCl_3$) −1.51 (3 H, s), 4.30 (3 H, s), 7.25 (1 H, s), 7.37 (1 H, d, *J* 6.9 Hz), 7.54 (1 H, t, *J* 6.9 Hz), 7.60 (1 H, d, *J* 6.9 Hz), 7.65 (1 H, d, *J* 3.4 Hz), and 7.91 (1 H, d, *J* 3.4 Hz); *m*/*z* 184 (M^+, base), 169, and 141.

2a,7b-*Dihydro*-2a,7b-*dimethyl*-2H-*cyclopent*[cd]*inden*-2-*one* (**15**).—(*a*) A solution of the ketone (**8**) (81 mg, 0.47 mmol) in dry THF (1 ml) was added to a stirred suspension of sodium hydride (50%; 90 mg, 1.9 mmol) in THF under nitrogen at room temperature. Hydrogen was immediately evolved, the iodomethane (0.25 ml, 4 mmol) was added. After 4 h at room temperature, the mixture was carefully poured into water, and extracted with ether. The ether extracts were combined, washed with water, dried (Na_2SO_4), evaporated, and the residue chromatographed to give (i) the methoxyannulene (**14**) (22 mg, 25%), and (ii) the *title compound* (**15**) (35 mg, 40%) as an orange–red oil, $\nu_{max.}$(neat) 2 890, 1 694, 1 620, 1 576, 1 074, 870, 854, 778, 668, and 622 cm^{-1}; $\lambda_{max.}$(EtOH) 252 (log ε 4.32), 335sh (3.09), and 450 nm (2.98); δ (250 MHz, $CDCl_3$), 1.18 (3 H, s), 1.47 (3 H, s), 4.90 (1 H, s), 5.55 (1 H, d, *J* 5.2 Hz), 6.02 (1 H, d, *J* 5.3 Hz), 6.13 (1 H, dd, *J* 5.2, 9.5 Hz), 6.32 (1 H, d, *J* 9.5 Hz), and 6.59 (1 H, d, *J* 5.3 Hz); *m*/*z* 184 (M^+), 169, 156, 155, 141 (base), and 115; 2,4-*dinitrophenylhydrazone*, red powder, m.p. 179—181 °C (from nitromethane) (Found: C, 62.7; H, 4.5; N, 15.0. $C_{19}H_{16}N_4O_4$ requires C, 62.6; H, 4.4; N, 15.4%).

(*b*) A solution of the ketone (**8**) (76 mg, 0.45 mmol) in dry THF (1 ml) was added to sodium hydride (50%; 80 mg, 1.7 mmol) in THF (2 ml) as described above. After 10 min, a solution of lithium bromide (174 mg, 2 mmol) in dry THF (2 ml) was added, followed by iodomethane (0.5 ml, 8.0 mmol). Work-up as above and chromatography gave (i) the 2-methoxyannulene (**14**) (16 mg, 19%) and (ii) the title ketone (**15**) (49 mg, 59%).

Reaction of the Methoxyannulene (**14**) *with PTAD*.—A mixture of the annulene (**14**) (19 mg, 0.1 mmol) and PTAD (18 mg, 0.1 mmol) was stirred at room temperature in dichloromethane (4 ml). After 15 min, the red colour of PTAD had disappeared. The solvent was evaporated, and the residue chromatographed to give the *adduct* (**16**) (7.5 mg, 14%) as an unstable solid which decomposed without melting at 135 °C, δ (250 MHz, $CDCl_3$) 1.12 (3 H, s), 3.81 (3 H, s), 4.90 (1 H, s), 6.13 (1 H, d *J* 9.2 Hz), 6.30 (1 H, d, *J* 5.4 Hz), 6.47 (1 H, dd, *J* 5.4, 9.2 Hz), 6.72 (1 H, d, *J* 5.9 Hz), 7.25—7.50 (10 H, m), and 7.75 (1 H, d, *J* 5.9 Hz).

Reaction of the Trimethylsiloxyannulene (**12**) *with PTAD*.—A mixture of the annulene (**12**) (25 mg, 0.11 mmol) and PTAD (18.9 mg, 0.11 mmol) was stirred at room temperature in dichloromethane (2 ml). After 10 min, the solvent was evaporated and the residue chromatographed on silica gel. Elution with ether gave 2a,7b-*dihydro*-7b-*methyl*-2a-(3,5-*dioxo*-4-*phenyl*-1,2,4-*triazolin*-2-*yl*)-2H-*cyclopent*[cd]*inden*-2-*one* (**17**) (19.4 mg, 54%) as orange–red crystals, m.p. 223—225 °C (decomp.) (Found: C, 69.4; H, 4.3; N, 12.1. $C_{20}H_{15}N_3O_3$ requires C, 69.6; H, 4.4; N, 12.2%); δ (250 MHz, $CDCl_3$) 1.66 (3 H, s), 5.21 (1 H, s), 5.68 (1 H, d, *J* 5.0 Hz), 6.13 (1 H, dd, *J* 5.0, 9.9 Hz), 6.32 (1 H, d, *J* 5.4 Hz), 6.40 (1 H, d, *J* 9.9 Hz), 6.70 (1 H, d, *J* 5.4 Hz), and 7.3—7.5 (5 H, m), NH not observed; *m*/*z* 345 (M^+), 330, 211, 183, 155, 141, and 119 (base).

6-*Methoxy*-7a-*methyl*-2,3,5,7a-*tetrahydro*-1H-*inden*-1-*one* (**19**).—A mixture of 6-methoxyindan-1-one (**18**)[12] (33.25 g, 0.205 mol) and t-butyl alcohol (33.85 g) in THF (80 ml) was added dropwise to a stirred solution of potassium (20.1 g, 0.51 g-atom) in liquid ammonia (1 000 ml) at −78 °C. A solution of anhydrous lithium bromide (46.6 g, 0.54 mol) in THF (140 ml) was added followed after 0.5 h by a simultaneous rapid addition of aqueous THF (50%; 180 ml) and iodomethane (30.7 g, 0.216 mol). Work-up as described previously,[10] and distillation of the crude product at 85—100 °C/0.2 mmHg gave the *title compound* (**19**) (28.5 g, 78%), δ (90 MHz, $CDCl_3$) 1.13 (3 H, s), 2.1—2.8 (6 H, m), 3.56 (3 H, s), 4.91 (1 H, br s), and 5.70 (1 H, m), which was used without further purification.

6-*Methoxy*-7a-*methyl*-5,7a-*dihydro*-1H-*iden*-1-*one* (**20**) *and its* 7,7a-*Dihydro Isomer* (**21**).—A solution of the dienone (**19**) (7.128 g, 0.04 mol) in dry THF (25 ml) was added dropwise with stirring to a solution of lithium di-isopropylamide [from di-isopropylamine (7.25 ml, 0.044 mol) and n-butyl-lithium (1.5M; 27 ml, 0.041 mol)] in THF at −78 °C under nitrogen. After 15 min, the mixture was cooled to −95 °C and a solution of phenylseleninyl chloride (7.66 g, 0.04 mol) in THF (20 ml) was added dropwise the temperature being maintained below −80 °C. After the addition, the mixture was allowed to warm to 0 °C, and was diluted with water, and the selenide extracted with ether. The combined extracts were washed with aqueous sodium hydrogen sulphate (10%) and saturated aqueous sodium hydrogen carbonate, dried, and evaporated. The crude selenide was redissolved in THF (70 ml) containing pyridine (10 ml), and treated with hydrogen peroxide (30%; 14 ml), the addition being regulated so that the temperature was maintained between 7 and 10 °C. When the reaction was complete (t.l.c.) the mixture was diluted with ether, and washed with saturated aqueous sodium hydrogen carbonate, aqueous sodium hydrogen sulphate (10%), and water, dried, and evaporated. The residue was chromatographed on silica gel to give a mixture of the trienones (**20**) and (**21**) (3.1 g, 45%). With time, the trienone (**20**) was slowly converted into the fully conjugated isomer (**21**) δ (250 MHz, $CDCl_3$) 1.13 (3 H, s), 2.27 (2 H, s), 3.70 (3 H, s), 5.25 (1 H, d), 6.18 (2 H, m), and 7.72 (1 H, d).

Conversion of the Trienone (**20**)/(**21**) *into the Tricyclic Adducts* (**24**), (**25**), *and* (**26**).—A solution of dimethyl acetylenedicarboxylate (683 mg, 5.56 mmol) in dry DME (5 ml) was added to a solution of the 3a*H*-indene (**22**) [generated from the trienones (**20**)/(**21**) (892 mg, 5.06 mmol) and potassium hydride (25%; 1.0 g) and 18-crown-6 (1.47 g, 5.56 mmol) followed by methyl fluorosulphonate as previously described[15]]. Work-up and chromatography gave the *adduct* (**23**) (720 mg, 43%) as a yellow oil. The adduct (**23**) (665 mg) was dissolved in methanol (1 ml) and cooled in ice. Concentrated sulphuric acid (1 ml) was added and the mixture was stirred at 0 °C for 10 min, and then poured into ether. The ether layer was separated, washed with saturated aqueous sodium hydrogen carbonate, dried, and evaporated. The residue was chromatographed to give (i) *dimethyl* 2a-*methoxy*-7b-*methyl*-1-*oxo*-2a,6,7a,7b-*tetrahydro*-*cyclopent*[cd]*indene*-1,2-*dicarboxylate* (**24**) (250 mg, 40%), m.p. 108—109 °C (Found: C, 64.1; H, 5.7. $C_{17}H_{18}O_6$ requires C, 64.1;

H, 5.7%); δ (250 MHz, $CDCl_3$) 1.30 (3 H, s), 2.84 (1 H, br d, *J* 18.6 Hz), 3.26 (1 H, dd, *J* 18.6, 4.1 Hz), 3.30 (3 H, s) 3.74 (1 H, s), 3.78 (3 H, s), 3.80 (3 H, s), 5.93 (1 H, m), 6.02 (1 H, d, *J* 7.5 Hz), and 7.16 (1 H, d, *J* 7.5 Hz); *m/z* 318 (M^+), 286 (base), 258, and 226; (ii) *dimethyl 7-methoxy-7b-methyl-7bH-cyclopent*[cd]*indene-1,2-dicarboxylate* (**26**) (48 mg, 8%) as a yellow oil, $\nu_{max.}$($CHCl_3$) 1 728 and 1 712 cm^{-1}; δ (250 MHz, $CDCl_3$) −1.13 (3 H, s), 3.96 (3 H, s), 4.03 (3 H, s), 4.05 (3 H, s), 7.04 (1 H, d, *J* 7 Hz), 7.62 (1 H, d, *J* 7 Hz), and 8.08 (2 H, ABq); *m/z* 300 (M^+) and 268 (base); and (iii) *dimethyl 1-hydroxy-7b-methyl-7bH-cyclopent*[cd]*indene-1,2-dicarboxylate* (**25**) (86 mg, 15%) as deep orange crystals, m.p. 83—84 °C (Found: C, 67.1; H, 4.9. $C_{16}H_{14}O_5$ requires C, 67.1; H, 4.9%); $\nu_{max.}$($CHCl_3$) 3 250br, 1 715, 1 665, and 1 574 cm^{-1}; δ (250 MHz, $CDCl_3$) −1.15 (3 H, s), 4.01 (3 H, s), 4.07 (3 H, s), 7.26 (1 H, d, *J* 7.5 Hz), 7.72 (1 H, d, *J* 7.5 Hz), 8.01 (1 H, d, *J* 3.8 Hz), 8.04 (1 H, d, *J* 3.8 Hz), and 10.05 (1 H, s); *m/z* 286 (M^+), 254, 233, 159, and 132 (base).

1-Methoxy-7a-methyl-2,3,5,7a-tetrahydro-1H-inden-1-one (**28**).—This compound was prepared from 4-methoxyindanone (**27**)[13] (26.2 g, 0.162 mol) in a manner identical to that described for the 6-methoxy isomer (**19**). Distillation of the crude product at 76—86 °C/0.3 mmHg gave the *title compound* (**28**) (21.6 g, 75%) as a liquid, δ (90 MHz, $CDCl_3$) 1.10 (3 H, s), 2.0—2.9 (6 H, m), 3.63 (3 H, s), and 5.6—6.0 (2 H, m); *semicarbazone*, m.p. 181—185 °C (Found: C, 61.0; H, 7.3; N, 17.7. $C_{12}H_{17}N_3O_2$ requires C, 61.3; H, 7.3; N, 17.9%).

5,7a-Dihydro-4-methoxy-7a-methyl-1H-inden-1-one (**29**).—This compound was prepared from the dienone (**28**) (7.128 g) in a manner identical to that described for the 6-methoxy isomer (**20**). Chromatography of the crude product gave the *title compound* (**29**) (3.6 g, 51%), δ (250 MHz, $CDCl_3$) 1.24 (3 H, s), 2.94 (2 H, m), 3.90 (3 H, s), 5.76 (1 H, m), 5.85 (1 H, d, *J* 6.5 Hz), 6.15 (1 H, m), and 8.08 (1 H, d, *J* 6.5 Hz), used without further purification.

Dimethyl 5-Methoxy-7b-methyl-7bH-cyclopent[cd]*indene-1,2-dicarboxylate* (**30**).—A solution of the trienone (**29**) (2.31 g, 0.013 mol) in dry DME (5 ml) was added dropwise to a stirred mixture of 18-crown-6 (3.8 g) and potassium hydride (25%; 3.1 g) in DME (10 ml) at −20 °C under nitrogen. The mixture turned deep red. Methyl fluorosulphonate (1.25 ml, 0.08 mol) was added and the colour immediately changed to yellow. After a further 5 min, dimethyl acetylenedicarboxylate (1.77 ml) in DME (2 ml) was added. The mixture was warmed to 40 °C, kept at this temperature for 1.5 h, and then finally heated at 60 °C for a few minutes. The dark mixture was filtered through Celite, diluted with ether, and washed with water. The ether extracts were dried, evaporated, and the residue chromatographed to give the *title annulene* (**30**) (2.60 g, 65%) as an orange oil, $\nu_{max.}$(CCl_4) 1 720 cm^{-1}; δ (250 MHz, $CDCl_3$) −1.19 (3 H, s), 4.00 (3 H, s), 4.04 (3 H, s), 4.27 (3 H, s), 7.31 (1 H, d, *J* 8 Hz), 7.97 (1 H, d, *J* 3.8 Hz), 8.03 (1 H, d, *J* 8 Hz), and 8.23 (1 H, d, *J* 3.8 Hz); *m/z* 300 (M^+) and 268 (base) Hydrolysis of the diester (**30**) in a 1:1 mixture of THF and hydrochloric acid (6M) gave *5-methoxy-7b-methyl-7bH-cyclopent*[cd]*indene-1,2-dicarboxylic acid*, m.p. 135—145 °C (Found: C, 65.6; H, 4.7. $C_{15}H_{12}O_5$ requires C, 66.2; H, 4.4%); δ (250 MHz, $CDCl_3$) −1.17 (3 H, s), 4.31 (3 H, s), 7.40 (1 H, d, *J* 8.1 Hz), 8.19 (1 H, d, *J* 4.1 Hz), 8.38 (1 H, d, *J* 4.1 Hz), and 8.42 (1 H, d, *J* 8.1 Hz); *m/z* 272 (M^+) and 254 (base).

5-Hydroxy-7b-methyl-7bH-cyclopent[cd]*indene-1,2-dicarbaldehyde* (**32**).—A solution of the diester (**30**) (1.00 g, 3.3 mmol) in dry ether (25 ml) was added to a stirred suspension of lithium aluminium hydride (0.48 g, 12.6 mmol) in ether (25 ml) at room temperature. The mixture was stirred for 1 h, and then ethyl acetate was added to destroy the excess of lithium aluminium hydride. Work-up gave the diol, which was treated with barium manganate in the usual way[5] to give 5-methoxy-7b-methyl-7bH-cyclopent[*cd*]indene-1,2-dicarbaldehyde (**31**) (0.52 g, 65%) as a red oil.

A solution of the dialdehyde (**31**) (32 mg) in dichloromethane (2 ml) was added to an excess of boron tribromide in dichloromethane at −78 °C. The mixture was warmed to room temperature, diluted with ether, and worked up with water. Chromatography gave the *title compound* (**32**) (10 mg, 33%) as a red solid, m.p. 174—175 °C, δ (250 MHz, $CDCl_3$) −1.00 (3 H, s), 7.44 (1 H, d, *J* 8.1 Hz), 8.24 (1 H, d, *J* 4 Hz), 8.35 (1 H, d, *J* 4 Hz), 8.37 (1 H, d, *J* 8.1 Hz), 10.81 (1 H, s), and 10.87 (1 H, s); *m/z* 226 (M^+, base), 211, and 159.

5-Methoxy-7b-methyl-7bH-cyclopent[cd]*indene* (**33**).—A mixture of the dialdehyde (**31**) (197 mg, 0.82 mmol) and tristriphenylphosphinerhodium(I) chloride (1.67 g, 1.80 mmol) was heated under reflux in benzene (25 ml) for 9 h. After cooling, the solution was treated with iodomethane (2 ml) to remove triphenylphosphine, and then evaporated. Chromatography of the residue gave the *title compound* (**33**) (98 mg, 65%) as a pale yellow oil, $\lambda_{max.}$(EtOH) 292 (log ε 4.68), 327sh (3.70), and 464 nm (2.61); δ (250 MHz, $CDCl_3$) −1.52 (3 H, s), 4.23 (3 H, s), 7.11 (1 H, d, *J* 7.5 Hz), 7.62 (1 H, d, *J* 7.5 Hz), 7.66 (1 H, d, *J* 3.5 Hz), 7.77 (1 H, d, *J* 3.0 Hz), 7.79 (1 H, d, *J* 3.0 Hz), and 8.00 (1 H, d, *J* 3.5 Hz); *m/z* 184 (M^+ base) and 169.

5-Hydroxy-7b-methyl-7bH-cyclopent[cd]*indene* (**9**).—A solution of the methoxyannulene (**33**) (18 mg) in dry dichloromethane (1 ml) was added to a large excess of boron tribromide in dichloromethane at −78 °C. After 15 min, the mixture was warmed to 0 °C, poured onto ice-water, and extracted with ether. The ether extracts were combined, washed with water, dried, and evaporated. The residue was chromatographed to give *2a-bromo-7b-methyl-2,2a,4a,7b-tetrahydrocyclopent*[cd]*inden-5-one* (**34**) as a colourless solid, δ (250 MHz, $CDCl_3$) 1.41 (3 H, s), 3.16 (2 H, AB q with additional splitting, *J* 17.6 Hz), 3.40 (1 H, m), 5.60 (1 H, dd), 5.92 (1 H, m), 6.02 (2 H, m), and 7.16 (1 H, d); *m/z* 252/250 (M^+) and 171 (base). The bromo trienone (**34**) was dissolved in benzene (10 ml) and treated with an excess of DBU at room temperature. After 30 min, the mixture was poured into dilute aqueous sodium hydrogen sulphate and extracted with ether. The ether extracts were combined, washed with dilute aqueous sodium hydrogen sulphate and water, dried, and evaporated. The residue was chromatographed to give the *title compound* (**9**) (10 mg, 60%) as a yellow oil, $\nu_{max.}$(CCl_4) 3 600 and 1 665 cm^{-1}; $\lambda_{max.}$(EtOH) 293 (log ε 4.48), 326sh (3.60), and 467 nm (2.54); δ (250 MHz, $CDCl_3$) −1.49 (3 H, s), 7.14 (1 H, d, *J* 7.1 Hz), 7.60 (1 H, d, *J* 7.1 Hz), 7.68 (1 H, d *J* 3.0 Hz), 7.81 (1 H, d, *J* 3.2 Hz), 7.90 (1 H, d, *J* 3.2 Hz), and 7.95 (1 H, d, *J* 3.0 Hz).

7-Chloroacetyl-7,7a-dihydro-7a-methyl-1H-inden-1-one (**36**).—A solution of the dichloro ketone (**35**)[10] (264 mg, 1.03 mmol) in dry degassed benzene (10 ml) containing azobisisobutyronitrile (50 mg, cat.) was added during 30 min to a refluxing solution of tri-n-butyltin hydride (0.3 ml, 1.03 mmol) in benzene (10 ml). The resulting mixture was refluxed for 5 h, the solvent evaporated, and the residue chromatographed to give (i) unchanged starting material (**35**) (60 mg, 19%), and (ii) the *title compound* (**36**) (139 mg, 52%, 65% based on unrecovered starting material) (Found: M^+, 222.0451. $C_{12}H_{11}{}^{35}ClO_2$ requires M^+, 222.0448); $\nu_{max.}$(neat) 1 710 cm^{-1}; δ (250 MHz, $CDCl_3$) 1.09 (3 H, s), 3.89 (1 H, d, *J* 7.1 Hz), 4.09 (2 H, AB q, *J* 15.3 Hz), 6.10 (1 H, d, *J* 5.4 Hz), 6.21 (1 H, dd, *J* 7.1, 9.2 Hz), 6.41 (1 H, dd, *J* 5.4, 9.2 Hz), 6.49 (1 H, d, *J* 5.6 Hz), and 7.75 (1 H, d, *J* 5.6 Hz); *m/z* 224/222 (M^+), 145 (base), 131, 117, 115, 102, and 91.

7-Acetyl-7,7a-dihydro-7a-methyl-1H-inden-1-one (**38**).—A mixture of the chloro ketone (**36**) (137 mg, 0.62 mmol) and sodium iodide (460 mg, 3.1 mmol) was stirred in acetone (10 ml) at room temperature for 1 h. The mixture was filtered and the filtrate evaporated. The residue was extracted with dichloromethane (5 × 2 ml), and the combined extracts were filtered and evaporated to give the *iodomethyl ketone* (**37**) (177 mg, 91%), δ (90 MHz, $CDCl_3$) 1.07 (3 H, s), 3.89 (2 H, AB q, *J* 11 Hz), 4.04 (1 H, d, *J* 7 Hz), 6.13 (1 H, d, *J* 5 Hz), 6.22 (1 H, dd, *J* 5, 9 Hz), 6.44 (1 H, dd, *J* 5, 9 Hz), 6.52 (1 H, d, *J* 6 Hz), and 7.77 (1 H, d, *J* 6 Hz).

A mixture of the iodomethyl ketone (**37**) (59 mg, 0.19 mmol) tri-n-butyltin hydride (0.1 ml, 0.3 mmol) and azobisisobutyronitrile (10 mg, cat.) was heated in refluxing benzene (5 ml) for 30 min. The solvent was evaporated and the residue chromatographed to give the *title compound* (**38**) (29 mg, 83%) as an oil, $\nu_{max.}$(neat) 1 696 cm^{-1}; δ (250 MHz, $CDCl_3$) 1.04 (3 H, s), 2.12 (3 H, s), 3.60 (1 H, d, *J* 6.7 Hz), 6.07 (1 H, d, *J* 5.0 Hz), 6.20 (1 H, dd, *J* 6.7, 9.0 Hz), 6.34 (1 H, dd, *J* 5.0, 9.0 Hz), 6.49 (1 H, d, *J* 5.3 Hz), and 7.71 (1 H, d, *J* 5.3 Hz); *m/z* 188 (M^+), 145 (base), 131, 117, and 115; *mono-2,4-dinitrophenylhydrazone*, m.p. 161—162 °C (from ethanol) (Found: C, 58.8; H, 4.4; N, 15.15. $C_{18}H_{16}N_4O_5$ requires C, 58.7; H, 4.4; N, 15.2%).

Acknowledgements

We thank the S.E.R.C. for a studentship (to R. McC.), the Swedish Natural Science Research Council for a postdoctoral award (to Z. L.), and Dr. H. S. Rzepa for valuable discussions.

References

1 Part 4, R. McCague, C. J. Moody, C. W. Rees, and D. J. Williams, *J. Chem. Soc., Perkin Trans. 1*, 1984, 909.
2 M.-C. Lasne, J.-L. Ripoll, and J.-M. Denis, *Tetrahedron Lett.*, 1980, **21**, 463.
3 E. Vogel, W. Schröck, and W. A. Böll, *Angew. Chem., Int. Edn. Engl.*, 1966, **5**, 732.
4 S. Masamune, D. W. Brooks, K. Morio, and R. L. Sobczak, *J. Am. Chem. Soc.*, 1976, **98**, 8277.
5 R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1984, 165.
6 R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1984, 175.
7 Preliminary communication, R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1982, 622.
8 Preliminary communication, Z. Lidert and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1983, 317.
9 H. S. Rzepa, *J. Chem. Res.*, 1982, (*S*) 324; (*M*) 3301.
10 R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2399.
11 P. Cazeau, F. Moulines, O. Laporte, and F. Duboudin, *J. Organomet. Chem.*, 1980, **201**, C9.
12 H. O. House and C. B. Hudson, *J. Org. Chem.*, 1970, **35**, 647.
13 J. D. Loudon and R. K. Razdan, *J. Chem. Soc.*, 1954, 4299.
14 Z. Lidert and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1982, 499.
15 T. L. Gilchrist, C. W. Rees, and D. Tuddenham, *J. Chem. Soc., Perkins Trans. 1*, 1981, 3214.

Received 11*th June* 1984; *Paper* 4/968