Tricyclic [10]Annulenes. Part 7.[1] Preparation, Properties, and Reactions of 7b-Benzyl-7b*H*-cyclopent[*cd*]indene

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The tricyclic [10]annulene containing a central benzyl group, 7b-benzyl-7b*H*-cyclopent[*cd*]indene [**1d**], has been prepared from 7-methoxyindan-1-one by a sequence involving reductive alkylation to give the dienone (**6**), introduction of an extra double bond, and reaction of the resulting trienone (**8**) with methoxyvinyl-lithium to give the alcohol (**9**). Methylation and acid hydrolysis gave the diketone (**4**) which underwent intramolecular aldol condensation in the key step to give the tricyclic ketone (**5**). Conversion of (**5**) into the annulene (**1d**) was accomplished by reduction of the ketone, dehydration of the resulting alcohol, and final elimination of methanol. The annulene (**1d**) rearranges to the 2a*H*-isomer (**13**) on heating, and is readily nitrated, acetylated, and formylated in the 10π system. The reactivity of compound (**1d**) is compared and contrasted with that of the methyl annulene (**1a**).

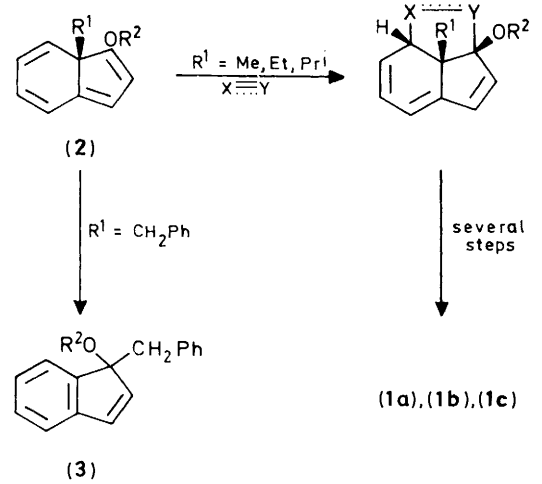
In previous papers in this series we have reported the preparation and properties of 7b-methyl- (**1a**),[2,3] 7b-ethyl- (**1b**),[1] and 7b-isopropyl-7b*H*-cyclopent[*cd*]indene (**1c**).[1] The properties of these compounds support their formulation as 10π aromatic systems, and in order to gain further insight into these novel species, we were interested in preparing the compound

(**1**)

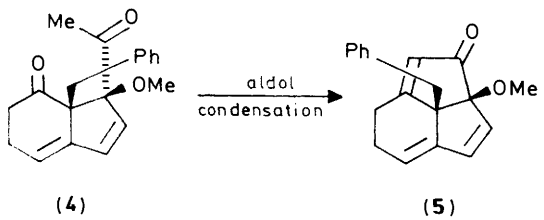
a; R = Me **c**; R = Pr^i
b; R = Et **d**; R = CH_2Ph

(**1d**) bearing a benzyl group at the central 7b-position. One particular feature of this compound is the possibility of interaction between the 10π-electron periphery and the 6π-electron system of the central substituent.

Routes to the tricyclic [10]annulenes (**1a**—**c**) are based on the [8 + 2] cycloaddition of 2π carbon dienophiles to the corresponding 3a*H*-indene (**2**; R^2 = Me or $SiMe_3$) (Scheme 1).[1-3] However, the benzyl-substituted 3a*H*-indene behaved differently, and underwent a rapid aromatising [1,5] sigmatropic shift of the benzyl group to give the indene (**3**) in preference to cycloaddition.[4] Clearly an alternative route was needed which avoided the intermediacy of this labile 3a*H*-indene. We now report full details of such a synthesis based on an intramolecular aldol condensation. Although this route was originally developed as an alternative to the cycloaddition approach to the methyl-substituted annulene (**1a**),[5] we illustrate its application to the preparation of 7b-benzyl-7b*H*-cyclopent-[*cd*]indene (**1d**), a previously unprepared tricyclic [10]annulene.



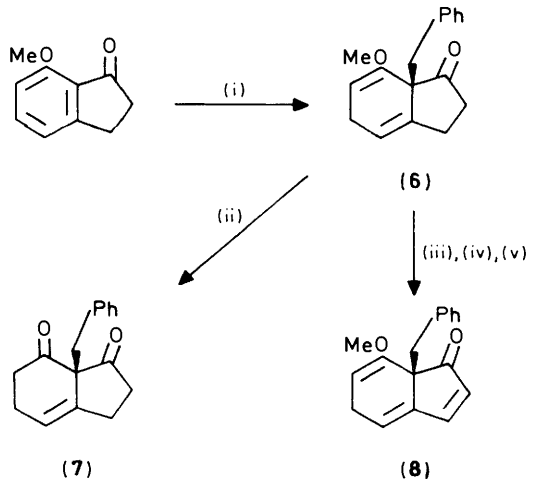
Scheme 1.



Results and Discussion

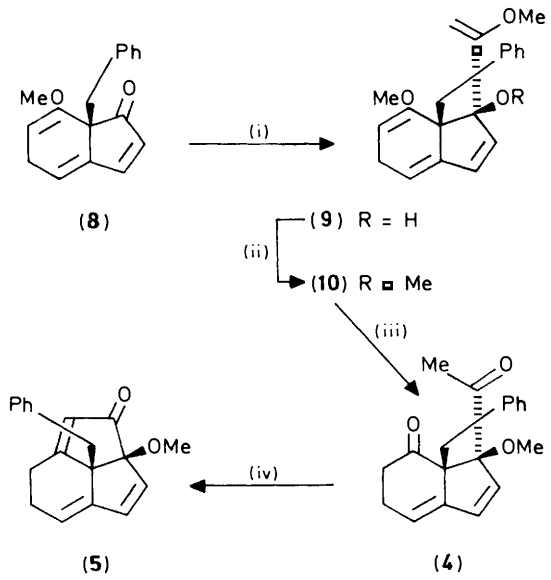
Preparation.—The key step in establishing the tricyclic skeleton of the annulene (**1d**) is the intramolecular aldol condensation of the diketone (**4**) to give the tricyclic ketone (**5**). The substrate (**4**) for the intramolecular aldol condensation was prepared from 7-methoxyindan-1-one. Addition of 7-methoxyindan-1-one[6,7] and t-butyl alcohol to a solution of potassium in liquid ammonia, followed by addition of lithium bromide and quenching with benzyl bromide, resulted in reductive alkylation and formation of the dienone (**6**) in 83% yield. Acid hydrolysis of the dienone (**6**) gave the diketone (**7**). The conversion of the dienone (**6**) into the trienone (**8**) (Scheme 2) was accomplished by α-phenylseleniation and oxidative fragmentation of the resulting selenide, although in common with related reactions[4] the yield was only moderate (34%).

The necessary two-carbon unit at C-1 was introduced using methoxyvinyl-lithium. This acyl anion equivalent[8] undergoes exclusive 1,2-addition to α,β-unsaturated ketones and is readily converted into the corresponding acetyl derivative by mild acid hydrolysis.[9] Thus addition of the trienone (**8**) to the organolithium reagent gave the alcohol (**9**). Methylation of the hydroxyl function was most efficiently carried out in a separate step (Scheme 3), and subsequent hydrolysis of both enol ethers gave the required diketone (**4**). The intramolecular aldol



Scheme 2. *Reagents and conditions:* (i) K, NH_3, −78 °C, Bu^{t}OH–THF; LiBr, THF; $PhCH_2Br$, water–THF; (ii) HCl, water–THF; (iii) $LiNPr^i_2$, THF, −78 °C; (iv) PhSeCl, −90 °C; (v) H_2O_2

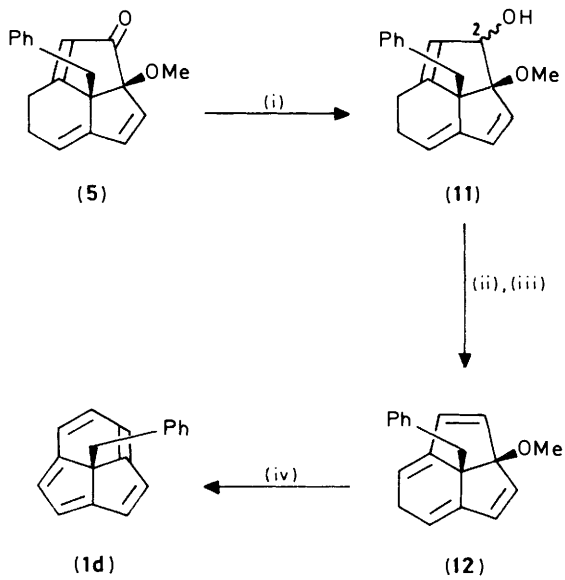
condensation was simply effected by heating the diketone (**4**) in 5% aqueous methanolic potassium hydroxide at 60 °C and gave the required tricyclic ketone (**5**). The intermediates (**9**), (**10**), and (**4**) were not purified and were taken straight on to the next step. The overall yield of the tricyclic ketone (**5**) from the trienone (**8**) was 46%.



Scheme 3. *Reagents and conditions:* (i) $H_2C{=}CLi(OMe)$, THF, −78 °C; aqueous work-up; (ii) $MeSOCH_2Na$, Me_2SO, MeI; (iii) 2M-HCl; (iv) 5% KOH, water–MeOH, 60 °C

Conversion of the tricyclic ketone (**5**) into the annulene (**1d**) was straightforward. Thus, treatment of the ketone with di-isobutylaluminium hydride (DIBAL) gave an epimeric mixture of alcohols (**11**) (93%). Although this mixture could be separated by chromatography into a minor and a major alcohol (ratio 1:3)* it was more convenient to dehydrate the mixture without purification. The dehydration was effected by treating the

* The stereochemistry of the major alcohol was assigned on the basis of nuclear Overhauser effect difference experiments in which pre-irradiation of 2-H caused an enhancement of the signal for the methoxy group, thus confirming the configuration of the hydroxy group, *i.e.* OH is *trans* to OMe.



Scheme 4. *Reagents and conditions:* (i) DIBAL, hexane, 0 °C; (ii) MTPI, $(Me_2N)_3PO$; (iii) 10% aq. NaOH; (iv) PTSA, CH_2Cl_2, 25 °C

alcohols (**11**) with methyltriphenoxyphosphonium iodide (MTPI) in a modified procedure.[10] The resulting tetraene (**12**) (Scheme 4) was not isolated but aromatised with loss of methanol to give the annulene (**1d**) on treatment with toluene-4-sulphonic acid (PTSA) in 79% overall yield from the ketone (**5**).

Physical Properties.—The tricyclic [10]annulene (**1d**) is a distillable bright yellow oil, whose electronic spectrum shows a long-wavelength absorption at 452 nm (log ε 2.49). The close similarity of the u.v. spectra of the annulenes (**1a**—**d**) suggest that all four annulenes have essentially identical electronic structures, and hence similar molecular geometries. In particular, the u.v. spectrum of the annulene (**1d**) suggested that there is no significant electronic interaction between the π-system of the benzyl substituent and the 10π-aromatic periphery.

The ^1H n.m.r. spectrum shows a signal for the central CH_2 of the benzyl group, upfield of tetramethylsilane, at δ −0.22, thus confirming the presence of an induced diamagnetic ring current in the applied magnetic field. The effect of the diamagnetic ring current extends as far as the *ortho*-protons of the phenyl ring (δ 6.29), although the effect on the *meta*- and *para*-protons is, as expected, much less (δ 6.95). The peripheral protons resonate in the range δ 7.5—7.95, and appear as the expected AB and AB_2 patterns (Figure 1).

The ^{13}C n.m.r. spectrum (Figure 2) supports the symmetrical nature of the structure, and in common with other tricyclic [10]annulenes contains a low-field signal (δ_C 176.5) for C-2a which reflects the ring strain present at this position. The spectral assignments which could be made with certainty are given in the Experimental section.

On being heated in solution the annulene (**1d**) rearranges to the 2a*H*-isomer (**13**) (78%). The rate of this rearrangement was determined by the u.v. method described previously,[2] and the half-lives for the process at 80, 109, and 138 °C were found to be 162, 7.2, and 1.3 minutes respectively. By comparison with the annulenes (**1a**) and (**1b**), this gives a relative rate of migration of the central methyl, ethyl, and benzyl groups of 1:11:540. The fact that the benzyl group migrates more easily than the methyl was expected on the basis of the relative thermal stability of the corresponding 3a*H*-indenes (**2**).[4] From the rates of migration of the benzyl group at different temperatures the activation energy

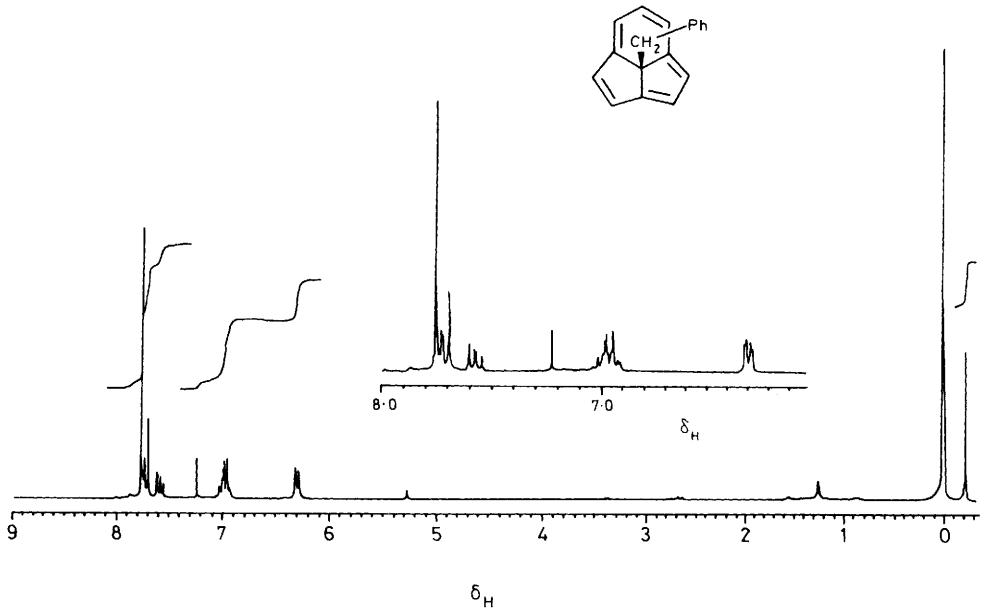


Figure 1. 250 MHz ^{1}H N.m.r. spectrum of 7b-benzyl-7b*H*-cyclopent[*cd*]indene (**1d**) in deuteriochloroform

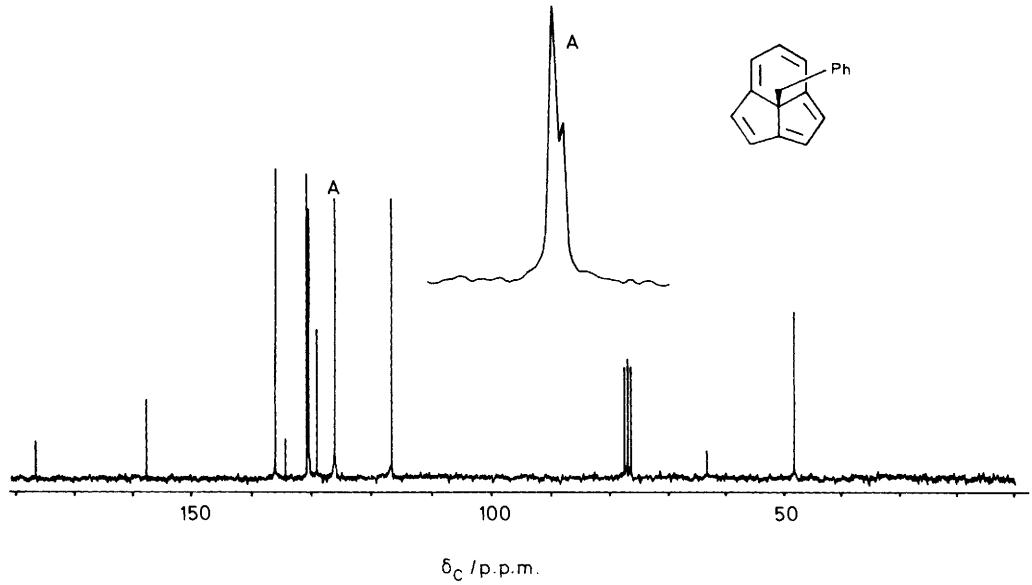
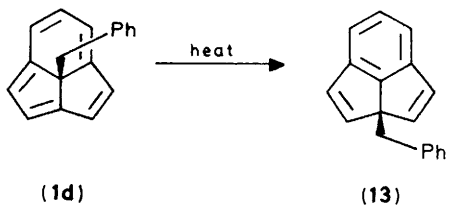


Figure 2. 62.9 MHz ^{13}C N.m.r. spectrum of 7b-benzyl-7b*H*-cyclopent[*cd*]indene (**1d**) in deuteriochloroform



(**1d**) (**13**)

for rearrangement was estimated as 24 (±1) kcal mol^{-1}. This compares with a value of 32.7 (±1) kcal mol^{-1} for rearrangement of the methyl-substituted annulene (**1a**).[2]

In contrast to the annulene (**1a**) which is essentially photostable,[2] irradiation of the benzyl annulene (**1d**) in light petroleum (b.p. 40—60 °C) at either 254 or 300 nm caused complete decomposition.

Chemical Reactions.—In accord with its aromatic structure the annulene (**1d**) underwent electrophilic substitution reactions, the attack occurring exclusively on the 10π periphery rather than on the benzene ring. The ratio of products, determined by n.m.r. integration, from the nitration, acetylation and formylation of the annulene (**1d**), carried out as for the corresponding reactions of the methyl annulene (**1a**),[3] are shown in the Table. The corresponding figures for the methyl annulene [3] are given for comparison. In the case of the methyl-substituted annulene (**1a**), the preference for 5- and 1-substitution was rationalised on the basis of the relative stability of the carbonium ion intermediates involved.[3] A similar rationale was expected to

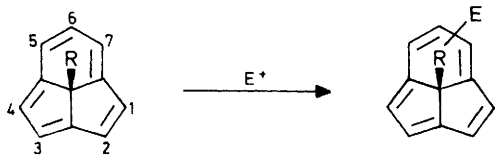
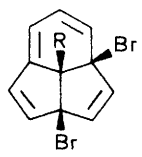


Table Electrophilic substitution reactions of the tricyclic [10]annulenes (**1d**) and (**1a**)

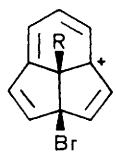
		% Distribution				
R	E	1-	2-	5-	6-	% Yield
$PhCH_2$	NO_2	0	0	48	52	37
$PhCH_2$	$COCH_3$	0	0	92	8	63
$PhCH_2$	CHO	0	0	96	4	31
Me	NO_2	40	5	40	15	41
Me	$COCH_2$	20	0	75	5	55
Me	CHO	4	0	93	3	28

apply for the benzyl annulene (**1d**), and therefore the lack of any 1-substituted products, together with the substantial amount of 6-substitution in the nitration reaction, was surprising.

The methyl and benzyl annulenes differ in their reaction towards pyridinium bromide perbromide. Whereas the methyl annulene gave a high yield of the addition product (**14**; R = Me),[3] presumably *via* initial electrophilic attack at C-2a to give (**15**; R = Me), the benzyl annulene was recovered (91%) under similar reaction conditions. One possible reason for the failure of the benzyl annulene to react is that the bulk of the benzyl group prevents the initial electrophilic attack from the top face, the intermediate (**15**; R = CH_2Ph) being sterically crowded.

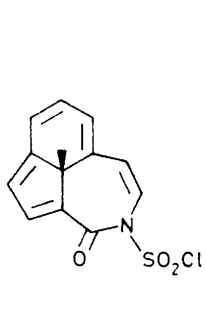


(**14**)

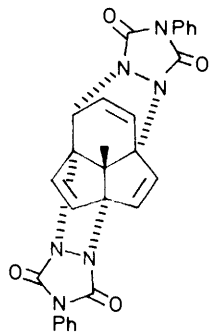


(**15**)

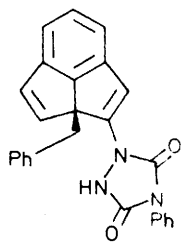
Differing reactivity between the two annulenes was also observed with chlorosulphonyl isocyanate (CSI) and 4-phenyl-1,2,4-triazole-3,5-dione (PTAD). The benzyl annulene was inert to CSI under conditions where the methyl annulene gave the ring-expanded indenoazepinone (**16**).[3] Since the formation of the indenoazepinone is believed to proceed by initial attack of the highly electrophilic CSI at C-2a, it is likely that the larger benzyl group again prevents approach of the electrophile from the top face.



(**16**)



(**17**)



(**18**)

Reaction of the methyl annulene with PTAD in refluxing 1,2-dimethoxyethane gave the 1:2 adduct (**17**).[3] However, under the same conditions the benzyl annulene was recovered, although on prolonged refluxing a new product was formed, and was assigned the 1:1 adduct structure (**18**). The adduct (**18**) is presumed to arise by electrophilic attack on the 2a*H*-isomer (**13**) which formed when the annulene (**1d**) is heated. This assumption was supported by the observation that treatment of compound (**13**) with PTAD in refluxing 1,2-dimethoxyethane also gave the adduct (**18**).

Attempted functionalisation of the benzylic CH_2 group by radical halogenation using *N*-bromosuccinimide or t-butyl hypochlorite failed.

Experimental

For general points see ref. 2. Light petroleum refers to that fraction boiling in the range 40—60 °C.

7a-*Benzyl*-7-*methoxy*-2,3,5,7a-*tetrahydro*-1H-*inden*-1-*one* (**6**).—To a stirred solution of potassium (4.45 g, 0.114 mol) in liquid ammonia (250 ml) at −78 °C under nitrogen was added a solution of 7-methoxyindan-1-one (5.00 g, 0.031 mol) and t-butyl alcohol (6.28 g, 0.084 mol) in dry THF (50 ml). After 30 min, a solution of lithium bromide (8.67 g, 0.1 mol) in THF (50 ml) was added. A further 30 min later a mixture of water (40 ml), THF (40 ml) and benzyl bromide (5.18 g, 0.030 mol) was added rapidly. The external cooling bath was removed and the ammonia allowed to evaporate off overnight. The residue was diluted with water (400 ml) and extracted with ether (3 × 300 ml). The combined extracts were dried ($MgSO_4$), evaporated, and chromatographed to give the title compound (**6**) (6.51 g, 83%) as an oil, $\nu_{max.}$ 1 740 cm^{-1}; δ (250 MHz; $CDCl_3$) 1.86 (1 H, m), 2.25—2.45 (2 H, m), 2.50—2.65 (3 H, m), 2.76 (1 H, d, *J* 13.0 Hz), 3.02 (1 H, d, *J* 13.0 Hz), 3.60 (3 H, s), 4.54 (1 H, t, *J* 3.7 Hz), 5.70 (1 H, t, *J* 4.6 Hz), 6.98—7.05 (2 H, m), and 7.15—7.22 (3 H, m); *m/z* 254 (M^+), 197, 163, 162, 135, 133, and 121 (base). Hydrolysis of the dienone (**6**) (100 mg) with hydrochloric acid (1.2 *M*; 10 ml) in THF (10 ml) for 1 h gave 7a-*benzyl*-2,3,5,7a-*tetrahydro*-1H-*indene*-1,7(6H)-*dione* (**7**) (81 mg, 86%), m.p. 172—174 °C (Found: C, 79.7; H. 7.0. $C_{16}H_{16}O_2$ requires C, 80.0; H, 6.7%); $\nu_{max.}$ 1 745, 1 695, and 1 675 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.00—2.70 (8 H, m), 2.86 (1 H, d, *J* 13.1 Hz), 3.23 (1 H, d, *J* 13.1 Hz), 6.06 (1 H, br d), and 7.07—7.76 (5 H, m).

7a-*Benzyl*-7-*methoxy*-5,7a-*dihydro*-1H-*inden*-1-*one* (**8**).—A solution of the dienone (**6**) (1.28 g, 5.05 mmol) in THF (5 ml) was added to a solution of lithium di-isopropylamide [from di-isopropylamine (0.9 ml, 6 mmol) in THF (10 ml) and n-butyl-lithium (1.6 M; 4 ml, 6 mmol)] at −78 °C under nitrogen. After 30 min, the solution was cooled to −90 °C and treated with phenylselenium chloride (1.34 g, 7 mmol) in THF (5 ml). The mixture was allowed to warm to 0 °C during 30 min, and was then poured into dil. hydrochloric acid (75 ml). The mixture was extracted with ether, and the extracts were dried and evaporated. The crude selenide was dissolved in THF (15 ml) and the solution was cooled to 0 °C. Pyridine (1 ml) was added and the mixture was treated dropwise with hydrogen peroxide (30%; 3 ml) while the temperature was maintained below 5 °C. After the addition was complete the mixture was poured into water and extracted with ether. The combined extracts were dried over $MgSO_4$, evaporated, and the residue was chromatographed to give the title compound (**8**) (433 mg, 34%) as an oil, $\nu_{max.}$ 1 700 cm^{-1}; δ(90 MHz; $CDCl_3$) 2.00 (1 H, br d), 2.54 (1 H, m), 2.75—3.06 (2 H, ABq, *J* 12 Hz), 3.60 (3 H, s), 4.50—4.60 (1 H, m), 5.80 (1 H, d, *J* 5 Hz), 5.97 (1 H, m), 6.90—7.20 (5 H, m) and 7.50 (1 H, d, *J* 5 Hz); *m/z* 252 (M^+), 234, 161, 160, 106 (base), and 105.

7b-*Benzyl*-2a-*methoxy*-2a,6,7,7b-*tetrahydro*-2H-*cyclopent*[cd]*inden*-2-*one* (**5**).—Methyl vinyl ether (10 ml) was distilled into a 100 ml three-necked flask at −78 °C under nitrogen. THF (20 ml) was added, followed by t-butyl-lithium (1.5 M; 2.3 ml, 3.45 mmol). The resulting yellow solution was then allowed to warm to −5 °C whereupon it became colourless. The mixture was then recooled to −78 °C and a solution of the trienone (**8**) (433 mg, 1.72 mmol) in THF (10 ml) was added. After being stirred at −78 °C for 10 min, the solution was allowed to warm up to 0 °C and was then quenched with aqueous ammonium chloride (20%; 20 ml). After dilution with water (50 ml) the mixture was extracted with ether (2 × 25 ml) and the ether extracts were dried and evaporated to give the crude alcohol (**9**).

Without further purification, the alcohol (**9**) was dissolved in dry DMSO (5 ml), and treated with dimsyl sodium [from sodium hydride (83 mg) and DMSO (20 ml)] at room temperature, followed by iodomethane (large excess). The reaction mixture was poured into water (30 ml) and extracted with ether (3 × 30 ml). The combined extracts were dried over $MgSO_4$, and evaporated. The crude product (**10**) was dissolved in THF (25 ml) and treated with hydrochloric acid (2M; 20 ml) at room temperature during 30 min. The reaction mixture was poured into water (30 ml) and extracted with ether (4 × 40 ml). The combined extracts were dried ($MgSO_4$) and evaporated to give the crude diketone (**4**).

Without further purification, the diketone (**4**) was dissolved in methanol (15 ml) and treated with 5% aqueous methanolic potassium hydroxide (15 ml) at 60 °C for 1 h. The mixture was poured into water (25 ml) and extracted with ether (4 × 35 ml). The combined extracts were dried ($MgSO_4$) and evaporated and the residue was chromatographed to give the *title compound* (**5**) (221 mg, 46%) as an oil, b.p. 120 °C at 0.2 mmHg (Kugelrohr) (Found: C, 81.9; H, 6.5. $C_{19}H_{18}O_2$ requires C, 82.0; H, 6.5%); $\nu_{max.}$ 1 690 and 1 605 cm^{-1}; δ (90 MHz; $CDCl_3$) 2.3—2.8 (4 H, m), 3.09 (2 H, br s), 3.68 (3 H, s), 5.65—5.78 (2 H, m), 5.99 (1 H, d, *J* 5 Hz), 6.17 (1 H, d, *J* 5 Hz), and 7.10—7.35 (5 H, m); *m/z* 278 (M^+) and 187 (base).

Reduction of the Tricyclic Ketone (**5**).—The tricyclic ketone (**5**) (350 mg, 1.26 mmol) was dissolved in light petroleum (15 ml) at 0 °C and was treated with a hexane solution of DIBAL (0.9 M; 2.8 ml, 2.5 mmol). After 1 h at 0 °C the mixture was quenched with methanol (5 ml) and then water (5 ml). Work-up gave an epimeric mixture of the alcohols (**11**) (329 mg, 93%) which was used directly in the next step. In a separate experiment the mixture obtained from reduction of the ketone (**5**) (90 mg) was chromatographed to give (i) the α-alcohol (11 mg, 15%), $\nu_{max.}$ 3 520 cm^{-1}); δ (250 MHz; $CDCl_3$) 2.20—2.70 (4 H, m), 2.98 (2 H, s), 3.43 (3 H, s), 4.27 (1 H, br d), 5.28 (1 H, br s), 5.64 (1 H, m), 6.03 (1 H, d, *J* 5.4 Hz), 6.19 (1 H, d, *J* 5.4 Hz), and 7.10—7.30 (5 H, m), and (ii) the β-alcohol (31 mg, 45%), $\nu_{max.}$ 3 580 cm^{-1}; δ (250 MHz; $CDCl_3$) 2.30—2.70 (4 H, m), 2.96—3.09 (2 H, ABq, *J* 15.0 Hz), 3.53 (3 H, s), 4.95—5.05 (1 H, br s), 5.03 (1 H, br s), 5.45 (1 H, dd, *J* 5.9 and 2.5 Hz), 6.13 (1 H, d, *J* 5.0 Hz), 6.24 (1 H, d, *J* 5.0 Hz), and 7.10—7.32 (5 H, m).

7b-*Benzyl*-7bH-*cyclopent*[cd]*indene* (**1d**).—The mixture of alcohols (**11**) (329 mg, 1.175 mmol) was dissolved in dry hexamethylphosphoramide (3 ml) and treated with MTPI (850 mg, 1.88 mmol). The reaction mixture was stirred at room temperature for 8 h and was then poured into aqueous sodium hydroxide (10%; 10 ml). After 1 h, the mixture was diluted with water and extracted with ether (4 × 30 ml). The combined extracts were dried ($MgSO_4$) and evaporated. The residue was dissolved in dichloromethane (10 ml), PTSA (few crystals) was added, and the mixture was stirred at room temperature for 30 min. The solvent was evaporated off, and the residue was chromatographed to give the *title compound* (**1d**) (230 mg, 85%) as a bright yellow oil, b.p. 80 °C at 0.2 mmHg (Kugelrohr) (Found: M^+, 230.1094. $C_{18}H_{14}$ requires *M*, 230.1095); $\nu_{max.}$ 3 030, 3 020, 2 920, 1 495, 1 450, 1 430, 1 375, 1 290, 1 030, and 955 cm^{-1}; $\lambda_{max.}$ (EtOH) 287 (log ε 4.60), 342sh (3.35), 426sh (2.28), 442sh (2.38), and 452 nm (2.49); δ (250 MHz; $CDCl_3$) −0.22 (2 H, s, CH_2Ph), 6.26—6.32 (2 H, m, *o*-ArH), 6.90—7.02 (3 H, m, *m*- and *p*-ArH), 7.53—7.72 (3 H, AB_2 system, giving δ_A 7.56, 6-H, and δ_B 7.70, J_{AB} 7.5 Hz, 5- and 7-H), and 7.73 (4 H, br s, 1-, 2-, 3-, and 4-H); δ_C($CDCl_3$) 48.1 (CH_2Ph), 63.2 (C-7b), 116.6 (C-5 and C-7), 125.9, 126.0, 128.9 (C-6), 130.1, 130.4, 134.2, 136.0 (C-1 and -4), 157.6 (C-4a and -7a), and 176.5 (C-2a); *m/z* 230 (M^+, base), 229, 214, and 129.

2a-*Benzyl*-2aH-*cyclopent*[cd]*indene* (**13**).—A solution of the annulene (**1d**) (13 mg) in toluene (5 ml) was heated under reflux for 30 min. The solvent was evaporated off and the residue was chromatographed to give the title compound (**13**) (10 mg, 78%) as a pale yellow oil, $\nu_{max.}$ 3 060, 3 030, 2 925, 2 855, 1 455, and 700 cm^{-1}; $\lambda_{max.}$(EtOH) 269 nm; δ (250 MHz; $CDCl_3$) 3.03 (2 H, s), 6.59 (2 H, d, *J* 5.0 Hz), 6.75 (2 H, d, *J* 5.0 Hz), and 6.97—7.29 (8 H, m).

Nitration of the Annulene (**1d**).—A solution of the annulene (**1d**) (11 mg, 48 μmol) in acetic anhydride (3 ml) at 0 °C was treated with freshly powdered copper(II) nitrate trihydrate (23 mg, 95 μmol). The mixture was stirred for 2 h, poured into water (5 ml), and the products were extracted with ether (3 × 5 ml). The combined extracts were washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated, and the residue was chromatographed to give a 1:1 mixture of 7b-benzyl-5-nitro-7b*H*-cyclopent[*cd*]indene and 7b-benzyl-6-nitro-7b*H*-cyclopent[*cd*]indene (5 mg, 37%) as an orange oil, $\lambda_{max.}$(EtOH) 277 (log ε 4.24), 320 (4.16), 3.85 (3.80), and 490sh nm (3.06); for the 5-nitro compound, δ (250 MHz; $CDCl_3$) 0.13 (2 H, ABq), 6.26—6.33 (2 H, m), 6.97—7.10 (3 H, m), 7.74 (1 H, d, *J* 8.1 Hz, 7-H), 7.83 (1 H, d, *J* 3.4 Hz, 1-H), 8.0 (1 H, d, *J* 3.4 Hz, 2-H), 8.06 (1 H, d, *J* 3.4 Hz, 3-H), 8.38 (1 H, *J*, 3.4 Hz, 4-H), and 8.49 (1 H, d, *J* 8.1 Hz, 6-H); for the 6-nitro isomer, δ (250 MHz; $CDCl_3$) 0.11 (2 H, s), 6.26—6.33 (2 H, m), 6.97—7.10 (3 H, m), 7.86 (2 H, d, *J* 3.4 Hz, 2- and 3-H), 8.13 (2 H, d, *J* 3.4 Hz, 1- and 4-H), and 8.65 (2 H, s, 5- and 7-H); for the mixture, *m/z* 275 (M^+), 258, 219, and 91 (base).

Acetylation of the Annulene (**1d**).—A solution of the annulene (**1d**) (13.8 mg, 60 μmol) in dry dichloromethane (3 ml) was treated with acetic anhydride (0.25 ml) and boron trifluoride–diethyl ether (0.1 ml). After 3 h at room temperature the mixture was poured into water (5 ml), and the products were extracted with dichloromethane (3 × 5 ml). The combined extracts were dried ($MgSO_4$), and evaporated, and the residue was chromatographed to give an 11:1 mixture of 5-acetyl-7b-benzyl-7b*H*-cyclopent[*cd*]indene and 6-acetyl-7b-benzyl-7b*H*-cyclopent[*cd*]indene (10.3 mg, 63%) as an orange oil, $\nu_{max.}$ 1 678 cm^{-1}; $\lambda_{max.}$(EtOH) 309, 354sh, 448sh, and 480 nm; *m/z* 272 (M^+), 257, 219, 138, and 91 (base); for the 5-acetyl isomer, δ (250 MHz; $CDCl_3$) −0.04 (2 H, s), 2.86 (3 H, s), 6.24—6.30 (2 H, m), 6.93—7.08 (3 H, m), 7.72 (1 H, d, *J* 7.6 Hz, 7-H), 7.78 (1 H, d, *J* 3.1 Hz, 1-H), 7.92 (1 H, d, *J* 3.1 Hz, 2-H), 7.94 (1 H, d, *J* 3.1 Hz, 3-H), 8.18 (1 H, d, *J* 3.1 Hz, 4-H), and 8.26 (1 H, d, *J* 7.6 Hz, 6-H); for the 6-acetyl isomer, δ (250 MHz; $CDCl_3$) 0.00 (2 H, s), 2.83 (3 H, s), 6.24 (2 H, m), 6.93—7.08 (3 H, m) 7.77 (2 H, d, *J* 3.1 Hz, 2- and 3-H), 8.00 (2 H, d, *J* 3.1 Hz, 1- and 4-H), and 8.33 (2 H, s, 5- and 7-H).

Formylation of the Annulene (**1d**).—A solution of the benzyl annulene (**1d**) (12 mg, 52 μmol) in dry dichloromethane (10 ml) was treated with dichloromethyl n-butyl ether[11] (0.1 ml) and

was cooled to −78 °C under nitrogen. Tin(IV) chloride (0.05 ml) was then added and the reaction mixture turned deep red. After 45 min at −78 °C the mixture was quenched with water, and the products were extracted with dichloromethane (3 × 5 ml). The combined extracts were dried ($MgSO_4$) and evaporated, and the residue was chromatographed to give a 24:1 mixture of 7b-benzyl-7b*H*-cyclopent[*cd*]indene-5-carbaldehyde and 7b-benzyl-7b*H*-cyclopent[*cd*]indene-6-carbaldehyde (4.2 mg, 31%) as a bright yellow oil, $\nu_{max.}$ 1 680 cm^{-1}; $\lambda_{max.}$(EtOH) 314, 352, 450sh, and 483 nm; *m/z* 258 (M^+), 219, and 91 (base); for the 5-aldehyde, δ (250 MHz; $CDCl_3$) 0.01 (2 H, br s), 6.24—6.30 (2 H, m), 6.93—7.03 (3 H, m), 7.78 (1 H, d, *J* 7.5 Hz, 7-H), 7.79 (1 H, d, *J* 3.1 Hz, 1-H), 7.93 (1 H, d, *J* 3.1 Hz, 2-H), 7.99 (1 H, d, *J* 3.1 Hz, 3-H), 8.10 (1 H, d, *J* 7.5 Hz, 6-H), 8.27 (1 H, d, *J* 3.1 Hz, 4-H), and 10.43 (1 H, s); for the 6-aldehyde, δ (250 MHz; $CDCl_3$) (*inter alia*) 8.03 (2 H, d, *J* 3.1 Hz, 1- and 4-H) and 8.23 (2 H, s, 5- and 7-H), the remaining signals being obscured.

Treatment of the Annulene (**1d**) *with* 4-*Phenyl*-1,2,4-*triazole*-3,5-*dione* (PTAD).—A mixture of the annulene (**1d**) (14.4 mg, 63 μmol) and PTAD (20.4 mg, 115 μmol) in dry 1,2-dimethoxyethane (10 ml) was heated under reflux for 3.5 h. The solvent was evaporated off and the residue was chromatographed to give 2a-*benzyl*-2-(3,5-*dioxo*-4-*phenyl*-1,2,4-*triazolidin*-1-*yl*)-2a*H*-*cyclopent*[cd]*indene* (**18**) (10.2 mg, 40%) as an oily solid (Found: M^+, 405.1476. $C_{26}H_{19}N_3O_2$ requires *M*, 405.1477); $\nu_{max.}$ 1 770 and 1 730 cm^{-1}; $\lambda_{max.}$(EtOH) 266sh nm; δ (250 MHz; $CDCl_3$) 2.77 (1 H, d, *J* 14.0 Hz), 3.09 (1 H, d, *J* 14.0 Hz), 5.41 (1 H, s, 1-H), 6.75 (1 H, d, *J* 5.3 Hz, 3-H), 6.88 (1 H, d, *J* 5.3 Hz, 4-H), 6.90 (2 H, m), 7.06—7.12 (2 H, m), and 7.20—7.41 (9 H, m), NH not observed; *m/z* 405 (M^+), 315, and 287.

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Received 3*rd September* 1984; *Paper* 4/1514