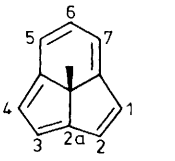
Tricyclic [10]Annulenes. Part 2.[1] Synthesis of 7b-Methyl-7b*H*-cyclopent[*cd*]indene

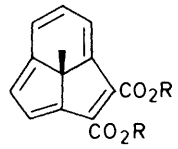
Raymond McCague, Christopher J. Moody, and Charles W. Rees
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY

Four routes have been developed to the tricyclic [10]annulene, 7b-methyl-7b*H*-cyclopent[*cd*]indene (1), starting from the diester (2a), the tricyclic nitrile (6), or the tricyclic ketone (9). The best overall procedure involves the ketones (9a) and (15). The 2-substituted annulene nitrile (7), aldehyde (8), acid (17), amide (18), and ester (19) have also been prepared. The spectral properties of these and of (1) are consistent with a 10π-electron aromatic structure. When heated (1) rearranges to the 2a*H*-isomer (23).

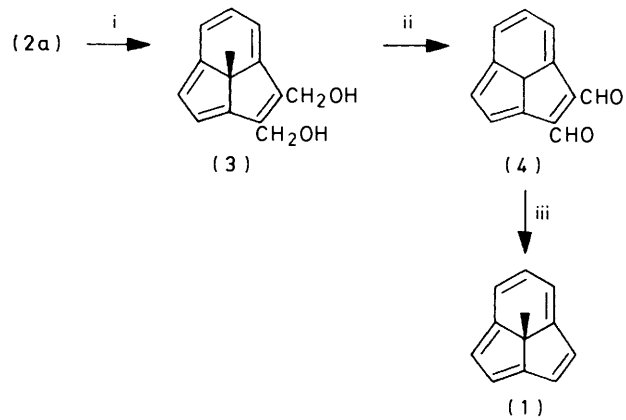
We have recently reported the preparation of the first derivatives of a new 10π-electron aromatic system, 7b-methyl-7b*H*-cyclopent[*cd*]indene (1).[1] The physical properties of the diester (2a) and the diacid (2b) support their formulation as delocalised [10]annulenes. In particular, the central methyl group of (2a) appears upfield of tetramethylsilane (TMS) in the ^{1}H n.m.r. spectrum at δ −1.34, consistent with the existence of a diamagnetic ring current. An *X*-ray crystal analysis of the diacid (2b) supports its aromatic structure.[2] In order to investigate the properties of this new aromatic system more fully, we required a route to the parent hydrocarbon (1). We now report details of the preparation and physical properties of this new hydrocarbon.



(1)



(2) a; R = Me
b; R = H



Scheme 1. *Reagents:* i, $LiAlH_4$, ether, room temp.; ii, $Ba[MnO_4]$, CH_2Cl_2, reflux; iii, $[Rh(PPh_3)_3]Cl$, C_6H_6, reflux

Preparation of 7b-*Methyl*-7bH-*cyclopent*[cd]*indene* (1)

From the Diester (2a).[3]—Preliminary experiments showed that although (1) could not be prepared by bis-decarboxylation of the diacid (2b), it could be obtained by bis-decarbonylation of the corresponding dialdehyde (4).[1] However, (1) was obtained in low yield and in an impure state. We have subsequently made improvements to this reaction sequence (Scheme 1).

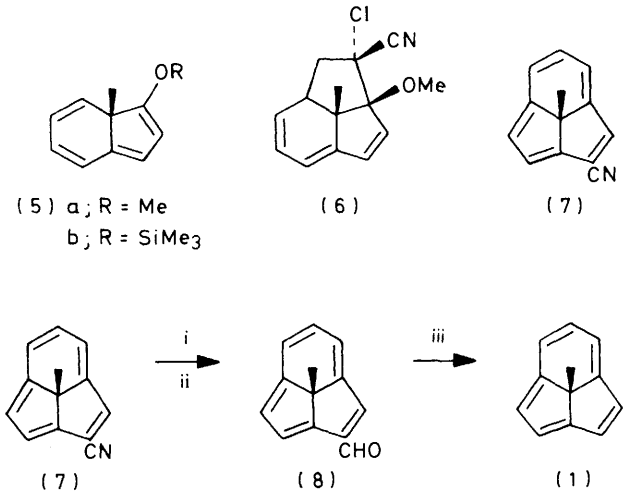
The diester (2a) was reduced with lithium aluminium hydride to give the diol (3). The diol (3) proved to be rather sensitive and was therefore oxidised immediately to the dialdehyde (4) [66% from (2a)] using barium manganate in refluxing dichloromethane, a reagent which is particularly effective for the oxidation of benzyl alcohols.[4] When the oxidation was carried out at room temperature or below, it was incomplete, and a mixture of the two possible mono-alcohol mono-aldehydes was obtained. The dialdehyde (4) is a stable orange-red crystalline solid, and its central methyl group resonates at δ −1.12 in the ^{1}H n.m.r. spectrum.

The dialdehyde was decarbonylated by treatment with two equivalents of tris(triphenylphosphine)rhodium(I) chloride in refluxing benzene [5] to give the parent hydrocarbon (1) (88%). It was found that the by-product, triphenylphosphine, was most conveniently separated from the hydrocarbon by quaternisation with iodomethane. Use of one equivalent of tris(triphenylphosphine)rhodium(I) chloride gave an inseparable mixture of monoaldehydes.

Although the annulene (1) can be prepared in good yield by the above route, a serious drawback is the expense of the rhodium reagent, of which two equivalents are necessary. Unfortunately, other reagents which are reported to effect decarbonylation catalytically were not suitable. Thus, bis(1,2-bisdiphenylphosphinoethane)rhodium(I) chloride,[6] bis(1,3-bisdiphenylphosphinopropane)rhodium(I) chloride,[6] and bis(triphenylphosphine)tetraphenylporphyrinatoruthenium(II) all decomposed during the attempted decarbonylation, and very little of the dialdehyde was consumed.

From the Cycloadduct (6).—The key step in the formation of the tricyclic ring structure of the annulene (2a) is the cycloaddition of dimethyl acetylenedicarboxylate to the 3a*H*-indene (5a). We have also investigated the cycloaddition of other 2π-components to (5a) and to the trimethylsilyl derivative (5b),[8] and we find that the resulting cycloadducts are also useful precursors to [10]annulenes.

Reaction of the 3a*H*-indene (5a) with 2-chloroacrylonitrile gave the crystalline adduct (6) as the major product.[8] Treatment of the adduct (6) with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) at 110 °C resulted in concomitant elimination of HCl and methanol to give the 2-cyanoannulene (7) (74%). The nitrile (7) is a yellow oil, and the central methyl group resonates upfield of TMS at δ −1.56. Conversion of (7) into the parent annulene (1) was readily achieved by reduction to the aldehyde (8) (66%) with di-isobutylaluminium hydride (DIBAL), followed by decarbonylation with tris(triphenyl-



Scheme 2. *Reagents:* i, DIBAL, light petroleum, 20 °C; ii, MeOH; iii, $[Rh(PPh_3)_3]Cl$, C_6H_6, reflux

phosphine)rhodium(I) chloride (92%) (Scheme 2). This route to (1) has advantages over the previous one in that only half as much of the rhodium reagent is required and the intermediate nitrile (7) gives access to other mono-substituted annulenes (q.v.). The overall yields of the two routes are comparable.

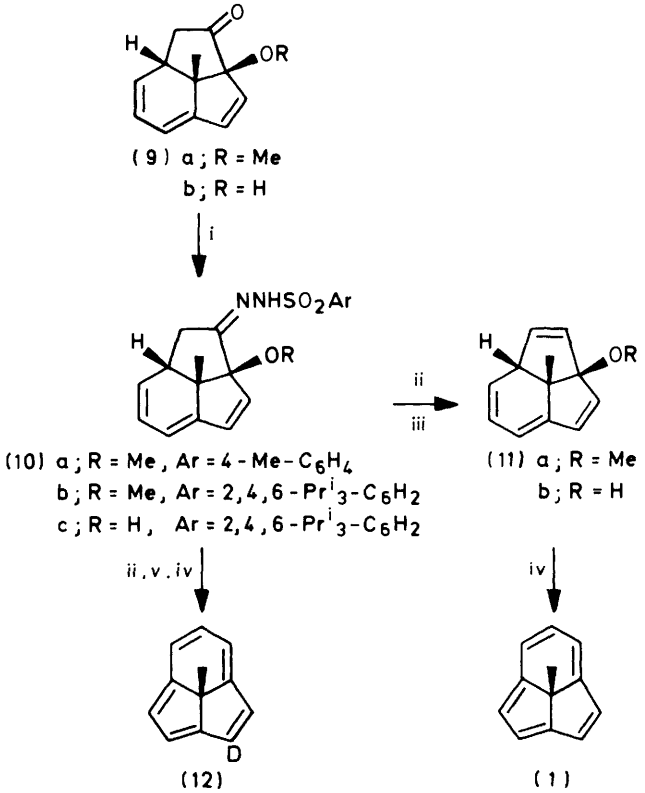
From the Tricyclic Ketones (9) via *the Shapiro Reaction.*[9]—Cycloaddition of the 3a*H*-indenes (5a) and (5b) to the ketene equivalent 2-chloroacryloyl chloride gave, after treatment of the initial adducts with sodium azide under the standard conditions,[10] the tricyclic ketones (9a) and (9b) respectively.[8] The conversion of these ketones into the unsubstituted annulene (1) is readily achieved by cleavage of the arenesulphonylhydrazone derivatives (10) with strong base (the Shapiro reaction) followed by elimination of methanol or water from the tetraene (11) (Scheme 3).

The hydrazone (10a) was prepared by heating the ketone (9a) with toluene-*p*-sulphonohydrazide in refluxing benzene with azeotropic removal of water. The product was isolated by chromatography and could be separated into two (*syn*/*anti*) isomers in a combined yield of 91%. The best conditions found for the cleavage of the tosylhydrazone (10a) was the use of a large excess of methyl-lithium in benzene. Elimination of methanol from (11a) to give the annulene (1) occurred to some extent in the strongly basic medium. By heating to 45 °C this conversion could be taken to completion.

Unfortunately the annulene prepared in this way was contaminated by olefinic material which could only be removed by chromatography on silica gel impregnated with silver acetate. Alternatively, the tetraene (11a), which showed no tendency for spontaneous elimination of methanol, could be converted into (1) by treatment with a catalytic amount of toluene-*p*-sulphonic acid (PTSA) in dichloromethane at room temperature.

Since the yield of (1) from the cleavage of hydrazone (10a) was only moderate, an improvement was sought. It is reported that 2,4,6-tri-isopropylbenzenesulphonyl (trisyl) hydrazones undergo fragmentation under milder conditions than the corresponding tosylhydrazones.[11,12] Therefore the trisylhydrazone (10b) was prepared by treatment of the ketone (9a) with trisylhydrazide in dichloromethane containing Amberlite IR120(H) resin at room temperature.[13] Reaction of (10b) with an excess of methyl-lithium in benzene gave improved yields of the annulene (1).

Similarly the trisylhydrazone (10c) prepared from ketone



Scheme 3. *Reagents:* i, $ArSO_2NHNH_2$; ii, MeLi, C_6H_6, RT; iii, H_2O quench; iv, cat. TsOH, CH_2Cl_2, RT; v, D_2O quench

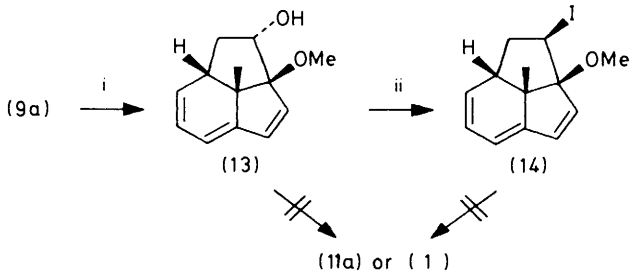
(9b) underwent fragmentation on treatment with methyl-lithium. However, the reaction was slow, and the tetraene (11b) was formed in only 35% yield. The annulene (1) was formed from (11b) on treatment with PTSA, but the overall yield from (9b) was not satisfactory.

The product of the Shapiro reaction before aqueous work-up is a vinyl-lithium species. Therefore when the hydrazone (10b) was treated with methyl-lithium at room temperature, followed by quenching with deuterium oxide and treatment with PTSA in dichloromethane, the product was the specifically 2-deuteriated annulene (12). The extent of deuterium incorporation was 65—70%, and there was no evidence for any deuterium scrambling.

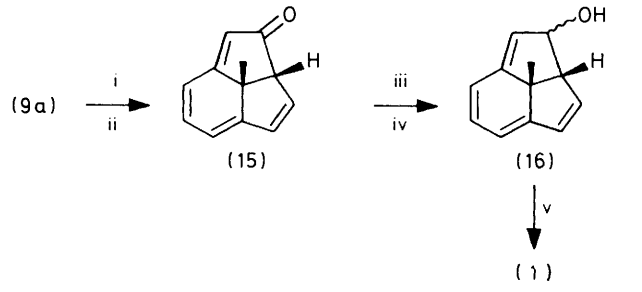
The successful application of the Shapiro reaction became all the more important when attempts to prepare the annulene by reduction of (9a) followed by dehydration and elimination of methanol failed (Scheme 4). The alcohol (13), prepared from (9a) by stereospecific reduction with sodium borohydride, could not be dehydrated by treatment with PTSA, thionyl chloride, or phosphorus oxychloride. Although the alcohol (13) could be converted into the iodide (14) by treatment with methyl(triphenoxy)phosphonium iodide in hexamethyl phosphoramide (HMPA)[14] all attempts to effect dehydroiodination with base failed.

From the Tricyclic Ketone (9a) via *the Tetraenone* (15); *the Best Overall Route.*—The conversion of the ketone (9a) into the tetraenone (15) has already been described.[15] Although the primary interest in (15) is the question of phenol-keto tautomerism in [10]annulenes,* the conversion of (15) into the

* A discussion of the properties of the tetraenone (15) and of phenol-keto tautomerism in general in [10]annulenes is not included here. This work will be published separately.



Scheme 4. *Reagents:* i, $NaBH_4$, EtOH; ii, $[PMe(OPh_3)]^+I^-$, HMPA

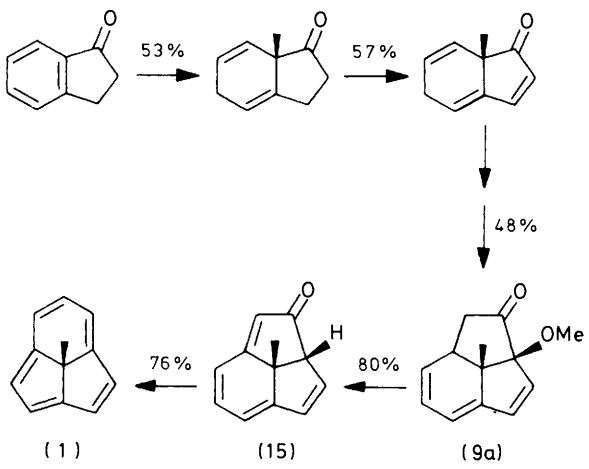


Scheme 5. *Reagents:* i, Me_3SiCl, NaI, Et_3N, MeCN, 80 °C; ii, H_2O, 0 °C; iii, DIBAL, hexane, 0 °C; iv, MeOH quench; v, TsOH, CH_2Cl_2, room temp.

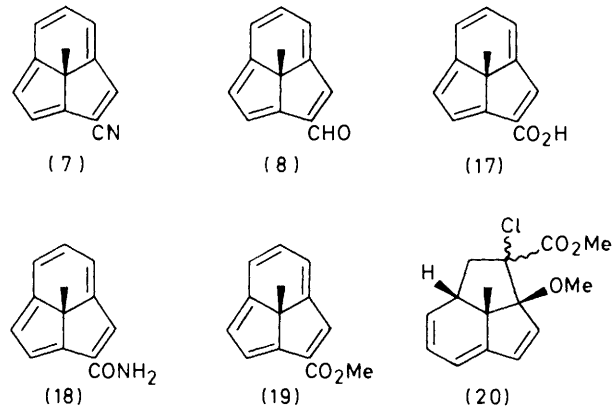
annulene (1) *via* the alcohol (16) provides the best overall route to (1) from (9a) (Scheme 5).

The tricyclic ketone (9a) was treated with an excess of chlorotrimethylsilane and sodium iodide in refluxing acetonitrile in the presence of triethylamine,[16] followed by addition of water at 0 °C to give the tetraenone (15) (80%) as previously described.[15] Reduction of (15) with DIBAL in hexane gave a mixture of epimeric alcohols (16), which were separable by chromatography. The less polar isomer, a pale yellow crystalline solid, is very unstable and rapidly polymerises with time to an insoluble solid. The more polar isomer is a pale yellow oil. Although neither isomer showed any tendency for spontaneous dehydration, both gave the annulene (1) on treatment with PTSA in dichloromethane. A consequence of the instability of the less polar epimer (16) is that the best yield of the annulene (1) [76% from (15)] was obtained when no attempt was made to isolate the alcohols (16). This procedure represents the most convenient route to (1). A 2 g sample was prepared in this way, and after chromatography and short-path distillation at 95 °C/3 mmHg the annulene (1) was analytically pure. The best overall route to the annulene (1) from indan-1-one (9% overall) *via* the key tricyclic ketone (9a) is summarised in Scheme 6.

Preparation of 2-*Substituted* [10]*Annulenes from the Cycloadducts* (6) *and* (20).—The conversion of the cycloadduct (6) of the 3a*H*-indene (5a) and 2-chloroacrylonitrile [8] into the 2-cyanoannulene (7) and hence the annulene-2-carbaldehyde (8) has already been discussed. Treatment of (6) with sodium hydroxide in ethanol and dimethyl sulphoxide under reflux gave the acid (17) in poor yield. However, the acid (17) could be prepared in higher yield by simple alkaline hydrolysis of the nitrile (7). Treatment of (6) with potassium t-butoxide in refluxing benzene gave the annulene-2-carboxamide (18) (20%). The formation of the amide was unexpected and it is likely that the hydrolysis of the nitrile was caused by the presence of potassium hydroxide in the potassium t-butoxide which was not freshly sublimed.



Scheme 6.



The methyl annulene-2-carboxylate (19) was conveniently prepared, albeit in poor yield, by treatment of the ester (20) with DBU. The ester (20) was obtained by cycloaddition of (5a) to 2-chloroacryloyl chloride followed by addition of methanol.[8]

Hence in addition to the parent unsubstituted annulene, a number of 2-substituted derivatives are available by cycloaddition reactions.

Physical Properties of 7b-*Methyl*-7bH-*cyclopent*[cd]*indene* (1).—The [10]annulene (1) is a free flowing bright yellow oil which has a green fluorescence in daylight. It is volatile and can be readily distilled under reduced pressure. On cooling in ice it solidifies to a pale yellow waxy solid, and an analytically pure sample melts at 12—13 °C. On exposure to air at room temperature, the annulene slowly becomes more viscous as a result of oxidative polymerisation. Consequently the annulene is best stored in solution at low temperature or under nitrogen below its freezing point.

U.v. spectrum. The electronic spectrum of (1) (Figure 1) shows a long wavelength absorption at 450 nm (log ε 2.64). Compared to the unsubstituted annulene, the diester (2a) shows a bathochromic shift of 21 nm owing to the effect of the substituents. The dialdehyde (4) and the 2-substituted annulenes (7), (8), and (17)—(19) all show similar shifts, and for comparison the long wavelength absorptions are given in Table 1.

It is interesting to note that the electronic spectrum of (1) bears a greater resemblance to that of 1,5-methano[10]annulene (21) [17,18] than that of 1,6-methano[10]annulene (22).[19,20]

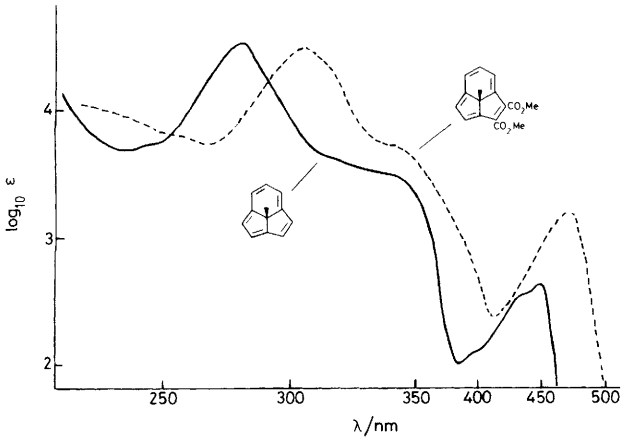
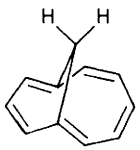
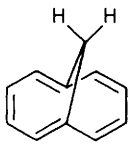


Figure 1. Electronic spectra of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) and dimethyl 7b-methyl-7b*H*-cyclopent[*cd*]indene-1,2-dicarboxylate (2a) in ethanol.



(21)



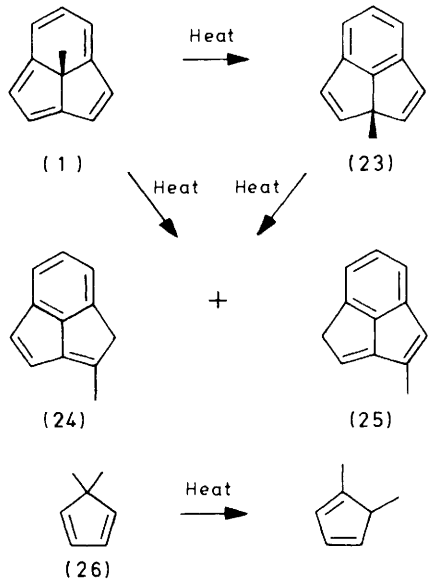
(22)

This is probably because of the significant transannular homoaromatic interaction in (22). This interaction is present to a lesser extent in (21), and is probably insignificant in (1) since the distance between the relevant carbon atoms (4a and 7a) has been calculated to be 2.55 Å,[21] much larger than the transannular distance of 2.26 Å encountered in (22).[22] Thus (1) may be the first ' genuine ' [10]annulene without this possibility for significant transannular interactions.

Photo-electron spectrum. * The photo-electron spectrum of (1) shows bands at 7.55, 8.05, and 10.00 eV which have been assigned to ionizations from the highest occupied π-orbitals of (1).[23] The photo-electron spectra for annulenes (21) and (22) have also been measured. The gross features show that the spectrum of (21) (7.63, 8.28, 9.56, and 10.17 eV) is similar to that of azulene,[24] whereas that of (22) (7.90, 8.38, 9.24, and 10.36 eV) is similar to naphthalene.[25]

N.m.r. spectra. The proton n.m.r. spectrum of (1) (Figure 2) shows a methyl singlet at δ −1.67 illustrating the presence of a diamagnetic ring current, and the aromatic protons in the range δ 7.4—8.2. The spectrum supports the symmetrical nature of the compound. The effect of a diamagnetic ring current is also seen in the n.m.r. spectra of the [10]annulenes (21) and (22). Thus the bridgehead protons in (21) resonate at δ −0.50 and −0.95.[17] and those in (22) at δ −0.50.[26] It is interesting that the upfield shift is greater in (1) than in either (21) or (22) despite the fact that the protons in question are one carbon atom further removed from the π-system. In all the substituted annulenes (2a), (4), (7), (8), and (17)—(19) the central methyl group resonates at lower field than in the parent annulene (1). These data are summarised in Table 1.

The carbon-13 spectrum of the annulene (1) (Figure 3) shows eight lines as expected for the symmetrical structure. The complete assignment was made with the aid of the deuteriated annulene (12). In the spectrum of (12) the lines due to C-1 and C-2a split into two, and the line due to C-1 (and C-3) is reduced in intensity; this is because C-2 when attached to a deuterium has none of the nuclear Overhauser enhancement that would occur if a proton were attached, and hence behaves as a quaternary carbon. The chemical shifts of the central carbon and the methyl group show little effect of the presence of a ring current because of the large chemical-shift range in carbon-13 spectra which dwarfs a shift of a few p.p.m. that the ring current might bring about. The unusual shift of C-2a (δ 178.7) probably reflects the strain at that position.



Thermal rearrangements. When heated in solution the annulene (1) rearranges to the 2a*H*-isomer (23). However, the rearrangement of (1) was achieved in best yield (78%) by flash-vacuum pyrolysis at 400 °C/0.3 mmHg. The 2a*H*-isomer (23) is an oil, and the ^{1}H n.m.r. spectrum confirms its symmetrical nature. When the flash-vacuum pyrolysis was carried out at high temperatures (700 °C) further rearrangement occurred to give a 2 : 1 mixture of the 1*H*-isomers (24) and (25). The structures were assigned by the similarity of their u.v. and n.m.r. spectra to those of the known unsubstituted compound, 1*H*-cyclopent[*cd*]indene.[27] The 1*H*-isomers are most probably formed from the 2a*H*-isomer (23) by a thermal [1,5] methyl shift followed by a series of rapid [1,5] hydrogen shifts. The results of these pyrolysis experiments imply that for the three cyclopent[*cd*]indenes, the order of stability is 1H > 2aH > 7bH.

The rearrangement of (1) to (23) in solution was most conveniently followed by observing the decrease in absorbance of the long wavelength band in the u.v. spectrum of (1). By this method, the half-life for rearrangement was determined as 12 h in refluxing xylene (138 °C). The rearrangement followed first-order kinetics consistent with a concerted unimolecular [1,5]sigmatropic shift of the methyl group. The rate of methyl migration was unchanged when dimethyl sulphoxide was used as the solvent (at the same temperature), and therefore for aprotic solvents the rearrangement is apparently not subject to a solvent effect. Subsequent work [28] has shown that the use of a protic solvent causes a slight increase in rate.

Rate data for the rearrangement of (1) were determined using decalin as solvent at several temperatures in the range 138—190 °C. A plot of the logarithm of the rate constant *versus* the reciprocal of the absolute temperature was linear, and from the slope the activation energy for the rearrange-

* For a full discussion of the photoelectron spectrum of (1) see ref. 23.

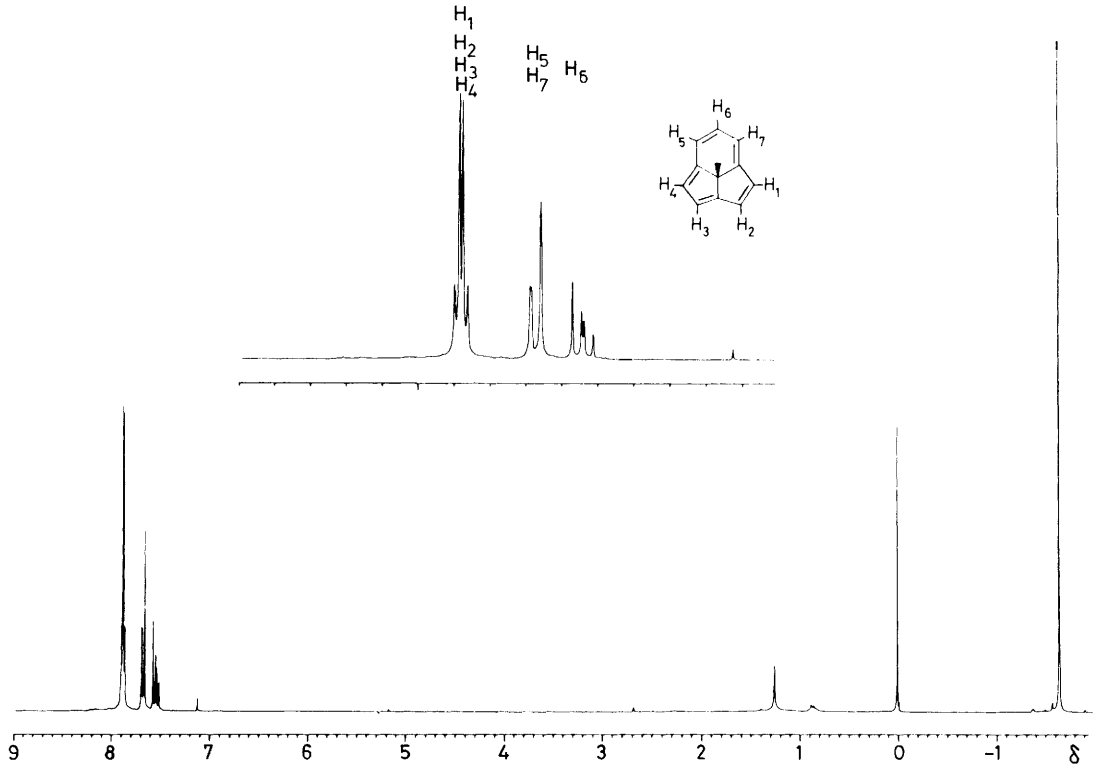


Figure 2. 250 MHz ^{1}H N.m.r. spectrum of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) in deuteriochloroform.

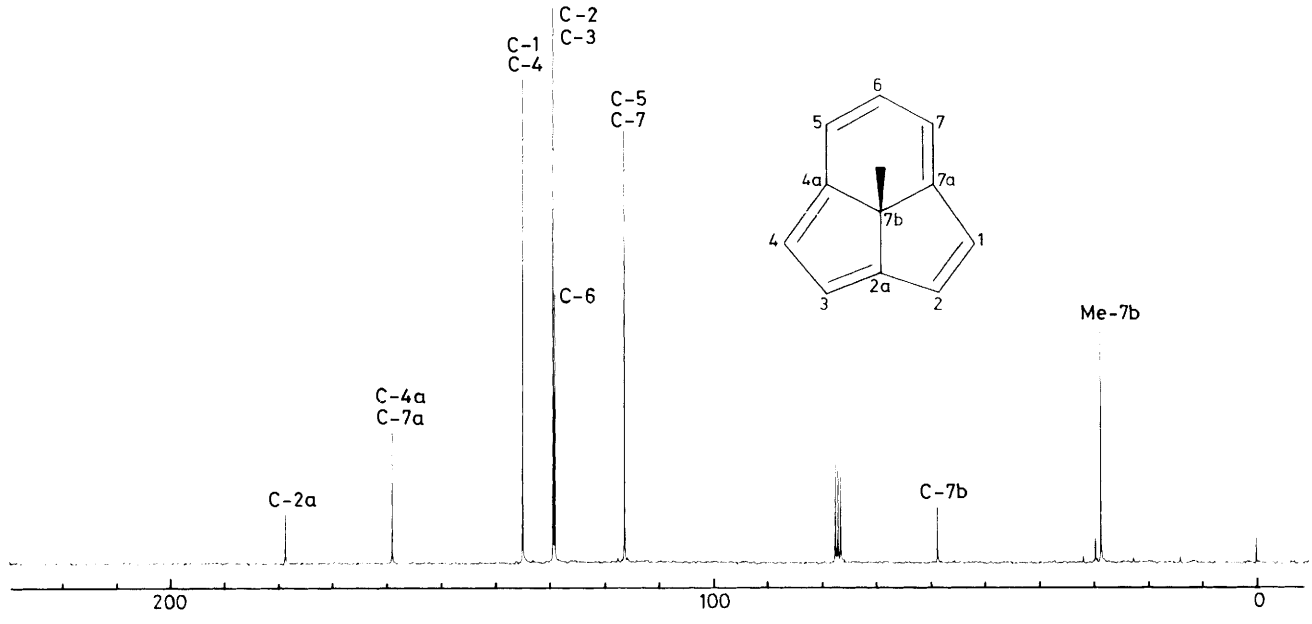


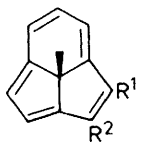
Figure 3. 62.9 MHz ^{13}C N.m.r. spectrum of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1) in deuteriochloroform

ment of (1) to (23) was found to be 32.7 (± 1) kcal mol^{-1}. For comparison, the [1,5] methyl shift in the cyclopentadiene (26) has an activation energy of 45 kcal mol^{-1}.[29] The greater ease of migration in the annulene (1) is presumably due to the extra driving force caused by the formation of a benzene ring, despite the fact that the starting material has some aromatic stabilisation.

The [10]annulenes (2a), (4), (7), (8), and (17)—(19) also rearrange when heated in solution. The half-lifes in boiling xylene, which are given in Table 1, were determined by the u.v. method described above. All reactions gave good first-order plots with the exception of the dialdehyde (4) which gave anomalous results due to rapid isomerisation to a new [10]-annulene, possibly a lactone, with a visible maximum of 474 nm in place of 498 nm. Introduction of any substituent into the 2-position increases the rate of rearrangement, the more electron-withdrawing substituents having the greater effect.

This effect of perturbation of the 10π-system by substituents is reflected by a reduction in the ring current of the annulene causing a downfield shift of the signal for the central methyl

Table. Selected u.v., ^{1}H n.m.r., and thermal rearrangement data for [10]annulenes



Compd.	R^1	R^2	$\lambda_{max.}$/nm (log ε)	δ(7b–Me)	$t_{\frac{1}{2}}$ (for rearrangement to 2a*H*-isomer at 138 °C) (h)
(1)	H	H	450 (2.64)	−1.67	12.0
(2a)	CO_2Me	CO_2Me	471 (3.25)	−1.34	3.4
(4)	CHO	CHO	498 (3.30)	−1.12	See text
(7)	H	CN	470 (3.15)	−1.56	2.0
(8)	H	CHO	488 (3.20)	−1.41	1.1
(17)	H	CO_2H	474 (3.17)	−1.40	2.0
(18)	H	$CONH_2$	471 (3.06)	−1.47	3.5
(19)	H	CO_2Me	475 (3.16)	−1.47	1.9

group in the ^{1}H n.m.r. spectrum, and a bathochromic shift of the long wavelength band in the electronic spectrum. These effects parallel the half-lives for rearrangement (Table 1), and the variation in rates may be explained in terms of the ground-state energy of the annulene. However, results obtained on some 5-substituted annulenes,[28] lead to the conclusion that the rate of rearrangement is increased when carbocation character is induced at the terminus of the migration (C-2a).

In contrast to its rearrangement on heating, the [10]annulene (1) is photostable. Thus, it was recovered unchanged after being irradiated in light petroleum at 300 nm for 15 h.

Conclusions.—A number of methods are now available for the synthesis of 7b-methyl-7b*H*-cyclopent[*cd*]indene (1), a new 10π-aromatic hydrocarbon. The physical properties of (1) are consistent with its aromatic structure. The chemical reactions of (1) will be described in the following paper.[28]

Experimental

For general points see ref. 8. ^{13}C N.m.r. spectra were recorded on a Bruker WM250 spectrometer operating at 62.9 MHz, and were fully proton decoupled.

7-*Methyl*-7bH-*cyclopent*[cd]*indene*-1,2-*dicarbaldehyde* (4).—A solution of dimethyl 7b-methyl-7b*H*-cyclopent[*cd*]indene-1,2-dicarboxylate (2a) [1] (3.42 g, 12.7 mmol) in dry ether (100 ml) was added dropwise to a stirred suspension of lithium aluminium hydride (1.85 g, 49 mmol) in dry ether (100 ml) at room temperature under nitrogen, and the resulting mixture stirred at room temperature for 1.5 h. After addition of ethyl acetate (30 ml) and ether (100 ml), the mixture was poured into ice–water (500 ml), and filtered through Celite. The organic layer was separated and the aqueous layer was extracted with ether (4 × 250 ml). The combined ether layers were dried ($MgSO_4$) and evaporated to give the crude diol (3) as a yellow oil (2.59 g). The oil was dissolved in dichloromethane (100 ml) and refluxed with barium manganate (15.0 g, 64 mmol) for 16 h. The cooled mixture was filtered through Celite, and the spent reagent washed with dichloromethane (2 × 25 ml). The combined filtrate and washings were concentrated, and the resulting oil chromatographed on silica gel using petroleum–ether (7 : 3) as eluant to give the *title compound* (4) (1.73 g, 66%) as an orange-red solid, m.p. 76—77 °C (from cyclohexane) (Found: C, 79.9; H, 4.75. $C_{14}H_{10}O_2$ requires C, 80.0; H, 4.8%); $\nu_{max.}$ 1 680 cm^{-1}; $\lambda_{max.}$ (EtOH) 217 (log ε 4.09), 242 (4.02), 318 (4.30), 3.75sh (3.66), and 498 nm (3.30); δ_H (250 MHz, $CDCl_3$) −1.12 (3 H, s, 7b-Me), 7.73 (1 H, d, *J* 7 Hz, 5-H), 7.84 (1 H, dd, *J* 7 Hz, 8 Hz, 6-H), 8.27 (1 H, d, *J* 4 Hz, 4-H), 8.34 (1 H, d, *J* 8 Hz, 7-H), 8.44 (1 H, d, *J* 4 Hz, 3-H), and 10.82 (2 H, s, 2 × C*H*O); δ_C ($CDCl_3$) 30.0 (7b-Me), 59.8 (C-7b), 118.7 (C-5), 122.5 (C-7), 133.9 (C-2), 135.4 (C-3 or C-6), 136.2 (C-6 or C-3), 140.1 (C-1), 142.8 (C-4), 162.4 (C-4a or C-7a), 163.1 (C-7a or C-4a), 176.9 (C-2a), 187.7 (CHO), and 189.1 (CHO) p.p.m.

7b-*Methyl*-7bH-*cyclopent*[cd]*indene* (1) *by Bisdecarbonylation of the Dialdehyde* (4).—A solution of the dialdehyde (4) (456 mg, 2.16 mmol) in benzene (55 ml) was refluxed with tris(triphenylphosphine)rhodium(I) chloride (4.00 g, 4.32) under nitrogen for 7 h. The reaction mixture was cooled to room temperature and treated with iodomethane (3 ml). After being stirred for 2 h at room temperature, the mixture was filtered, and the residue washed with benzene until the filtrate was colourless. The combined filtrate and washings were evaporated and the residue chromatographed on silica gel. Elution with petroleum gave the *annulene* (1) (295 mg, 88%) as a yellow oil; spectral data are given later.

7b-*Methyl*-7bH-*cyclopent*[cd]*indene*-2-*carbonitrile* (7).—A stirred mixture of the adduct (6) [8] (1.06 g, 4.3 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (1.0 g, 6.6 mmol) was heated at 110 °C for 6 h under nitrogen. The resulting black viscous mixture was chromatographed on silica gel. Elution with petroleum–ether (4 : 1) gave the *title compound* (7) (0.57 g, 74%) as a mobile yellow oil (Found: *m/z* 179.0736. $C_{13}H_9N$ requires 179.0735); $\nu_{max.}$ (neat) 2 224 cm^{-1}; $\lambda_{max.}$ (EtOH) 251 (log ε 3.87), 2.97 (4.66), 329 (3.84), and 470 nm (3.15); δ_H (250 MHz, $CDCl_3$) −1.56 (3 H, s, 7b-Me), 7.60 (1 H, t, *J* 7 Hz, (6-H), 7.70 (1 H, d, *J* 7 Hz, 5-H), 7.82 (1 H, d, *J* 7.4 Hz, 7-H), 7.90 (1 H, s, 1-H), 7.97 (1 H, d, *J* 3.5 Hz, 4-H), and 8.03 (1 H, d, *J* 3.5 Hz, 3-H); δ_C ($CDCl_3$) 28.6 (7b-Me), 59.6 (7b-C), 107.7 (CN or C-2), 116.5 (C-2 or CN), 118.5 (C-5), 121.0 (C-7), 130.5 (C-3 or C-6), 130.8 (C-6 or C-3), 136.4 (C-4), 139.6 (C-1), 157.3 (C-4a or C-7a), 159.5 (C-7a or C-4a), and 179.4 p.p.m. (C-2a); *m/z* 179 (M^+, base) 178, 164, 152, and 151.

7b-*Methyl*-7bH-*cyclopent*[cd]*indene*-2-*carbaldehyde* (8).—A solution of di-isobutylaluminium hydride in hexane (1M; 3 ml, 3 mmol) was added to a stirred ice-cooled solution of the nitrile (7) (228 mg, 1.3 mmol) in petroleum (10 ml) under nitrogen. After 15 min, methanol (0.5 ml) was added, followed by a solution of ammonium chloride (0.3 g) in water (2 ml), and the resulting mixture was stirred at room temperature for 2 h. The mixture was poured into water (20 ml) and extracted with ether (3 × 25 ml). The combined extracts were dried ($MgSO_4$), evaporated, and the residue chromatographed on silica gel. Elution with petroleum–ether (4 : 1) gave the *title compound* (9) (154 mg, 66%) as an orange oil, $\nu_{max.}$ (neat) 1 666 cm^{-1}; $\lambda_{max.}$ (EtOH) 257 (log ε 4.07), 312 (4.51), 350 (3.85), and 488 nm (3.20); δ_H (250 MHz, $CDCl_3$) −1.41 (3 H, s, 7b-Me), 7.57 (1 H, t, *J* 7 Hz, 6-H), 7.71 (1 H, d, *J* 7.1 Hz, 5-H), 7.90 (1 H, d, *J* 7.5 Hz, 7-H), 8.11 (1 H, d, *J* 3.6 Hz, 4-H), 8.16 (1 H, d, *J* 3.6 Hz, 3-H), 8.21 (1 H, s, 1-H), and 10.38 (1 H, s, C*H*O); δ_C ($CDCl_3$) 28.7 (7b-Me), 60.5 (7b-C), 118.7

(C-5), 122.5 (C-7), 130.2 (C-3 or C-6), 130.7 (C-6 or C-3), 134.5 (C-4), 137.3 (C-2), 140.7 (C-1), 157.7 (C-4a or C-7a), 159.2 (C-7a or C-4a), 179.4 (C-2a), and 188.3 p.p.m. (CHO). The aldehyde (8) gave a 2,4-*dinitrophenylhydrazone*, as brick-red needles, m.p. 220—222 °C (decomp.) (from dimethylformamide–acetonitrile) (Found: C, 62.65; H, 3.9; N, 15.25. $C_{19}H_{14}N_4O_4$ requires C, 63.0; H, 3.9; N, 15.45%).

7b-*Methyl*-7bH-*cyclopent*[cd]*indene* (1) *by Decarbonylation of the Aldehyde* (8).—A solution of the aldehyde (8) (163 mg, 0.89 mmol) in benzene (20 ml) was refluxed with tris(triphenylphosphine)rhodium(I) chloride (850 mg, 0.92 mmol) under nitrogen for 6.5 h. Work-up and chromatography as described earlier gave the *annulene* (1) (126 mg, 92%); spectral data given later.

2a-*Methoxy*-7b-*methyl*-1,2a,7a,7b-*tetrahydro*-2H-*cyclopent*-[cd]*inden*-2-*one* p-*Tolylsulphonylhydrazone* (10a).—A solution of the ketone (9a) [8] (1.24 g, 6.1 mmol) and toluene-*p*-sulphonohydrazide (1.21 g, 6.5 mmol) in benzene (15 ml) was refluxed under nitrogen for 3 h with azeotropic removal of water. The solvent was evaporated and the residue chromatographed on silica gel. Elution with petroleum–ether–dichloromethane (4 : 3 : 3) gave the *title hydrazone* (10a) (2.05 g, 91%) as a gum which solidified on trituration with ether.

In a separate experiment, the hydrazone was separated into two isomers by careful chromatography: *the minor isomer* had m.p. 157—160 °C (from petroleum–dichloromethane) (Found: C, 65.2; H, 6.0; N, 7.65; S, 8.5. $C_{20}H_{22}N_2O_3S$ requires C, 64.85; H, 6.0; N, 7.55; S, 8.65%); *the major isomer* had m.p. 172—175 °C (from petroleum–dichloromethane) (Found: C, 65.0; H, 6.1; N, 7.55; S, 8.65%).

Reaction of the p-*Tolylsulphonylhydrazone* (10a) *with Methyl-lithium.*—(a) *At room temperature.* A stirred solution of the hydrazone (10a) (195 mg, 0.53 mmol) in benzene (10 ml) was treated with an ethereal solution of methyl-lithium (2M; 5 ml, 10 mmol) under nitrogen. The mixture was stirred at room temperature for 20 h, and quenched by careful addition of water (1 ml). The resulting slurry was poured into water (30 ml) and extracted with ether (3 × 30 ml). The combined extracts were dried ($MgSO_4$), evaporated, and the residue chromatographed on silica gel. Elution with petroleum gave the impure annulene (1) (20 mg, 17%), which could only be purified by further chromatography on silica gel impregnated with silver acetate (10% w/w). Elution with petroleum–ether (19 : 1) gave, after a forerun of aromatic material (39 mg), 4a,7b-*dihydro*-2a-*methoxy*-7b-*methyl*-2aH-*cyclopent*[cd]*indene* (11a) (26 mg, 26%) as an oil (Found: *m/z* 186.1050. $C_{13}H_{14}O$ requires *m/z* 186.1045); $\lambda_{max.}$ (EtOH) 309 nm (log ε 3.66); δ_H (250 MHz, $CDCl_3$) 1.01 (3 H, s, 7b-Me), 3.31 (3 H, s, OMe), 3.32 (1 H, m, 4a-H), 5.77 (3 H, m, simplified by decoupling at δ 3.32, 3-H, 5-H, and 7-H), 6.02 (1 H, ddd, $J_{4a,6}$ 0.9 Hz, $J_{6,7}$ 5.2 Hz, $J_{5,6}$ 9.4 Hz, 6-H), 6.07 (1 H, dd, $J_{4,4a}$ 1.7 Hz, $J_{3,4}$ 5.6 Hz, 4-H), 6.24 (1 H, d, *J* 5.6 Hz, 1-H or 2-H), and 6.32 (1 H, d, *J* 5.6 Hz, 2-H or 1-H).

(b) *At* 45 °C. A stirred solution of the hydrazone (10a) (667 mg, 1.8 mmol) in benzene (40 ml) was treated with an ethereal solution of methyl-lithium (2M; 15 ml, 30 mmol) under nitrogen. The mixture was then heated at 45 °C for 10 h. Work-up as before, and chromatography on silica gel impregnated with silver acetate (10% w/w) gave the *annulene* (1) (110 mg, 40%); spectral data given later.

7b-*Methyl*-7bH-*cyclopent*[cd]*indene* (1) *from the Tetraene* (11a).—A solution of the tetraene (11a) (52 mg) in dichloromethane (12 ml) was stirred with toluene-*p*-sulphonic acid (5 mg) at room temperature for 3 h. The resulting solution was washed with saturated aqueous sodium hydrogen carbonate (3 × 10 ml) and water (10 ml), dried ($MgSO_4$), evaporated, and the residue chromatographed on silica gel. Elution with petroleum gave the annulene (1) (35 mg, 81%).

2a-*Methoxy*-7b-*methyl*-1,2a,7a,7b-*tetrahydro*-2H-*cyclopent*-[cd]*inden*-2-*one* 2,4,6-*Tri-isopropylphenylsulphonylhydrazone* (10b).—A solution of the ketone (9a) (4.05 g, 20 mmol) in dichloromethane (50 ml) containing Amberlite IR 120 (H) (5 g) was treated with a solution of 2,4,6-tri-isopropylbenzenesulphonylhydrazide (6.60 g, 22 mmol) in dichloromethane (50 ml). The mixture was stirred at room temperature for 3 h, filtered, and the filtrate evaporated; the residue was chromatographed on silica gel. Elution with petroleum–ether–dichloromethane (2 : 1 : 1) gave the *title hydrazone* (10b) (8.1 g, 83%), m.p. 174—177 °C (from petroleum–dichloromethane) (Found: C, 69.3; H, 7.95; N, 5.7. $C_{28}H_{38}N_2O_3S$ requires C, 69.65; H, 7.9; N, 5.8%).

Reaction of the 2,4,6-*Tri-isopropylphenylsulphonylhydrazone* (10b) *with Methyl-lithium followed by Quenching with Deuterium Oxide.*—(a) *At room temperature.* A stirred solution of the hydrazone (10b) (274 mg, 0.57 mmol) in benzene (10 ml) was treated with an ethereal solution of methyl-lithium (2M; 7.5 15 mmol) under nitrogen. The mixture was stirred at room temperature for 2 h, and then quenched by addition of deuterium oxide (99.7 atom %; 0.5 ml). After 5 min, the mixture was poured into water (30 ml) and extracted with ether (3 × 30 ml). The combined extracts were dried ($MgSO_4$), evaporated, and the residue chromatographed on silica gel. Elution with petroleum gave the annulene (1) (6 mg, 7%). Elution with petroleum–ether (19 : 1) gave 4a,7b-*dihydro*-2a-*methoxy*-7b-*methyl*-2aH-[$^2H_3$]*cyclopent*[cd]*indene* (*ca.* 65% deuterium incorporation) (67 mg, 63%); δ_H (250 MHz, $CDCl_3$) as for undeuteriated sample except δ 5.77 (2.35 H, m) and 6.07 (1 H, m, 4-H; decoupling of 4a-H at δ 3.03 gives a singlet and a doublet, *J* 5.6 Hz).

(b) *At* 45 °C. A stirred solution of the hydrazone (10b) (980 mg, 2.0 mmol) in benzene (50 ml) was treated with an ethereal solution of methyl-lithium (2M; 27 ml, 54 mmol) under nitrogen. The mixture was stirred at 45 °C for 7 h. Quenching and work-up as above gave the annulene (1) (193 mg, 61%), the extent of 2-deuterium incorporation was *ca.* 20%; and the tetraene (11a) (84 mg, 22%), the extent of deuterium incorporation was not determined.

7b-*Methyl*-7bH-[$^2H_2$]*cyclopent*[cd]*indene* (12) *from the Deuteriated Tetraene.*—A solution of the deuteriated tetraene (65% deuterium incorporated) in dichloromethane was treated with toluene-*p*-sulphonic acid as described for the undeuteriated material. Work-up and chromatography gave *the deuteriated annulene* (12) (65% deuterium incorporation), δ_H (250 MHz, $CDCl_3$) 1.64 (3 H, s, 7b-Me), 7.52—7.72 (3 H, AB_2 system, $J_{A,B}$ 7 Hz, δ_A 7.57, 6-H; δ_B 7.69, 5-H and 7-H), 7.90 (1.3 H, d, *J* 3 Hz and 2-H of undeuteriated material), and 7.92 (2 H, s + d, *J* 3 Hz, 1-H and 4-H); δ_C ($CDCl_3$) 28.7 (7b-Me), 58.8 (C-7b), 116.3 (C-5 and C-7) 129.0 (C-6), 129.3 (intensity reduced relative to undeuteriated sample C-2 and C-3), 134.87 (C-1 of deuteriated compound) 134.92 (C-4 and C-1 of undeuteriated compound), 159.2 (C-4a and C-7a), 178.8 (C-2a of deuteriated compound), and 178.9 p.p.m. (C-2a of undeuteriated compound).

2a-*Hydroxy*-7b-*methyl*-1,2a,7a,7b-*tetrahydro*-2H-*cyclopent*[cd]*inden*-2-*one* 2,4,6-*Tri-isopropylphenylsulphonylhydrazone* (10c).—A mixture of the ketone (9b) [8] (234 mg, 1.24 mmol), 2,4,6-tri-isopropylbenzenesulphonohydrazide (408 mg, 1.36 mmol), and Amberlite IR120 (H) (100 mg) in dichloro-

methane (6 ml) was stirred at room temperature for 2 h. The cloudy mixture was dried (Na_2SO_4), filtered, evaporated, and the residue chromatographed on silica gel. Elution with petroleum–ether–dichloromethane (2 : 1 : 1) gave the *title hydrazone* (10c) (mixture of isomers; 554 mg, 95%) as a foam.

Reaction of the 2,4,6-*Tri-isopropylphenylsulphonylhydrazone* (10c) *with Methyl-lithium*.—(a) A solution of the hydrazone (10c) (200 mg, 0.43 mmol) in benzene (8 ml) was treated with an ethereal solution of methyl-lithium (1.3 M; 2.0 ml, 2.6 mmol) under nitrogen at 0 °C, and then for 1 h at room temperature. The mixture was quenched with water (10 ml), and the products were extracted with ether (2 × 10 ml). The combined ether extracts were washed with water (10 ml), dried (Na_2SO_4), evaporated, and the residue chromatographed on silica gel. Elution with petroleum–ether (7 : 3) gave 4a,7b-*dihydro*-7b-*methyl*-2aH-*cyclopent*[cd]*inden*-2a-*ol* (11b) (26 mg, 35%), as an unstable solid, m.p. 88—90 °C (from cold petroleum) (Found: *m/z* 172.0884. $C_{12}H_{12}O$ requires 172.0888); $\nu_{max.}$ 3 610 and 3 500—3 000 cm^{-1}; $\lambda_{max.}$ (EtOH) 310 nm (log ε 3.65); δ_H (250 MHz, $CDCl_3$) 1.02 (3 H, s, 7b-Me), 1.86 (1 H, br s, OH), 3.34 (1 H, m, 4a-H), 5.7—5.85 (3 H, m, 3-H, 5-H, and 7-H), 5.96 (1 H, dd, $J_{4.4a}$ 1.8 Hz, $J_{4a.5}$ 5.8 Hz, 4a-H), 6.02 (1 H, dd, $J_{6.7}$ 5.2 Hz, $J_{5.6}$ 9.2 Hz, 6-H), 6.18 (1 H, d, *J* 5.5 Hz, 3-H or 4-H), and 6.34 (1 H, d, *J* 5.5 Hz, 4-H or 3-H); *m/z* 172 (M^+), 157 (base), 129, and 128. Further elution with petroleum–ether (2 : 1) gave an isomer of the starting hydrazone (71 mg, 36%). This isomer was recovered unchanged after further treatment with excess of methyl-lithium.

(b) A solution of the hydrazone (10c) (100 mg, 0.21 mmol) was treated with an ethereal solution of methyl-lithium (1.3 M; 3 ml, 3.9 mmol) as described above. After the aqueous work-up, the residue was dissolved in dichloromethane (2 ml) and stirred with toluene-*p*-sulphonic acid (15 mg) at room temperature for 3 h. The solution was washed with saturated aqueous sodium hydrogen carbonate (2 ml), dried, and evaporated. Chromatography of the residue on silica gel gave the annulene (1) (7.1 mg, 22%).

2a-*Methoxy*-7b-*methyl*-2,2a,7a,7b-*tetrahydro*-1H-*cyclopent*[cd]*inden*-2-*ol* (13).—A stirred emulsion of the ketone (9a) (622 mg, 3.1 mmol) in ethanol (10 ml) was treated with a solution of sodium borohydride (400 mg, 10.5 mmol) in ethanol (10 ml). After 0.5 h, the clear solution was poured into water (90 ml), and the product extracted with ether (3 × 60 ml). The combined extracts were washed with water (50 ml), dried ($MgSO_4$), evaporated, and the residue chromatographed on silica gel. Elution with petroleum–ether (3 : 2) gave *the title compound* (13) (383 mg, 61%), as a viscous oil (Found: *m/z* 204.1156. $C_{13}H_{16}O_2$ requires *m/z* 704.1150); $\nu_{max.}$ (neat) 3 420 cm^{-1}; $\lambda_{max.}$ (EtOH) 304 nm (log ε 3.89); δ_H (250 MHz, $CDCl_3$) 0.84 (3 H, s, 7b-Me), 1.05 (1 H, ddd, $J_{1\alpha.1\beta}$ 10.8 Hz, $J_{1\alpha.2}$ 9.4 Hz, $J_{1\alpha.7a}$ 10.8 Hz, 1-H_α), 1.52 (1 H, br s, OH), 2.22 (1 H, ddd, $J_{1\alpha.1\beta}$ 10.8 Hz, $J_{1\beta.2}$ 6.0 Hz, $J_{1\beta.7a}$ 6.1 Hz, 1-H_β), 2.35 (1 H, ddd, $J_{1\beta.7a}$ 6.1 Hz, $J_{1\alpha.7a}$ 10.8 Hz, $J_{7.7a}$ 6.1 Hz, 7a-H), 3.45 (3 H, s, OMe), 4.08 (1 H, br 2-H), 5.75 (1 H, d, $J_{5.6}$ 5.1 Hz, 5-H), 5.86 (1 H, dd, $J_{6.7}$ 9.2 Hz, $J_{7.7a}$ 6.1 Hz, 7-H), 6.03 (1 H, dd, $J_{5.6}$ 5.1 Hz, $J_{6.7}$ 9.2 Hz, 6-H), 6.39 (1 H, d, $J_{3.4}$ 5.7 Hz, 3-H), and 6.61 (1 H, d, $J_{3.4}$ 5.7 Hz, 4-H); *m/z* 204 (M^+), 160 (base), and 145.

2-*Iodo*-2a-*methoxy*-7a-*methyl*-2,2a,7a,7b-*tetrahydro*-1H-*cyclopent*[cd]*indene* (14).—A solution of the alcohol (13) (28.7 mg, 0.14 mmol) in dry hexamethylphosphoramide (0.5 ml) was treated with methyltriphenoxyphosphonium iodide (186 mg, 0.41 mmol), and the resulting mixture was stirred overnight at room temperature. Sodium hydroxide solution (10% w/v; 5 ml) was added, and the mixture stirred at room temperature for 1 h, and then extracted with ether (3 × 5 ml). The combined extracts were dried (Na_2SO_4), evaporated, and the residue chromatographed on silica gel. Elution with petroleum–ether (9 : 1) gave *the title compound* (14) (10.8 mg, 47%) as an oil (Found: *m/z* 314.0175. $C_{13}H_{15}IO$ requires *m/z* 314.0170); δ_H (90 MHz, $CDCl_3$) 0.99 (3 H, s, 7b-Me), 1.72 (1 H, ddd, $J_{1\alpha.1\beta}$ 14 Hz, $J_{1\alpha.2}$ 6 Hz, $J_{1\alpha.7a}$ 12 Hz, 1-H_α), 2.30 (1 H, ddd, $J_{1\alpha.1\beta}$ 14 Hz, $J_{1\beta.2}$ 2 Hz, $J_{1\beta.7a}$ 6 Hz, 1-H_β), 2.91 (1 H, dt, $J_{1\alpha.7a}$ 12 Hz, $J_{1\beta.7a} = J_{7.7a}$ 6 Hz, 7a-H), 4.40 (1 H, dd, $J_{1\alpha.2}$ 6 Hz, $J_{1\beta.2}$ 2 Hz, 2-H), 5.79 (1 H, ddd, $J_{5.6}$ 5 Hz, $J_{6.7}$ 9 Hz, 6-H), 6.28 (1 H, d, *J* 6 Hz, 3-H or 4-H), and 6.49 (1 H, d, *J* 6 Hz, 4-H or 3-H); *m/z* 314 (M^+), 160, and 145.

2a,7b-*Dihydro*-7b-*methyl*-2H-*cyclopent*[cd]*inden*-2-*one* (15).—Chlorotrimethylsilane (14.5 ml, 120 mmol) was added to a solution of sodium iodide (17 g, 120 mmol) in dry acetonitrile (160 ml) at room temperature under nitrogen. A mixture of the ketone (9a) (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 (150 ml), dried (Na_2SO_4), evaporated and the residue chromatographed on silica gel. Elution with petroleum–ether (7 : 3) gave the *title compound* (15) (3.1 g, 80%) as an orange-red oil; 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%); the full spectral data for the ketone (15) will be published separately.

2a,7b-*Dihydro*-7b-*methyl*-2H-*cyclopent*[cd]*inden*-2-*ol* (16).—A stirred solution of the ketone (15) (76 mg, 0.45 mmol) in petroleum (5 ml) was treated with a hexane solution of di-isobutylaluminium hydride (1M; 0.5 ml, 0.5 mmol) at 0 °C under nitrogen. After 20 min, methanol (0.5 ml) was added, followed by water (2 ml). After 1 h at room temperature, the mixture was filtered through Celite and the residue was washed with hot methanol (4 × 5 ml). The combined filtrate and washings were poured into water (50 ml), and the products extracted with ether (3 × 15 ml). The combined extracts were washed with water (30 ml), dried (Na_2SO_4), evaporated, and the residue chromatographed on silica gel. Elution with petroleum–ether (7 : 3) gave unchanged ketone (15) (4 mg). Elution with petroleum–ether (3 : 2) gave the less polar isomer of the title alcohol (25 mg, 32%), as an unstable pale yellow solid, m.p. 74—76 °C (from cold petroleum), δ_H (60 MHz, $CDCl_3$) 1.03 (3 H, s, 7b-Me), 1.20 (1 H, m,) 3.37 (1 H, d, *J* 10 Hz), 4.84 (1 H, m), 4.96 (1 H, m), 5.71 (1 H, m), and 6.1—6.4 (4 H, m). Elution with petroleum–ether (2 : 1) gave the more polar isomer of the title alcohol (36 mg, 47%) as a pale yellow oil; $\nu_{max.}$ (neat) 3 340 cm; $\lambda_{max.}$ (EtOH) 232 (log ε 4.13) and 348 nm (3.40); δ_H (250 MHz, $CDCl_3$) 1.18 (3 H, s, 7b-Me), 2.22 (1 H, br s, OH), 2.66 (1 H, m, 2a-H), 4.64 (1 H, m, 2-H), 4.89 (1 H, d, *J* 2.5 Hz, 1-H), 5.66 (1 H, d, *J* 4.9 Hz, 5-H), 6.08 (1 H, dd, *J* 4.9 Hz, 9.9 Hz, 6-H), 3.20 (2 H, m, 4-H and 7-H), and 6.54 (1 H, dd, *J* 2.8 Hz, 5.3 Hz, 3-H); *m/z* 172 (M^+), 157, 143, 129, 128 (base), 127, and 115.

7b-*Methyl*-7bH-*cyclopent*[cd]*indene* (1) *from the Ketone* (15).—A stirred solution of the ketone (15) (3.08 g, 18 mmol) in petroleum (100 ml) was treated with a hexane solution of di-isobutylaluminium hydride (1M; 18.2 ml, 18.2 mmol) at 0 °C under nitrogen. After 20 min, methanol (20 ml) was added and the mixture stirred for 3 h at room temperature, filtered through Celite and the residue washed with hot methanol. The combined filtrate and washings were evaporated, and the residue was dissolved in dichloromethane (100 ml) and stirred

with toluene-*p*-sulphonic acid (1 g) for 15 min at room temperature. The solution was washed with saturated aqueous sodium hydrogen carbonate (100 ml) and water (100 ml), dried (Na_2SO_4), evaporated, and the residue chromatographed on silica gel. Elution with petroleum gave 7b-*methyl*-7bH-*cyclopent*[cd]*indene* (1) (2.11 g, 76%) as a yellow oil; an analytical sample was prepared by distillation (Kugelrohr) and had b.p. 95 °C (oven) at 3 mmHg, m.p. 12—13 °C (Found: C, 93.3; H, 6.6. $C_{12}H_{10}$ requires C, 93.45; H, 6.55%); $\nu_{max.}$ (neat) 3 055m, 2 970m, 2 920m, 2 860w-m, 1 574w-m, 1 442m, 1 376w-m, 1 360w-m, 1 338w-m, 1 332m, 1 292m, 1 242m, 1 036w-m, 940m, 840s, 830s, 768m, 722s, 684s, 656m, and 622m cm^{-1}; $\lambda_{max.}$ (EtOH) 249sh (log ε 3.74), 282 (4.54), 335sh (3.52), 398sh (2.11), 439sh (2.57), and 450 nm (2.64); δ_H (250 MHz, $CDCl_3$) −1.67 (3 H, s, 7b-Me), 7.53—7.83 (3 H, AB_2 system giving δ_A 7.57, 6-H; δ_B 7.69, 5-H and 7-H; $J_{A,B}$ 7 Hz), and 7.89—7.92 (4 H, AB system giving δ_A 7.90, δ_B 7.92; $J_{A,B}$ 3 Hz, 1-H, 2-H, 3-H, and 4-H); δ_C ($CDCl_3$) 28.7 (7b-Me), 58.7 (C-7b), 116.2 (C-5 and C-7), 129.0 (C-6), 129.3 (C-2 and C-3), 134.9 (C-1 and C-4), 159.1 (C-4a and C-7a) and 178-7 p.p.m. (C-2a); *m/z* 154 (M^+), 153 (base), 139, and 76.

7b-*Methyl*-7bH-*cyclopent*[cd]*indene*-2-*carboxylic Acid* (17).—A mixture of the nitrile (7) (118 mg, 0.66 mmol), sodium hydroxide (250 mg) and water (5 ml) was refluxed under nitrogen for 2 h. Water (20 ml) was added, and the mixture was extracted with dichloromethane (2 × 30 ml). The extracts were discarded, and the aqueous layer was acidified with sulphuric acid (6M) and extracted with dichloromethane (3 × 30 ml). These extracts were washed with water (50 ml), dried ($MgSO_4$), and evaporated, and the residue chromatographed on silica gel. Elution with petroleum–ether (1 : 1) gave the *title compound* (17) (89 mg, 68%) as light orange crystals, m.p. 152—153.5 °C [from petroleum (b.p. 60—80 °C)] (Found: C, 78.85; H, 5.1. $C_{13}H_{10}O_2$ requires C, 78.8; H, 5.1%); $\nu_{max.}$ 3 400—2 300br and 1 680 cm^{-1}; $\lambda_{max.}$ (EtOH) 250 (log 3.89), 299 (4.62), 332 (3.82), 418sh (2.15), and 474 nm (3.17); δ_H (250 MHz, $CDCl_3$) −1.40 (3 H, s, 7b-Me), 7.59 (1 H, t, *J* 7 Hz, 6-H), 7.71 (1 H, d, *J* 6.6 Hz, 5-H), 7.91 (1 H, d, *J* 7.3 Hz, 7-H), 8.12 (1 H, d, *J* 3.5 Hz, 4-H), 8.23 (1 H, d, *J* 3.5 Hz, 3-H), 8.31 (1 H, s, 1-H), and 10.3-12.0 (1 H, br, CO_2H); δ_C ($CDCl_3$) 28.8 (7b-Me), 60.2 (C-7b), 118.2 (C-5), 121.7 (C-7), 129.4 (C-2), 129.9 (C-3 or C-6), 131.8 (C-6 or C-3), 136.4 (C-4), 140.1 (C-1), 157.6 (C-4a or C-7a), 159.2 (C-7a or C-4a), 170.9 (CO_2H), and 180.2 p.p.m. (C-2a); *m/z* 198 (M^+), 153 (base), and 152.

7b-*Methyl*-7b*h*-*cyclopent*[cd]*indene*-2-*carboxamide* (18).—A solution of the adduct (6) (1.25 g, 5.0 mmol) in benzene (20 ml) was refluxed with potassium t-butoxide (1.8 g, 16 mmol) under nitrogen for 0.5 h. The dark brown mixture was poured into water (100 ml) acidified with acetic acid, and extracted with dichloromethane (3 × 50 ml). The combined extracts were washed with water (100 ml), dried ($MgSO_4$), evaporated, and the residue chromatographed on silica gel. Elution with ether–ethyl acetate (4 : 1) gave *the title amide* (18) (0.20 g, 20%) as yellow needles, m.p. 150.5—155 °C (from ethyl acetate) (Found: C, 78.9; H, 5.65; N, 7.1. $C_{13}H_{11}NO$ requires C, 79.15; H, 5.6; N, 7.1%); $\nu_{max.}$ 1 678 cm^{-1}; $\lambda_{max.}$ (EtOH) 245sh (log ε 3.89), 299 (4.61). 333 (3.81), and 471 nm (3.06); δ_H (250 MHz, $CDCl_3$) −1.47 (3 H, s, 7b-Me), 6.5 (3 H, br, NH_2), 7.60 (1 H, t, *J* 7 Hz, 6-H), 7.74 (1 H, d, *J* 7.2 Hz, 5-H), 7.83 (1 H, d, *J* 7.4 Hz, 7-H), 8.05 (2 H, AB system, *J* 3.1 Hz, 3-H and 4-H), and 8.28 (1 H, s, 1-H); *m/z* 197 (M^+), 160, 154, 153, 152, and 144.

Methyl 7b-*Methyl*-7bH-*cyclopent*[cd]*indene*-2-*carboxylate* (19).—A mixture of the ester (20) [8] (204 mg, 0.73 mmol) and 1,8-diazabicyclo[5.4.0]undec-7-ene (300 mg, 2.0 mmol) was heated at 110 °C under nitrogen for 4 h. The resulting dark viscous mixture was chromatographed on silica gel, with petroleum–ether (4 : 1) as eluant, to give *the title ester* (19) (19 mg, 12%) as a yellow oil, $\nu_{max.}$ 1 718 cm^{-1}; $\lambda_{max.}$ (EtOH) 251 (log ε 3.89), 302 (4.60), 336 (3.81), and 475 nm (3.16); δ_H (250 MHz, $CDCl_3$) −1.47 (3 H, s, 7b-Me), 4.00 (3 H, s, OMe), 7.48 (1 H, t, *J* 7.2 Hz, 6-H), 7.71 (1 H, d, *J* 7.2 Hz, 5-H), 7.87 (1 H, d, *J* 7.2 Hz, 7-H), 8.08 (1 H, d, *J* 3.4 Hz, 4-H), 8.16 (1 H, d, *J* 3.4 Hz, 3-H), and 8.26 (1 H, s, 1-H).

Thermal Rearrangement of Annulene (1) *by Flash Vacuum Pyrolysis.*—(a) *At* 400 °C. The annulene (1) (33.0 mg) was distilled at 3 mmHg through a tube heated to 400 °C. The product was collected on a cold finger at −78 °C. Since analysis of the product by t.l.c. showed that some (1) had remained unchanged, the crude product was resubjected to the pyrolysis conditions to give 2a-*methyl*-2aH-*cyclopent*[cd]*indene* (23) (25.3 mg, 78%) as an oil; $\lambda_{max.}$ (EtOH) 258 (log ε 4.04), 318sh (2.50), and 331sh nm (2.41); δ_H (250 MHz, $CDCl_3$) 1.48 (3 H, s, 2a-Me), 6.59 (2 H, d, *J* 5 Hz, 2-H and 3-H), 6.70 (2 H, d, *J* 5 Hz, 1-H and 4-H), and 6.95—7.20 (3 H, AB_2 system giving δ_A 6.14, 6-H and δ_B 5.99 5-H and 7-H; $J_{A,B}$ 7 Hz); δ_C ($CDCl_3$) 23.6 (2a-Me), 118.5, 129.7, 131.8, 142.5, 145.1, and 169.5 p.p.m.

(b) *At* 700 °C. The annulene (1) (28.4 mg) was pyrolysed at 700 °C and 0.2 mmHg. Chromatography of the pyrolysate on silica gel with petroleum as eluant gave a 2 : 1 mixture of 2-*methyl*-1H-*cyclopent*[cd]*indene* (24) and 3-*methyl*-1H-*cyclopent*[cd]*indene* (215) (18.0 mg, 62%) as an oil; δ_H (250 MHz, $CDCl_3$) 2.30 [3 H × ⅓, fine d, 3-Me of (25)], 2.39 [3 H × ⅔, s, 2-Me of (24)], 3.99 (2 H, br s, CH_2), 6.4—7.0 (2 H, m), and 7.1—7.4 (3 H, m). A third minor component was also present, but was not identified.

Thermal Rearrangement of Tricyclic [10]*Annulenes in Solution: Kinetic Measurements.*—A solution of the annulene (*ca.* 5 mg) in redistilled decalin (8 ml) was heated in the vapour of a suitable solvent, boiling in the range 109—190 °C. After the temperature of the annulene solution had stabilised (*ca.* 10 min) aliquots were withdrawn at intervals of 15 min–2 h, and measurements made of the absorbance of the solution at the long wavelength maximum (400—500 nm). Plots of the logarithm of the absorbance/initial absorbance against time were generally linear, and rate constants were determined from the gradient of the plot. The results, given as half-lives for the rearrangement, are summarised in Table 1.

Photolysis of 7b-*Methyl*-7bH-*cyclopent*[cd]*indene* (1).—A solution of the annulene (1) (28.1 mg) in petroleum (200 ml) was irradiated at 300 nm (in a Rayonet reactor) for 15 h. The mixture was concentrated, and chromatographed on silica gel. Elution with petroleum gave starting material (27.7 mg, 99% recovery).

Acknowledgements

We thank the S.E.R.C. for a studentship (to R. McC.) Drs. T. L. Gilchrist and D. Tuddenham for early work, Professor D. Dolphin for a gift of bis(triphenylphosphine)tetraphenylporphyrinatoruthenium(II), Professor R. Gleiter for determining the photoelectron spectrum of (1), Professor S. Masamune for allowing us to quote his unpublished results on the photoelectron spectrum of (21), and Dr. H. S. Rzepa for useful discussions on all theoretical aspects.

References

1 Part 1, T. L. Gilchrist, C. W. Rees, and D. Tuddenham, *J. Chem. Soc., Perkin Trans. 1*, 1983, 83.

2 T. L. Gilchrist, C. W. Rees, D. Tuddenham, and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1980, 691.
3 Preliminary communication, T. L. Gilchrist, D. Tuddenham, R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1981, 657.
4 H. Firouzabadi and E. Ghaderi, *Tetrahedron Lett.*, 1978, 839.
5 J. Tsuji and K. Ohno, *Synthesis*, 1969, 157.
6 D. H. Doughty and L. H. Pignolet, *J. Am. Chem. Soc.*, 1978, **100**, 7083.
7 G. Domazetis, B. Tarpey, D. Dolphin, and B. R. James, *J. Chem. Soc., Chem. Commun.*, 1980, 939.
8 R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, 1983, 2399.
9 Preliminary communication, R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1982, 497.
10 E. J. Corey, T. Ravindranathan, and S. Terashima, *J. Am. Chem. Soc.*, 1971, **93**, 4326.
11 N. J. Cusack, C. B. Reese, A. C. Risius, and B. Roozpeikar, *Tetrahedron*, 1976, **32**, 2157.
12 A. R. Chamberlin, J. E. Stemke, and F. T. Bond, *J. Org. Chem.*, 1978, **43**, 147.
13 R. M. Adlington and A. G. M. Barrett, *J. Chem. Soc., Perkin Trans. 1*, 1981, 2848.
14 R. O. Hutchins, M. G. Hutchins, and C. A. Milewski, *J. Org. Chem.*, 1972, **37**, 4190; M. Casey, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1982, 714.
15 Preliminary communication, R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Chem. Commun.*, 1982, 622.
16 P. Cazeau, F. Moulines, O. Laporte, and F. Duboudin, *J. Organomet. Chem.*, 1980, **201**, C9.
17 S. Masamune and D. W. Brooks, *Tetrahedron Lett.*, 1977, 3239.
18 L. T. Scott, W. R. Brunsvold, M. A. Kirms, and I. Erden, *J. Am. Chem. Soc.*, 1981, **103**, 5216.
19 H.-R. Blattmann, W. A. Böll, E. Heilbronner, G. Hohlneicher, E. Vogel, and J.-P. Weber, *Helv. Chim. Acta*, 1966, **49**, 2017.
20 H. J. Dewey, H. Deger, W. Frölich, B. Dick, K. A. Klingensmith, G. Hohlneicher, E. Vogel, and J. Michl, *J. Am. Chem. Soc.*, 1980, **102**, 6412.
21 H. S. Rzepa, personal communication.
22 M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 1965, **48**, 1429.
23 R. Gleiter, R. Haider, and P. Bischof, to be published.
24 S. Masamune and D. W. Brooks, unpublished results.
25 R. Boschi, W. Schmidt, and J.-C. Gfeller, *Tetrahedron Lett.*, 1972, 4107.
26 E. Vogel, *Pure Appl. Chem.*, 1982, **54**, 1015 and references therein.
27 P. Eilbracht and K. Hafner, *Angew. Chem., Int. Ed. Engl.*, 1971, **10**, 751.
28 R. McCague, C. J. Moody, and C. W. Rees, *J. Chem. Soc., Perkin Trans. 1*, following paper.
29 C. W. Spangler, *Chem. Rev.*, 1976, **76**, 187.

Received 6th June 1983; *Paper* 3/910