

## Tricyclic [10]Annulenes. Part 6.<sup>1</sup> Preparation and Properties of 7b-Ethyl- and 7b-Isopropyl-7bH-cyclopent[cd]indenes

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Previous syntheses of 7b-methyl-7bH-cyclopent[cd]indene (**1a**) have been extended to the 7b-ethyl (**1b**) and 7b-isopropyl (**1c**) analogues. All three compounds have similar u.v. and n.m.r. spectra, entirely consistent with their delocalised  $10\pi$  aromatic structure. The 7b-ethyl compound undergoes thermal sigmatropic rearrangement to the 2aH-isomer eleven times faster than the 7b-methyl analogue.

We have recently described the preparation of 7b-methyl-7bH-cyclopent[cd]indene (**1a**), an aromatic tricyclic [10]annulene.<sup>2</sup> The aromatic structure, particularly the diamagnetic ring current induced in an applied magnetic field, is supported by its n.m.r. spectrum in which the central methyl group resonates upfield of tetramethylsilane (TMS) at  $\delta -1.67$ . With a view to learning more about the aromaticity of these tricyclic [10]annulenes, especially the effect of the induced ring current on the n.m.r. chemical shift of the central substituent, we have now prepared the corresponding 7b-ethyl (**1b**) and 7b-isopropyl derivatives (**1c**).

### Results and Discussion

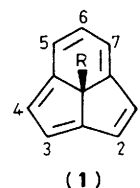
As part of a study<sup>3</sup> on 3-methoxy-3a-substituted-3aH-indenes and their 3-trimethylsiloxy analogues, we prepared the adduct (**3**) of 3a-ethyl-3-methoxy-3aH-indene (**2**) and dimethyl acetylenedicarboxylate. The removal of the elements of methanol from the adduct (**3**) was simply effected by treatment with concentrated sulphuric acid in methanol at 0 °C to give the annulene diester (**4**) (79%). The n.m.r. spectrum of compound (**4**) confirmed its aromatic structure, and showed, in addition to the expected pattern for the peripheral protons ( $\delta$  7.59–8.23), an ABX<sub>3</sub> system in the region upfield of TMS (Figure 1) for the central ethyl group. The methyl group resonated at  $\delta -0.35$ , whilst the methylene group appeared as a sixteen-line multiplet centred at  $\delta -0.98$ . This multiplet arises from the non-equivalence of the two CH<sub>2</sub> protons.

The diester (**4**) was converted into the dialdehyde (**5**) by the method previously described for the 7b-methyl analogue.<sup>2</sup> Decarbonylation of the dialdehyde using two equivalents of tris(triphenylphosphine)rhodium(I) chloride in refluxing benzene gave the required 7b-ethyl-7bH-cyclopent[cd]indene (**1b**) in 77% yield (Scheme 1).

The [10]annulene containing a central isopropyl group was prepared from the tricyclic ketone (**6**).<sup>3</sup> Thus reaction of the ketone (**6**) with 2,4,6-tri-isopropylbenzenesulphonyl hydrazide gave a mixture of the hydrazones (**7**), which was converted into the tetraene (**8**) by the Shapiro reaction.<sup>4</sup> Fragmentation of the hydrazones under the basic conditions was rather slow, and this is attributed to the need to form a trianion. The final elimination of water proceeded smoothly to give 7b-isopropyl-7bH-cyclopent[cd]indene (**1c**) in an overall yield of 28% from the ketone (**6**) (Scheme 2).

The tricyclic [10]annulenes (**1b**) and (**1c**) are both bright yellow oils, whose u.v. spectra show a close similarity to that of the methyl-substituted annulene (**1a**) (Table 1). This suggests, not surprisingly, that changing the central alkyl group has very little effect on the electronic structure of the annulene.

The aromatic nature of the annulenes (**1b**) and (**1c**) was confirmed by their <sup>1</sup>H n.m.r. spectra (Figures 2 and 3), the resonances associated with the central alkyl group appearing



(1)

a; R = Me  
b; R = Et  
c; R = Pr<sup>i</sup>

Table 1. Electronic spectral data of 7b-substituted-7bH-cyclopent[cd]indenes (**1**)

Compound	$\lambda_{\max}$ (nm)
( <b>1a</b> )	282, 335sh, 450
( <b>1b</b> )	286, 341sh, 451
( <b>1c</b> )	286, 342sh, 452

Table 2. Chemical shifts of the central groups of 7b-substituted-7bH-cyclopent[cd]indenes (**1**)

Compound	Protons	Observed value ( $\delta$ )	Reference <sup>6</sup> value ( $\delta$ )	Upfield shift
( <b>1a</b> )	CH <sub>3</sub>	-1.67	0.9	2.57
( <b>1b</b> )	CH <sub>2</sub> CH <sub>3</sub>	-1.33	1.4	2.73
( <b>1c</b> )	CH(CH <sub>3</sub> ) <sub>2</sub>	-1.13	1.5	2.63
( <b>1b</b> )	CH <sub>2</sub> CH <sub>3</sub>	-0.48	0.9	1.38
( <b>1c</b> )	CH(CH <sub>3</sub> ) <sub>2</sub>	-0.33	0.9	1.23

upfield of TMS as a result of the induced diamagnetic ring current. As studies on tetracyclic [14]annulenes, the *trans*-10b,10c-dihdropyrenes, have shown that the ring-current effect is essentially independent of the central substituent,<sup>5</sup> a similar analysis of the 7bH-cyclopent[cd]indenes was performed by correlating the observed chemical shifts of the central substituents against appropriate reference values<sup>6</sup> (Table 2). Although this rudimentary analysis does not take all factors into account, it does show that the absolute magnitude of the ring current effect, as measured by the upfield shift of the group with respect to the reference value, is approximately independent of the nature of the central substituent.

The peripheral protons of the annulenes (**1b**) and (**1c**) resonated in the region  $\delta$  7.5–7.95 and appeared as the expected AB and AB<sub>2</sub> patterns.

On heating, the annulene (**1b**) rearranged to the 1aH-isomer (**9**) by a [1,5] sigmatropic shift of the ethyl group. The driving force for this rearrangement is believed to be the formation of a benzene ring, and relief of the ring-strain at the 2a-position.

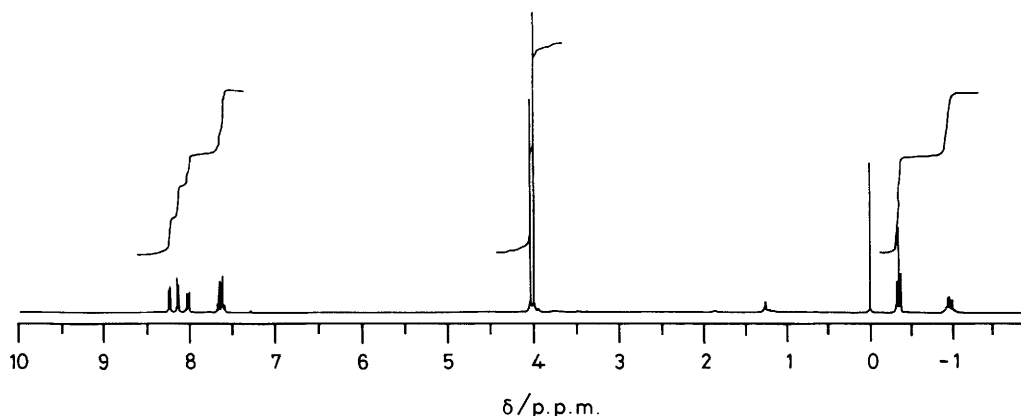
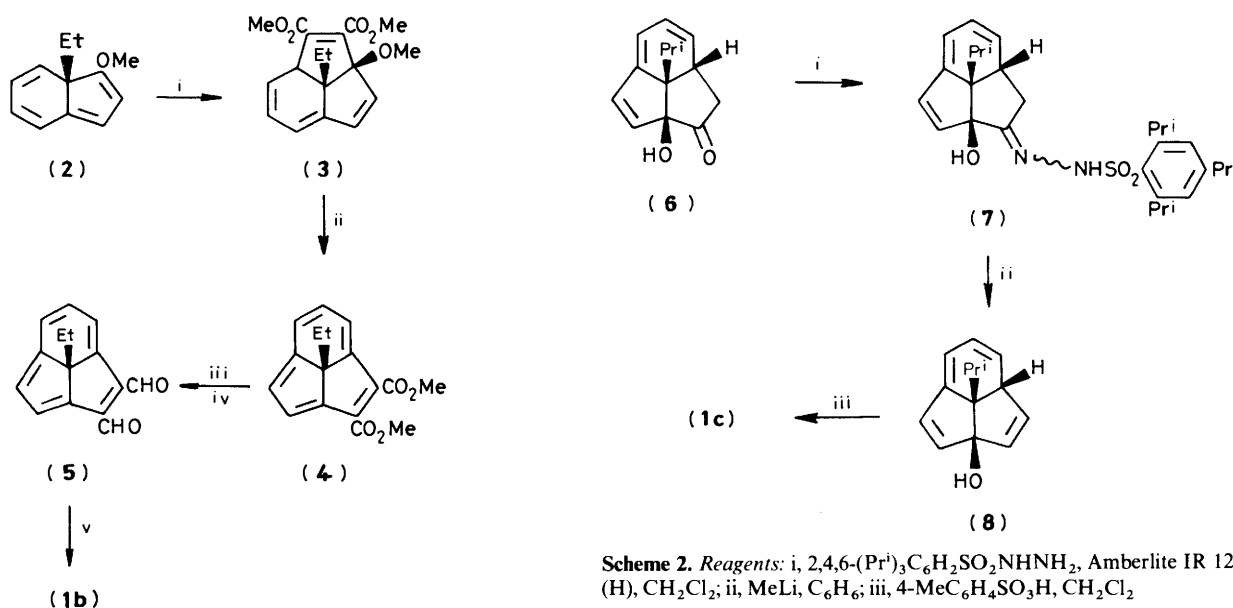


Figure 1. 250 MHz  $^1\text{H}$  N.m.r. spectrum of dimethyl 7b-ethyl-7bH-cyclopent[cd]indene-1,2-dicarboxylate (**4**) in deuteriochloroform (region upfield of TMS)



Scheme 1. Reagents: i, dimethyl acetylenedicarboxylate; ii, conc.  $\text{H}_2\text{SO}_4$ , MeOH,  $0^\circ\text{C}$ ; iii,  $\text{LiAlH}_4$ ,  $\text{Et}_2\text{O}$ ; iv,  $\text{BaMnO}_4$ ,  $\text{CH}_2\text{Cl}_2$ , reflux; v,  $\text{Rh}(\text{PPh}_3)_3\text{Cl}$ ,  $\text{C}_6\text{H}_6$ , reflux

Scheme 2. Reagents: i, 2,4,6-(Pr<sup>i</sup>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>SO<sub>2</sub>NHNH<sub>2</sub>, Amberlite IR 120 (H),  $\text{CH}_2\text{Cl}_2$ ; ii, MeLi,  $\text{C}_6\text{H}_6$ ; iii, 4-MeC<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>H,  $\text{CH}_2\text{Cl}_2$

The half-life for this rearrangement was measured by the u.v. method described previously<sup>2</sup> and found to be 275 min at  $109^\circ\text{C}$ . This contrasts with the corresponding rearrangement of the methyl derivative ( $t_{1/2}$  720 min at  $138^\circ\text{C}$ ) and gives a relative rate of migration of methyl to ethyl groups of 1:11. This is in line with previous work by Dolbier *et al.* which showed that ethyl has a higher migratory aptitude than methyl in sigmatropic shifts.<sup>7</sup> The rearrangement of peripherally substituted tricyclic [10]annulenes was previously found to be faster than the parent annulene (**1a**),<sup>2</sup> and, in accord with this, the diester (**4**) rearranged faster ( $t_{1/2}$  77 min at  $109^\circ\text{C}$ ) than the unsubstituted annulene (**1b**). This rapid rearrangement of annulenes containing electron-withdrawing groups caused a problem during the preparation of compound (**1b**) in that the intermediate dialdehyde (**5**) partially rearranged during the decarbonylation step. Consequently the annulene (**1b**) was always contaminated with a few percent of the rearranged isomer (**9**).

## Experimental

For general points see refs. 2 and 3.

**Dimethyl 7b-Ethyl-7bH-cyclopent[cd]indene-1,2-dicarboxylate (4).**—The adduct (**3**) (144 mg, 0.46 mmol) was dissolved in methanol (3 ml) and cooled to  $0^\circ\text{C}$ . Concentrated sulphuric acid (3 ml) was added, and after 15 min the mixture was poured into ice-water (15 ml), and extracted with ether ( $3 \times 15$  ml). The combined extracts were dried ( $\text{MgSO}_4$ ), evaporated, and the residue chromatographed to give the *title compound* (**4**) (102 mg, 79%) as a bright yellow oil (Found:  $M^+$ , 284.1045.  $\text{C}_{17}\text{H}_{16}\text{O}_4$  requires  $M^+$ , 284.1049);  $\nu_{\text{max}}$ , 2950, 2920, 1715, 1440, 1245, 1220, 1155, 1130, and  $820\text{ cm}^{-1}$ ;  $\lambda_{\text{max}}$  (EtOH) 311 (log  $\epsilon$  4.56) 340 (3.78), and 471 nm (3.30);  $\delta$  (250 MHz;  $\text{CDCl}_3$ )  $-0.98$  (2 H, m),  $-0.35$  (3 H, t), 4.00 (3 H, s), 4.04 (3 H, s), 7.59 (1 H, d,  $J$  6.7 Hz), 7.65 (1 H, t,  $J$  6.7 Hz), 8.01 (1 H, d,  $J$  6.7 Hz), 8.13 (1 H, d,  $J$  3.8 Hz), and 8.23 (1 H, d,  $J$  3.8 Hz);  $m/z$  284 ( $M^+$ ), 253, 252 (base), 238, 224, 193, 165, and 138.

**7b-Ethyl-7bH-cyclopent[cd]indene-1,2-dicarbaldehyde (5).**—A solution of the diester (**4**) (400 mg, 1.41 mmol) in dry ether (25 ml) was added dropwise to a stirred suspension of lithium

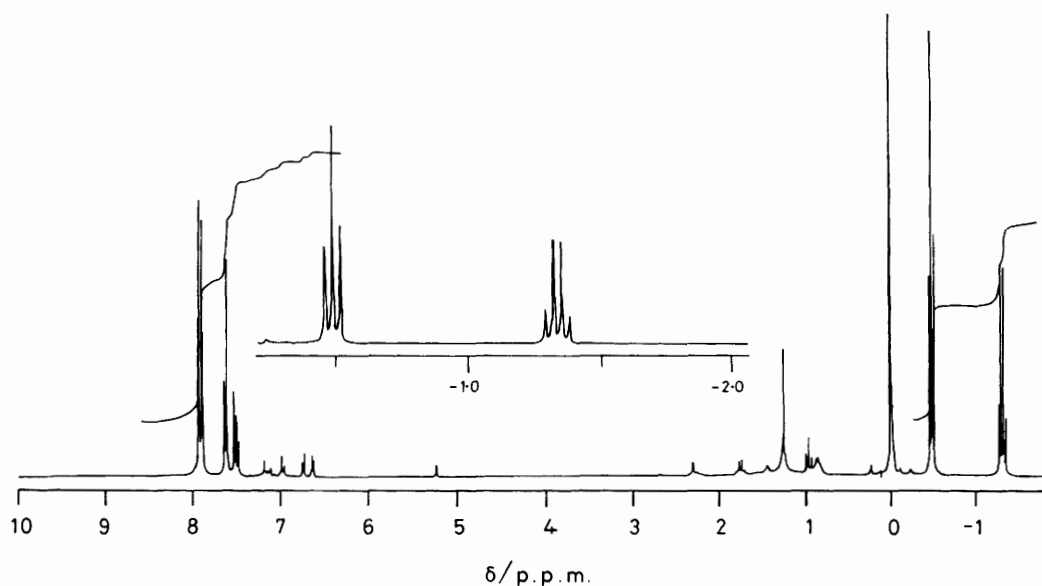


Figure 2. 250 MHz  $^1\text{H}$  N.m.r. spectrum of 7b-ethyl-7bH-cyclopent[cd]indene (**1b**) in deuteriochloroform

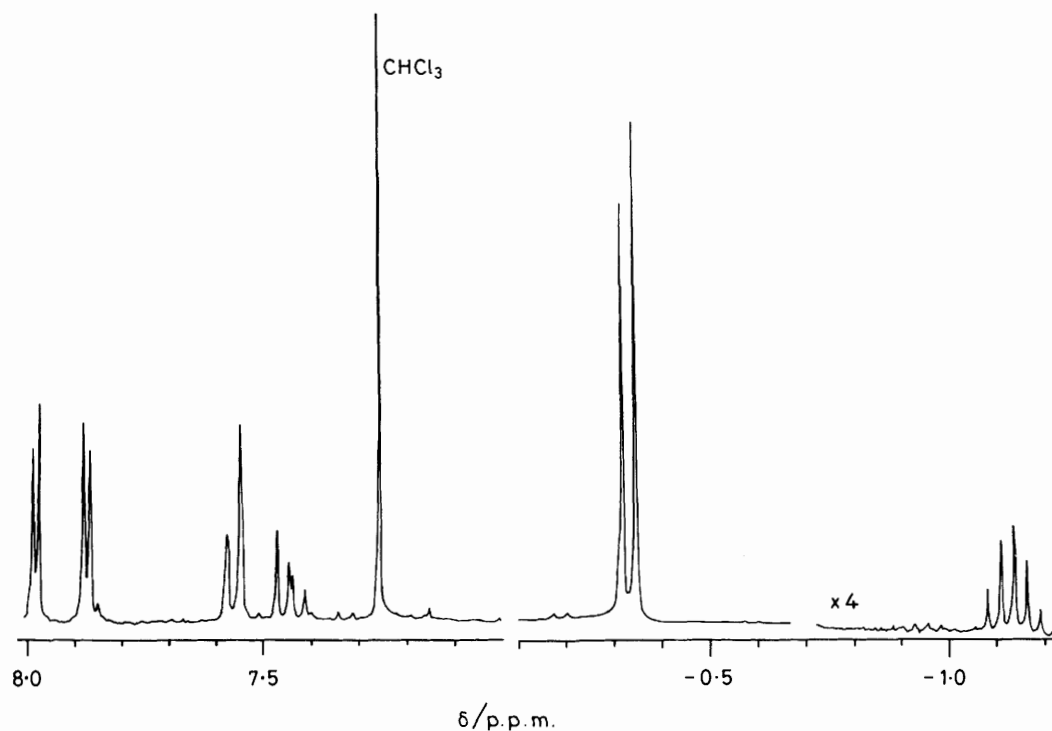
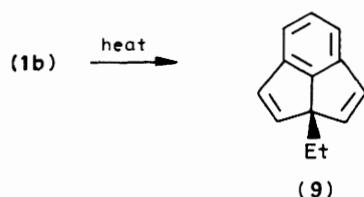


Figure 3. 250 MHz  $^1\text{H}$  N.m.r. spectrum of 7b-isopropyl-7bH-cyclopent[cd]indene (**1c**) in deuteriochloroform



aluminium hydride (268 mg, 7.1 mmol) in ether (10 ml) under nitrogen at room temperature. The resulting mixture was stirred for 1.5 h at room temperature, and worked up in the standard

way to give a dark-red oil. This oil was redissolved in dichloromethane (50 ml), treated with barium manganate (3.60 g, 14.0 mmol), and the mixture heated under reflux for 16 h. After cooling, the solution was filtered through Celite, evaporated and chromatographed to give the *title compound* (**5**) (190 mg, 60%) as a red oil,  $\nu_{\text{max}}$  2 940, 1 685, 1 515, 1 430, 1 225, 950, and 830  $\text{cm}^{-1}$ ;  $\lambda_{\text{max}}$  (EtOH) 337 (log  $\epsilon$  3.98), 363sh (3.24) and 512 nm (3.04);  $\delta$  (250 MHz;  $\text{CDCl}_3$ ) -0.79 (2 H, q), -0.31 (3 H, t), 7.67 (1 H, d,  $J$  7.1 Hz), 7.78 (1 H, t,  $J$  7.1 Hz), 8.29 (1 H, d,  $J$  7.1 Hz), 8.3 (1 H, d,  $J$  3.8 Hz), 8.45 (1 H, d,  $J$  3.8 Hz), 10.78 (1 H, s), and 10.80 (1 H, s);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 7.1, 36.9, 64.5, 118.9, 122.8, 135.0, 135.6, 137.2, 141.5, 143.6, 162.7, 163.6, 176.8, 187.4, and 188.9;  $m/z$  224 ( $M^+$ ), 195 (base), 167, and 139.

7b-Ethyl-7bH-cyclopent[cd]indene (**1b**).—A solution of the dialdehyde (**5**) (112 mg, 0.5 mmol) and tris(triphenylphosphine)rhodium(i) chloride (925 mg, 1 mmol) in dry benzene (15 ml) was heated under reflux under nitrogen for 8 h. After cooling, the mixture was treated with iodomethane (2 ml), stirred for a further 1.5 h at room temperature, filtered, and evaporated. The residue was chromatographed to give the *title compound* (**1b**) (65 mg, 77%) as a bright yellow oil (Found:  $M^+$ , 168.0934.  $C_{13}H_{12}$  requires  $M^+$ , 168.0939);  $\nu_{\max}$ . 3 025, 2 960, 2 925, 2 865, 2 850, 1 450, 1 370, 1 290, 1 235, 950, 925, 840, 830, 788, 765, 720, 675, 645, and 620  $cm^{-1}$ ;  $\lambda_{\max}$ (EtOH) 286 (log  $\epsilon$  4.52), 341sh (3.40), 428sh (2.47), 440sh (2.56), and 451 nm (2.61);  $\delta$  (250 MHz;  $CDCl_3$ ) -1.33 (2 H, q), -0.48 (3 H, t), 7.47—7.65 (3 H,  $AB_2$ ,  $\delta_A$  7.50, 6-H;  $\delta_B$  7.62, 5-H and 7-H,  $J_{AB}$  7.5 Hz), and 7.88—7.95 (4 H, AB,  $\delta_A$  7.90,  $\delta_B$  7.92,  $J_{AB}$  3.3 Hz, 1-H, 2-H, 3-H, and 4-H);  $\delta_C$ ( $CDCl_3$ ) 6.5, 34.2, 63.1, 116.3, 129.2, 130.3, 136.0, 159.2, and 178.3;  $m/z$  168 ( $M^+$ ), 153 (base), 140, and 139. Closer examination of the n.m.r. spectrum revealed the presence of a small amount of compound (**9**) as an impurity. Data for compound (**9**) are given below.

*Thermal Rearrangement of the Annulene (1b)*.—A solution of the annulene (**1b**) (15 mg) in toluene (5 ml) was heated under reflux for 24 h. Evaporation of the solvent, and chromatography of the residue gave 2a-ethyl-2aH-cyclopent[cd]indene (**9**) (11 mg, 73%) as a pale yellow oil,  $\nu_{\max}$ . 3 045, 2 960, 2 920, 2 840, 1 450, 1 370, 1 325, 930, 835, and 780  $cm^{-1}$ ;  $\lambda_{\max}$ (EtOH) 258 (log  $\epsilon$  3.91), 284 (3.84) and 346sh nm (2.24);  $\delta$  (250 MHz;  $CDCl_3$ ) 0.98 (3 H, t), 1.78 (2 H, q), 6.63 (2 H, d,  $J$  5.0 Hz), 6.75 (2 H, d,  $J$  5.0 Hz), and 6.96—7.17 (3 H,  $AB_2$ , 7.0 Hz).

*Thermal Rearrangement of the Annulene Diester (4)*.—A solution of the annulene diester (**4**) (40 mg) was heated under reflux in xylene (10 ml) for 3 h. Evaporation of the solvent and chromatography of the residue gave dimethyl 2a-ethyl-2aH-cyclopent[cd]indene-1,2-dicarboxylate (33 mg, 83%) as a pale yellow oil,  $\nu_{\max}$ . 2 950, 2 925, 1 710, 1 550, 1 455, and 1 430  $cm^{-1}$ ;  $\lambda_{\max}$ (EtOH) 253sh, and 314sh nm;  $\delta$  (250 MHz;  $CDCl_3$ ) 0.84 (3 H, t), 1.88—2.28 (2 H, qq), 3.85 (3 H, s), 3.94 (3 H, s), 6.67 (1 H, d,  $J$  5.0 Hz), 6.75 (1 H, d,  $J$  5.0 Hz), and 7.08—7.27 (3 H, m).

7b-Isopropyl-7bH-cyclopent[cd]indene (**1c**).—A mixture of the tricyclic ketone (**6**) (15 mg, 69  $\mu$ mol), 2,4,6-tri-isopropyl-

benzenesulphonyl hydrazide (21 mg, 70  $\mu$ mol), and Amberlite resin IR120 (H) (25 mg) was stirred in dichloromethane (10 ml) at room temperature for 2 h. Work-up and chromatography gave (i) the recovered ketone (**6**) (4.1 mg) and (ii) the hydrazones (**7**) (21.5 mg, 62%).

The mixture of the hydrazones (**7**) (21.5 mg, 43  $\mu$ mol) was dissolved in benzene and treated with methyl-lithium (1.35M; 0.3 ml, 0.47 mmol) at room temperature. The mixture was then warmed to 40 °C for 1 h, and then quenched with water. The mixture was extracted with ether (3  $\times$  15 ml), and the combined extracts dried and evaporated. The residue was dissolved in dichloromethane (5 ml) and stirred with toluene-4-sulphonic acid (10 mg) for 0.5 h at room temperature. The solvent was evaporated and the residue chromatographed to give the *title compound* (**1c**) (3.6 mg, 28%) as a bright yellow oil (Found:  $M^+$ , 182.1093.  $C_{14}H_{14}$  requires  $M^+$ , 182.1095);  $\lambda_{\max}$ (EtOH) 288, 344sh, 425sh, 439sh, and 452 nm;  $\delta$  (250 MHz;  $CDCl_3$ ) -1.13 (1 H, septet), -0.33 (6 H, d), 7.62—7.78 (3 H,  $AB_2$ ,  $\delta_A$  7.64, 6-H; and  $\delta_B$  7.76, 5-H and 7-H;  $J_{AB}$  7.5 Hz), and 7.93 (4 H, AB,  $\delta_A$  7.87,  $\delta_B$  7.93,  $J_{AB}$  3.1 Hz, 1-H, 2-H, 3-H, and 4-H);  $m/z$  182 ( $M^+$ ) and 139 (base).

### Acknowledgements

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