A New Synthesis of the Tricyclic [10]Annulene 7b-Methyl-7b*H*-cyclopent-[*cd*]indene

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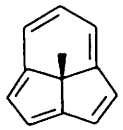
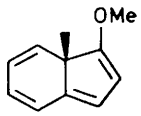
In a new versatile synthesis of the tricyclic [10]annulene, 7b-methyl-7b*H*-cyclopent[*cd*]indene, the third ring is formed by an intramolecular aldol condensation rather than a cycloaddition reaction.

We have recently reported the synthesis of the tricyclic [10]-annulene (**1**),[1] and certain of its peripherally substituted derivatives, based on the [8 + 2] cycloaddition reactions of 3-methoxy-3a-methyl-3a*H*-indene (**2**).[2] We now report an alternative synthesis of (**1**) which avoids this cycloaddition of the labile 3a*H*-indene (**2**), provides a route to differently substituted derivatives of (**1**), and circumvents the very rapid aromatising rearrangement which 3a*H*-indenes undergo when the ring junction substituent is other than a simple alkyl group.[3]

Birch reduction and methylation of 7-methoxyindan-1-one (**3**),[4] in the standard way,[2] gave the methoxydienone (**4**),† b.p. 84—87 °C at 0.1 mmHg, which was converted by phenylselenation and oxidation into the methoxytrienone (**5**),† m.p 79—81 °C, in 30% overall yield from (**3**). Acid hydrolysis of the dienone (**4**) gave the expected diketone (**6**) (75%), m.p. 75—76 °C, a useful synthetic intermediate.



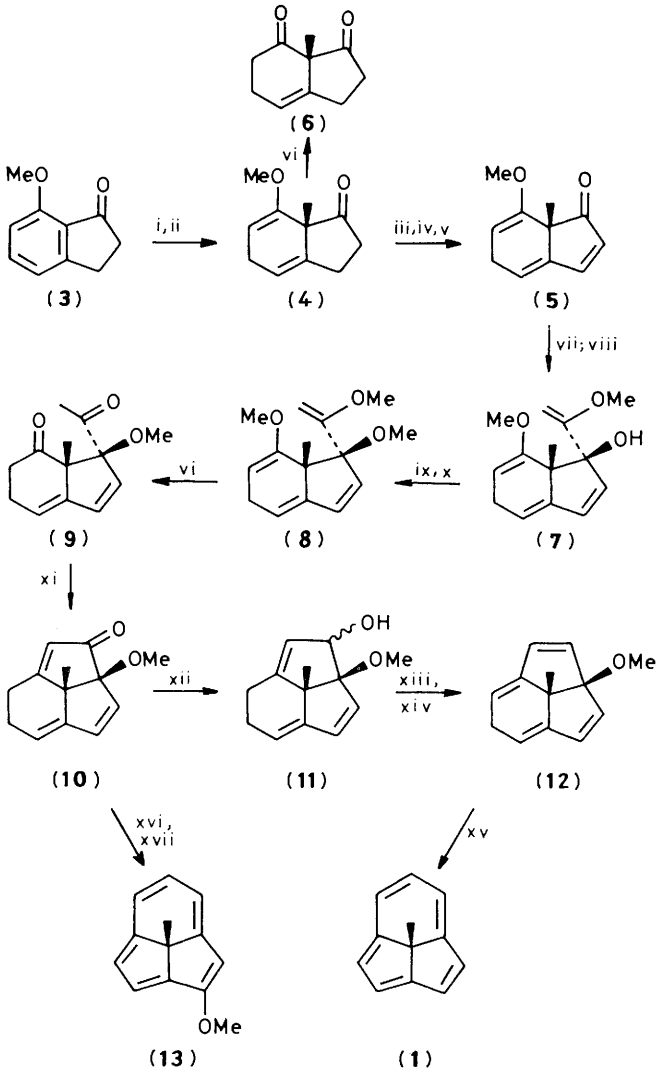
(**1**)



(**2**)

The methoxytrienone (**5**) was converted into the tricyclic ketone (**10**) in 50% overall yield, as follows. Treatment of (**5**) with lithium methyl vinyl ether in tetrahydrofuran (THF) at −78 °C[5] gave the alcohol (**7**) which was deprotonated with dimsyl-sodium in dimethyl sulphoxide and methylated with methyl iodide[6] to give (**8**). Acid hydrolysis of (**8**), without purification, gave the diketone (**9**) which was then cyclised with 5% aqueous methanolic potassium hydroxide, followed

† Spectral data for selected intermediates: (**4**) ν_{max} (film) 1743 cm^{-1}; δ ($CDCl_3$) 1.33 (3H, s, 7a-Me), 2.2—2.9 (6H, m, 2-, 3-, and 5-CH_2), 3.62 (3H, s, MeO), 4.68 (1H, br.t, *J* 4 Hz, 6-CH), 5.70—5.75 (1 H, m, 4-CH). (**5**) ν_{max} (film) 1705 cm^{-1}; δ ($CDCl_3$) 1.39 (3H, s, 7a-Me), 2.89 (1H, dt, *J* 22 and 6 Hz) and 3.04 (1H, dt, *J* 22 and 2 Hz), (5-CH_2), 3.62 (3H, s, MeO), 4.65 (1H, dd, *J* 6 and 2 Hz, 6-CH), 6.00 (1H, d, $J_{2,3}$ 5 Hz, 2-CH), 6.06 (1H, dd, *J* 6 and 2 Hz, 4-CH), 7.65 (1H, d, $J_{2,3}$ 5 Hz, 3-CH). (**10**) δ ($CDCl_3$) 1.30 (3H, s, 7b-Me), 2.75—2.90 (4H, m, 6- and 7-CH_2), 3.55 (3H, s, MeO), 5.68—5.72 (2H, m, 1-CH and 5-CH), 5.91 (1H, d, *J* 6 Hz) and 6.26 (1H, d, *J* 6 Hz) (3- and 4-CH).



Scheme 1. Reagents: i, K, Bu^{t}OH, THF, LiBr, NH_3, −78 °C; ii, MeI, THF, NH_3, −78 °C; iii, $LiNPr^i_2$, THF, −78 °C; iv, PhSeCl, THF, −90 °C; v, H_2O_2, THF, pyridine, 0 to 5 °C; vi, 2M HCl, H_2O, THF; vii, CH_2=C(Li)OMe, THF, −78 to 0 °C; viii, 20% NH_4Cl, H_2O; ix, $MeSOCH_2^-Na^+$, 20 °C; x, MeI; xi, 5% KOH, H_2O, MeOH; xii, di-isobutylaluminium hydride, hexane; xiii, MTPI, HMPA; xiv, 10% NaOH, H_2O; xv, *p*-$MeC_6H_4SO_3H$ (catalytic), CH_2Cl_2; xvi, KH, 18-crown-6, DME, −20 °C; xvii, FSO_3Me, −20 °C to reflux (DME).

by chromatography on silica gel, to give the pure tricyclic ketone (**10**)† as a viscous oil.

Reduction of the ketone (**10**) with di-isobutylaluminium hydride in hexane gave a mixture of the epimeric alcohols (**11**), which could be separated chromatographically. However, the mixture (**11**) was readily dehydrated with methyltriphenoxyphosphonium iodide (MTPI) in hexamethylphosphoric triamide (HMPA) at room temperature, followed by stirring with 10% aqueous sodium hydroxide for 1 h.[7] Immediate treatment of the tetraene (**12**) with a catalytic amount of 4-toluenesulphonic acid in methylene dichloride at room temperature for 5 min gave the [10]annulene (**1**), identical with that reported earlier,[1] in 42% overall yield from (**10**).

The tricyclic ketone (**10**) is a versatile intermediate for synthesising [10]annulene derivatives. Thus, with two equivalents of potassium hydride in 1,2-dimethoxyethane (DME) containing 18-crown-6, followed by addition of methyl fluorosulphonate and subsequent heating to reflux for 30 min, it gave the 2-methoxy compound (**13**) as a yellow oil (70%) identical with that prepared by an alternative route.[8]

Our efforts to introduce substituents other than alkyl groups on to the central carbon of the annulene (**1**) will be reported later.[3]

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