

3-Methoxy-3a-methyl-3aH-indene

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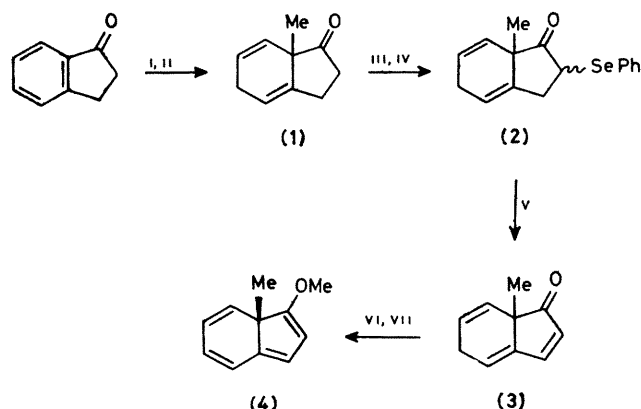
Summary 3-Methoxy-3a-methyl-3aH-indene (**4**) has been synthesised and is isolated as an unstable, readily oxidised oil, which undergoes [8 + 2]cycloaddition with 4-phenyltriazoline-3,5-dione and with dimethyl acetylenedicarboxylate.

THE isomer of indene with the tetrahedral carbon atom at a ring junction (3aH-indene) has been suggested as an intermediate in a variety of rearrangements,¹ but no

simple 3aH-indene derivative has hitherto been isolated.² We have prepared 3-methoxy-3a-methyl-3aH-indene (**4**) from indan-1-one by a rational route; we report here its synthesis (Scheme) and some of its chemistry.

Indan-1-one was converted (on a 20 g scale) by a Birch reduction-alkylation sequence³ into the ketone (**1**) (58%), which was characterised as its 2,4-dinitrophenylhydrazone, m.p. 156.5–158 °C. A by-product of the reaction was a dimethylated compound, 2,7a-dimethyl-5,7a-dihydroindan-

1-one, and this was separated from the ketone (1) by column chromatography. A double bond was then introduced adjacent to the carbonyl group of (1) by phenylselenation followed by oxidation. The α -(phenylseleno)-ketone (2) could be isolated as a mixture of diastereoisomers, b.p. 110 °C at 0.02 mmHg, but the conversion of (1) into the trienone (3) was more efficiently carried out as a 'one-pot' procedure, without isolation of the intermediates. Compound (3), isolated in 63% yield, was characterised as its 2,4-dinitrophenylhydrazone, m.p. 179.5–181.5 °C. The deprotonation of the trienone (3) required both potassium hydride and 18-crown-6, in 1,2-dimethoxyethane at –18 °C the purple colour of the enolate anion was rapidly generated. Methyl fluorosulphonate was added 30 min later to give a reaction mixture containing the 3aH-indene (4).

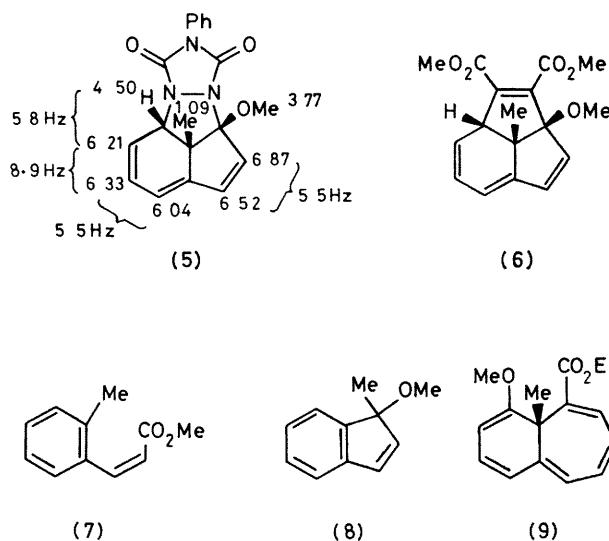


SCHEME Reagents i, K-Bu^tOH-THF-LiBr-NH₃, –78 °C, ii, MeI-THF-NH₃, –78 °C, iii, LiNPr₂-THF, –78 °C, iv, Ph₂-Se₂-Br₂-THF, –78 to 20 °C, v, H₂O₂-THF, –10 to 20 °C, vi, KH-18-crown-6-dimethoxyethane, –18 °C, vii, MeOSO₂F

The enolisation and alkylation could also be carried out, less efficiently, in diethyl ether, and this allowed isolation of the 3aH-indene. The ether was removed at –20 °C and the residue was subjected to column chromatography at –78 °C (alumina, ether-pentane) which gave in low yield, a pure specimen of (4) (CCl₄) 1.26 (3a-Me), 3.71 (3-Ome), 4.88 (d, 2-H), 5.7 (dq, 5-H, 6-H), 5.98 (d, 1-H), and 6.18 (dq, 4-H, 7-H), $J_{1,2}$ 2.2, $J_{4,5}$ 8.9, $J_{5,6}$ 5.0 and $J_{6,7}$ 8.9 Hz, λ_{\max} (ether-pentane) 219, 253, and 388 nm. The compound was a yellow oil which decomposed at room temperature.

Addition of 4-phenyltriazoline-3,5-dione to the solution of (4) in dimethoxyethane at –18 °C gave a 1:1 adduct [45% based on (3)], m.p. 101–102 °C. Cycloaddition took place across the 3 and 4 positions, as shown by the ¹H n.m.r. spectrum of the adduct (5) the assigned chemical shifts and coupling constants are shown on the diagram.

A similar adduct (6) (60%), m.p. 94–95 °C, was formed with dimethyl acetylenedicarboxylate. The n.m.r. spectrum of (6) includes signals for the bridgehead methyl group at δ 0.93, for the ring-junction hydrogen atom at δ 3.59, and for the olefinic hydrogen atoms between δ 5.83 and 6.49. The unsaturated periphery of (4) has thus acted as a unit in these cycloadditions which are [8 + 2] rather than either of the two possible modes of [4 + 2] addition. Formal [8 + 2] addition has been observed with indolizine, the 3a-aza analogue of our indene, and dimethyl acetylenedicarboxylate.⁴



Compound (4) is stable for several hours at or above room temperature in dilute solution and in the absence of air. It is oxidised to the Z-cinnamic ester (7)[†] (36%) in tetrachloromethane in the presence of air, when heated in hexane or dimethoxyethane in the absence of air it is slowly converted into the indene (8) together with other products which are as yet unidentified. The methyl shift to give (8) could be a thermal process or it could be catalysed by traces of acid.

Bicyclic conjugated polyenes which are fully unsaturated save for a tetrahedral carbon at one ring junction represent an interesting but virtually unknown family of hydrocarbons. The instability and high reactivity of compound (4), the first tetraene to be isolated in this series, is in contrast with the related pentaene (9) which was recently reported to be a stable red oil.⁵

(Received, 26th March 1980, Com 326)

[†] The structure of the ester was established from the n.m.r. spectrum, the Z-configuration of the double bond being indicated by the coupling constant (J 13 Hz), and by comparison with material independently synthesised by Lindlar catalytic hydrogenation of methyl 2-methylphenylpropynoate.

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² Benzo-fused derivatives are known: H. W. Moore and H. R. Snyder, *J. Org. Chem.*, 1963, **28**, 535; L. A. Cort and M. A. Mahesar, *J. Chem. Soc., Perkin Trans. I*, 1979, 2034.

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