3-Methoxy-3a-methyl-3a*H*-indene

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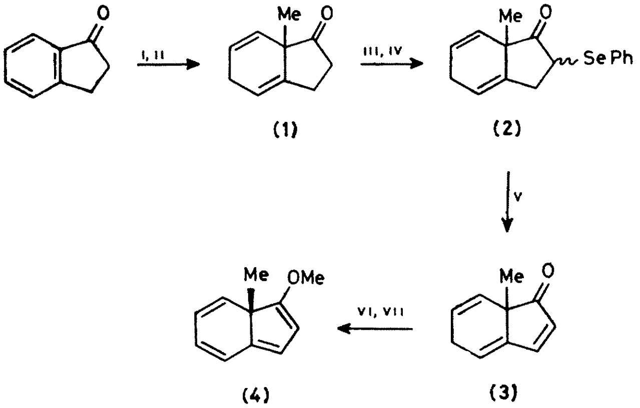
Summary 3-Methoxy-3a-methyl-3a*H*-indene (**4**) has been synthesised and is isolated as an unstable, readily oxidised oil, which undergoes [8 + 2]cycloaddition with 4-phenyltriazoline-3,5-dione and with dimethyl acetylenedicarboxylate.

THE isomer of indene with the tetrahedral carbon atom at a ring junction (3a*H*-indene) has been suggested as an intermediate in a variety of rearrangements,[1] but no simple 3a*H*-indene derivative has hitherto been isolated.[2] We have prepared 3-methoxy-3a-methyl-3a*H*-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 sequence[3] 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 3a*H*-indene (**4**)

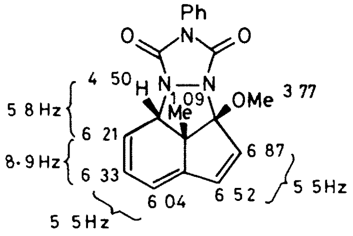


SCHEME Reagents i, K–Bu^{t}OH–THF–LiBr–NH$_3$, −78 °C, ii, MeI–THF–NH$_3$, −78 °C, iii, LiNPr$^i_2$–THF, −78 °C, iv, Ph$_2$Se$_2$–Br$_2$–THF, −78 to 20 °C, v, H$_2$O$_2$–THF −10 to 20 °C, vi, KH–18-crown-6–dimethoxyethane, −18 °C, vii, MeOSO$_2$F

The enolisation and alkylation could also be carried out, less efficiently, in diethyl ether, and this allowed isolation of the 3a*H*-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**) δ (CCl$_4$) 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_{45} 8·9, J_{56} 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 ^{1}H 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]



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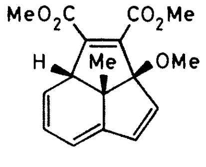

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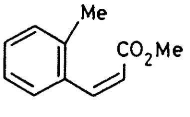

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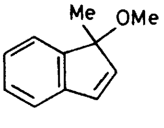

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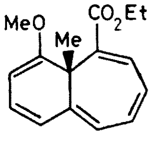

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Compound (**4**) is stable for several hours at or above room temperature in dilute solution and in the absence of air It is oxidised to the *Z*-cinnamic ester (**7**)‡ (36%) in tetrachloromethane in the presence of air, when heated in hexane or dimethoxyethane 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]

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‡ 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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