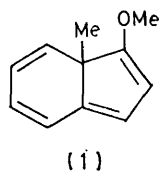


Generation of 3-Methoxy-3a-methyl-3aH-indene and Study of its Cycloaddition Reactions¹

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The title compound (1) has been prepared from indan-1-one by Birch reduction and methylation followed by the introduction of a further double bond, enolisation of the ketone, and *O*-methylation. The tetraenol ether (1) is the first 3aH-indene derivative to be isolated. It is shown to be oxidised by air to the *Z*-cinnamic ester (5), and to undergo ready rearrangement to the 1H-indene (7). Cycloadditions of *N*-phenyltriazolinedione, diethyl azodiformate, and dimethyl acetylenedicarboxylate to the termini of the tetraene are observed. These formal [8 + 2] cycloadditions are in contrast to the [4 + 2] addition which is observed with *N*-phenylmaleimide. The [4 + 2] adduct rearranges on heating to give a mixture of [8 + 2] adducts: it is suggested that this process involves dissociation of the adduct into its components and their re-combination.

BICYCLIC conjugated polyenes in which the peripheral unsaturation is interrupted by a tetrahedral carbon atom at a ring junction have hitherto been explored very little. Three aspects of their chemistry make their study worthwhile: (i) there is, in principle, the possibility of homoaromatic stabilisation or destabilisation of the π -electron system; (ii) they are, potentially, excellent substrates for investigating sigmatropic group migrations, and (iii) they offer a variety of possibilities for cycloaddition reactions, including that of extended cycloadditions across the termini of the π -system. In this paper we give details of the first synthesis of an isolable 3aH-indene derivative, 3-methoxy-3a-methyl-3aH-indene (1), and its modes of rearrangement and cycloaddition.



3aH-Indene and derivatives bearing a hydrogen atom at the bridgehead position have been suggested as intermediates in a variety of rearrangements.^{2,3} Molecular orbital calculations based on the MNDO method indicate that 3aH-indene is less stable than the 1H-isomer by about 113 kJ mol⁻¹ and indeed is the least stable of all the isomers of indene.⁴ It is obvious from the earlier observations of rearrangements involving 3aH-indenes only as transient intermediates, that the ready [1,5]hydrogen shift to the 1H-isomers precludes their isolation. We therefore aimed to prepare derivatives with groups other than hydrogen at the ring junction.

A direct route to the required carbon skeleton is the Birch reduction and alkylation of indan-1-one. Reactions of this type have been reported previously to lead to the introduction of a group at the bridgehead (7a) position adjacent to the carbonyl group.⁵ We found that, by this means, the ketone (2) could be isolated in fairly good yields (of up to 58%), but that it was always

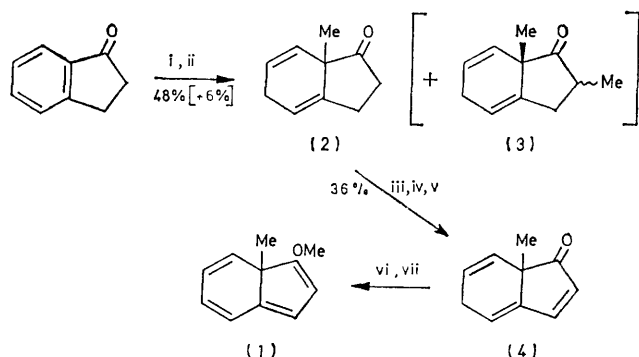
contaminated by small amounts of a dimethylated compound, the ketone (3). The pure ketone (2) was separated by column chromatography.

The planned route from the ketone (2) to the 3aH-indene system involved the introduction of a double bond into the five-membered ring as the next step. This proved to be difficult. The phenylseleno-group was introduced by means of base and benzeneselenenyl bromide, and the mixture of diastereoisomeric α -seleno-ketones was then oxidised to give the ketone (4) in moderate yield. In the best procedure, the α -seleno-ketones were oxidised *in situ* with hydrogen peroxide, the exothermic reaction being controlled by cooling. Methods involving the use of 2,3-dichloro-5,6-dicyanobenzoquinone, benzeneseleninic anhydride, or *N*-bromosuccinimide for the introduction of the double bond were unsuccessful. The structure of the trienone (4), a mobile yellow oil, was established from its u.v. spectrum, with a maximum at 286.5 nm (log ϵ 3.95) consistent with the presence of a conjugated dienone rather than a conjugated trienone, from its n.m.r. spectrum, and from the properties of its crystalline 2,4-dinitrophenylhydrazone.

The fully conjugated 3aH-indene system was generated from this ketone by the removal of a proton from C-5 of the ketone (4). Following earlier work on 'extended' enolisation of this type,⁶ we found that this reaction was most efficiently carried out by the use of potassium hydride and an equivalent of 18-crown-6 in 1,2-dimethoxyethane at -18 °C. With this base system the deep purple enolate anion was generated; the anion was then intercepted as the enol ether (1) by adding freshly distilled methyl fluorosulphonate. The route to the enol ether is summarised in Scheme 1.

The presence of the 3aH-indene derivative (1) was established by intercepting it with dienophiles as described below, but it was not possible to isolate it from the solution because of its thermal instability. Experiments were then performed in which diethyl ether was used in place of dimethoxyethane as the solvent for the last steps of the preparation. This was a poorer reaction medium but, because of its volatility, it could

be removed at -18°C under vacuum. Attempts to distil the product from the residue were unsuccessful. In another experiment the residue was suspended in a mixture of ether and pentane and the mixture was applied to an alumina column which was maintained at -78°C by a cooling jacket. This gave, in low yield, a solution containing the yellow enol ether (1). The u.v. spectrum of the solution showed maxima at 219, 252, and 388 nm. The solvent was then removed and the residue was immediately redissolved in carbon tetrachloride to allow the ^1H n.m.r. spectrum to be recorded.



SCHEME 1 Reagents: i, $\text{K-Bu}^t\text{OH-THF-NH}_3$, LiBr-THF , -78°C ; ii, $\text{MeI-THF-H}_2\text{O}$, -78°C ; iii, $\text{LiNPr}_2\text{-THF}$, -78°C ; iv, $\text{Ph}_2\text{Sc}_2\text{-Br}_2\text{-THF}$, -78 to 20°C ; v, $\text{H}_2\text{O}_2\text{-THF}$, 0°C ; vi, $\text{KH-18-crown-6-dimethoxyethane}$, -18°C ; vii, MeOSO_2F

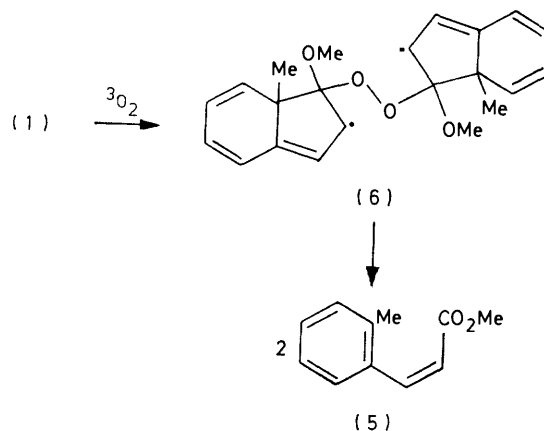
The spectrum shows signals for the $3\alpha\text{H}$ -methyl group at δ 1.26 and for the *O*-methyl group at 3.71. The olefinic region contains two doublets at δ 4.88 and 4.98 (J 2.2 Hz) which are assigned to H-1 and H-2 in the five-membered ring. The signals for H-5 and H-6 are centred at δ 5.77 and those for H-4 and H-7 at δ 6.18: the coupling constants ($J_{4,5}$ 8.9, $J_{5,6}$ 5.0, $J_{6,7}$ 8.9 Hz) are in accord with those expected for the tetraene (1).

Oxidation and Rearrangement of the Tetraene (1).—The tetraene had a lifetime of at least 1 h in dilute solution at room temperature in the absence of air. When the solution was concentrated, however, the yellow colour of the tetraene was discharged within 30 min at 0°C under vacuum. The colourless oil which remained was shown to consist mainly of an oxidation product, the ester (5). This ester was also obtained, in an overall yield of 36%, from the trienone (4) when a solution containing the tetraene (1) was kept at room temperature in air. The structure of the ester (5) was established by an independent synthesis in which the methyl ester of 2-methylphenylpropionic acid was reduced by hydrogenation over Lindlar's catalyst. The *Z*-configuration of the double bond was shown by the coupling constant (J 12 Hz) for the olefinic hydrogen atoms.

The oxidative cleavage of the tetraene (1) is probably initiated by the attack of oxygen at C-3. We speculate that the *Z*-cinnamic ester may be formed by fragmentation of the dimeric intermediate (6) (Scheme 2).

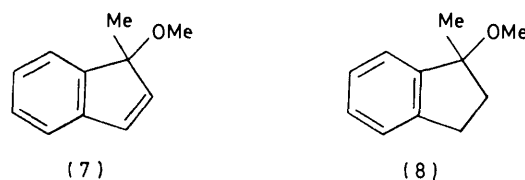
In an attempt to observe the fate of the tetraene in the absence of air, a specimen of the crude tetraene was

heated in de-gassed hexane under reflux. The yellow colour of the tetraene persisted for $2\frac{1}{2}$ h. The mixture of products was separated into two fractions by layer chromatography. The major fraction appeared to be a mixture: the mass spectrum showed an ion at m/e 200



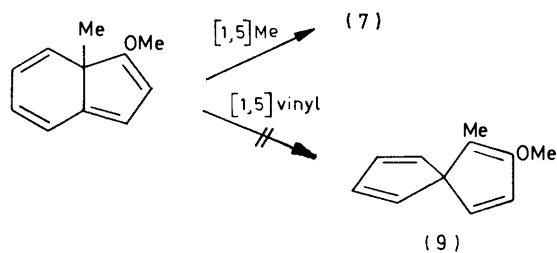
SCHEME 2

but the n.m.r. spectrum was complex, containing signals for aromatic and aliphatic hydrogen atoms. No structure was assigned but it was concluded that the solvent, hexane, was involved in the reaction. The minor fraction, an oil, was a single substance which was identified as 1-methoxy-1-methylindene (7). The n.m.r. spectrum of this product showed signals for the hydrogen atoms at C-2 and C-3 as doublets at δ 6.3 and 6.8 with a coupling constant of 6 Hz, which is that expected for a 1*H*-indene. The structure (7) was further supported by catalytic reduction of the compound and comparison of the properties of the reduction product with those of a specimen of 2,3-dihydro-1-methoxy-1-methylindene (8), which was prepared independently from the known 7 1-methylindan-1-ol.



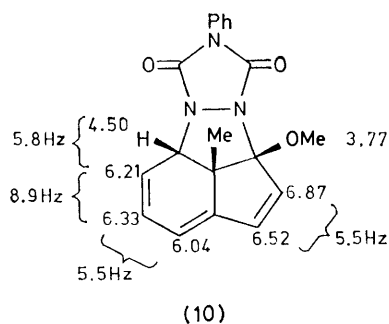
The indene (7) was also isolated later from reactions which involved heating the tetraene (1) in dimethoxyethane and from the melt pyrolysis of cycloadducts of the tetraene (as described below). It therefore seems likely that this is the major product of unimolecular thermal rearrangement of the tetraene. It can be regarded as the product of a [1,5] sigmatropic shift of a methyl group. Alternative [1,5] shifts, such as the vinyl shift to give the spiro compound (9) (Scheme 3), apparently do not take place—at least, we were unable to detect products arising from such a rearrangement—despite the fact that the reaction might have been expected to occur with a low activation energy.³

Cycloaddition Reactions.—The $3\alpha\text{H}$ -indene (1), when

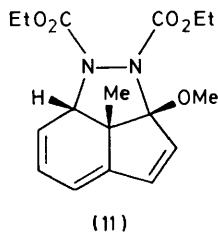


SCHEME 3

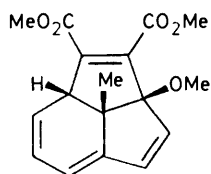
generated in dimethoxyethane, could be intercepted by the addition of 4-phenyltriazoline-3,5-dione at -18°C . The product, a 1:1 adduct, is a colourless crystalline solid which was isolated in 45% yield. It was assigned the structure (10), mainly on the basis of the ^1H n.m.r. spectrum. The assigned chemical shifts and coupling constants are as shown.



The unsaturated periphery of the tetraene has thus acted as a unit in this reaction, the process being an $[8 + 2]$ cycloaddition. We found that analogous reactions took place with diethyl azodiformate at -18°C , and with dimethyl acetylenedicarboxylate at room temperature. With diethyl azodiformate the addition was much less efficient than with *N*-phenyltriazoline-dione, and the adduct was obtained in an impure state; however, the n.m.r. spectrum showed it to have the structure (11). The crystalline adduct (12) was obtained with dimethyl acetylenedicarboxylate in a yield of 60%.



(11)



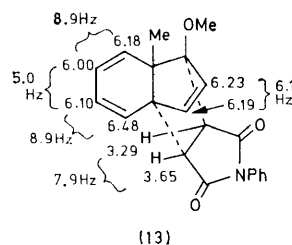
(12)

Formal $[8 + 2]$ cycloaddition has previously been observed with indolizine, the 3a-aza-analogue of compound (1), and dimethyl acetylenedicarboxylate.⁸ This thermally allowed cycloaddition thus appeared to be the preferred mode of reaction of the tetraene.

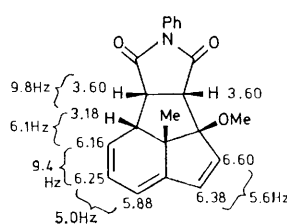
We investigated the possibility of extending this cycloaddition reaction to olefinic dienophiles, with unexpected results. Both maleic anhydride and *N*-phenylmaleimide

reacted readily with the tetraene. The reaction with maleic anhydride gave a single adduct as the initial product. This was partially purified by rapid chromatography but when a solution of the adduct was left at room temperature, another product began to appear. The n.m.r. spectrum of the product mixture did not allow definite assignments of structure to be made, although the mass spectrum showed that a 1:1 adduct was present.* A crystalline 1:1 adduct was isolated in 64% yield from the reaction with *N*-phenylmaleimide, but it was not an $[8 + 2]$ adduct. The n.m.r. spectrum showed that it was a $[4 + 2]$ adduct (13), formed by addition across the 3- and 7a-positions of the five-membered ring. The chemical shifts and coupling constants were assigned as shown: the presence of six olefinic signals clearly rules out possible alternative $[8 + 2]$ and $[4 + 2]$ structures for the adduct.

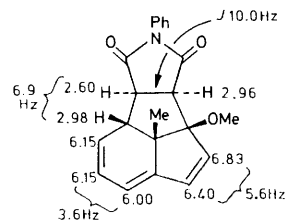
When an attempt was made to regenerate the tetraene by flash vacuum pyrolysis of the adduct (13), it was found that most of the adduct failed to sublime at $80-100^{\circ}\text{C}$, but rearranged to a mixture of two new substances. These substances, which were thermally stable and which were not interconverted in boiling xylene, were separated by layer chromatography. The more polar component was identified as the *endo*- $[8 + 2]$ adduct (14), and the less polar component as the *exo*-isomer (15), on the basis of their n.m.r. spectra; the ratio of (14) to (15) in the product mixture was 1.6:1. The assigned chemical shifts and coupling constants for the two adducts are as shown.



(13)



(14)



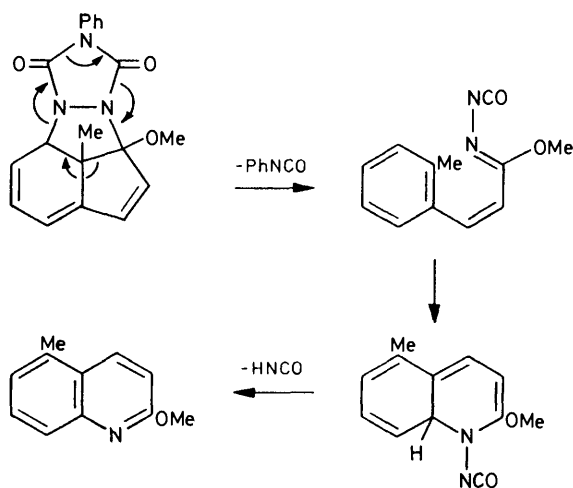
(15)

Thus it appears that, in the cycloaddition to *N*-phenylmaleimide, the $[4 + 2]$ adduct (13) is the kinetically favoured product but that it is thermally unstable and rearranges to the $[8 + 2]$ adducts above about 80°C . There is strong circumstantial evidence that this rearrangement involves dissociation and re-addition of the

* This and related reactions have subsequently been studied in more detail (R. McCague) and the results will be reported separately. The configurations shown for the adducts (13), (14), and (15) are based in part on this further work.

components. The major factor supporting this view is that there are two products of rearrangement which are not interconvertible and which are therefore being formed independently. This observation incidentally also indicates that there is little preference for *endo*- over *exo*-addition in the [8 + 2] process, the ratio of adducts being 1.6 : 1, whereas in the [4 + 2] process only the *endo*-adduct is formed. Another observation which favours the hypothesis of a dissociation-recombination mechanism is that the products which did sublime in the attempted flash pyrolysis were those expected for dissociation: *N*-phenylmaleimide and the indene (7). It remains to be established whether [4 + 2] addition is the kinetically favoured process with other olefinic dienophiles. A limitation is the low thermal stability of the tetraene (1): for example, it failed to react with phenyl vinyl sulphoxide even in boiling dimethoxyethane, the only product being the indene (7).

Thermolysis of the *N*-Phenyltriazolinedione Adduct (10).—This adduct was also subjected to flash vacuum pyrolysis in an attempt to regenerate the tetraene (1) in the vapour phase and thus to study its mode of rearrangement. In this objective we were unsuccessful because, although the adduct sublimed and partly decomposed when its vapour was passed through a tube heated to 600 °C, it did not revert to its original components. Instead, the major product was a nitrogen-containing substance which is tentatively identified as 2-methoxy-5-methylquinoline (16). The basis of this structural assignment was a comparison of the u.v. and n.m.r. spectra of the product with those of a specimen of the known⁹ 2-methoxyquinoline, which were closely similar. A possible route to this product, involving the fragmentation of the triazolinedione ring as the first step, is shown in Scheme 4.



Conclusions.—We have developed a viable route to the tetraenol ether (1) which is, in principle, extendible to the preparation of other 3*aH*-indenes. We have shown that the tetraene (1) can undergo both [4 + 2] and [8 + 2] cycloadditions and that, rather surprisingly, the major

pathway for thermal rearrangement appears to involve a [1,5] methyl shift rather than a vinyl shift. The presence of a methoxy-substituent on the periphery of the tetraene is, of course, likely to have a considerable influence on the properties of the 3*aH*-indene system: it would clearly be desirable to prepare derivatives without this substituent, or with other types of substituents in addition. In following papers we will describe other reaction sequences designed to prepare different 3*aH*-indenes.

EXPERIMENTAL

All n.m.r. spectra were recorded for solutions in CDCl₃ with tetramethylsilane as the internal standard. ¹H n.m.r. spectra were obtained using a Perkin-Elmer R34 spectrometer at 220 MHz; ¹³C spectra were recorded using a Varian XL-100 spectrometer at 25.2 MHz. Mass spectra were recorded on an A.E.I. MS12 instrument at 70 eV using a direct insertion probe; high resolution spectra giving accurate mass information were obtained on a MS 902 instrument coupled to a Ferranti Argos 500 computer. Solvents used for the generation of anions were dried by distillation from lithium aluminium hydride. Petrol refers to the fraction b.p. 60–80 °C.

2,3,5,7a-Tetrahydro-7a-methyl-1*H*-inden-1-one (2).—Potassium (15.7 g, 0.4 mol) was added in small pieces, with stirring, to a solution of indan-1-one (21.2 g, 0.16 mol), dry *t*-butyl alcohol (30.4 cm³, 0.32 mol), and dry tetrahydrofuran (130 cm³) in ammonia (1 l) at –78 °C. Anhydrous lithium bromide (34.3 g, 0.39 mol) in dry tetrahydrofuran (150 cm³) was then added, followed after 0.5 h by iodomethane (50 cm³, 0.81 mol) and 50% aqueous tetrahydrofuran (150 cm³). The ammonia was allowed to evaporate and water (1 l) added. The aqueous solution was extracted with ether (3 × 100 cm³) and the combined extracts were washed with brine, dried, and evaporated to leave a mobile oil. Column chromatography [silica (600 g); petrol-ether 19 : 1] gave (i) 2,3,5,7a-tetrahydro-2,7a-dimethyl-1*H*-inden-1-one (3) (1.33 g, 6%), b.p. 72–74 °C at 0.16 mmHg; ν_{\max} 1 730 and 1 680 cm⁻¹; δ 1.05 (3 H, d, *J* 8.8 Hz, Me-2), 1.13 (3 H, Me-7a), 2.18 (1 H, d, *J* 14.2 Hz, H-3), 2.62–2.69 (3 H, m, 2 H-5 + H-2), 3.0 (1 H, m, H-3'), 5.72 (1 H, m, H-4), 5.80 (1 H, m, H-6), and 5.95 (1 H, dd, H-7). Reaction of the ketone with 2,4-dinitrophenylhydrazine in ethanolic hydrochloric acid gave the 2,4-dinitrophenylhydrazone (67%), m.p. 183–185 °C (from dichloromethane-petrol) (Found: C, 59.4; H, 5.4; N, 16.2. C₁₇H₁₈N₄O₄ requires C, 59.65; H, 5.3; N, 16.4%). (ii) A second fraction from the column consisted of a mixture (1.77 g) of the ketones (2) and (3). (iii) Further elution gave 2,3,5,7a-tetrahydro-7a-methyl-1*H*-inden-1-one (2)⁵ (11.44 g, 48%) as a mobile oil; ν_{\max} 1 730 and 1 635 cm⁻¹; δ 1.10 (3 H, Me-7a), 2.25 (1 H, m, H-3), 2.55 (1 H, m, H-3') 2.65 (4 H, m, 2 H-2 + 2 H-5), 5.72br (1 H, H-4), 5.82 (1 H, m, H-6), and 5.95 (1 H, d, H-7); 2,4-dinitrophenylhydrazone (55%), m.p. 156.5–158 °C (from dichloromethane-petrol) (Found: C, 58.25; H, 5.2; N, 17.2. C₁₆H₁₆N₄O₄ requires C, 58.5; H, 4.9; N, 17.1%).

5,7a-Dihydro-7a-methyl-1*H*-inden-1-one (4).—A solution of the dienone (2) (3.5 g, 23.6 mmol) in dry tetrahydrofuran (15 cm³) was cooled to –78 °C under nitrogen. A solution of lithium di-isopropylamide, prepared at 0 °C from di-

isopropylamine (5.0 cm³, 35.7 mmol) and butyl-lithium (1.5M; 24.0 cm³, 36.0 mmol) in tetrahydrofuran (30 cm³), was added dropwise, giving an orange-red solution. After 30 min a mixture of diphenyl diselenide (4.4 g, 14.1 mmol) and bromine (0.75 cm³, 14.1 mmol) in tetrahydrofuran (20 cm³) was added dropwise. The solution was stirred at -78 °C for 5 min then at room temperature for 30 min. It was poured into hydrochloric acid (0.5M; 400 cm³) and the acid solution was washed with ether (3 × 50 cm³). The combined ether extracts were washed with brine, dried, and evaporated to leave an orange-brown oil. A solution of the oil in tetrahydrofuran (100 cm³) was cooled to 0 °C and aqueous hydrogen peroxide (30%; 13 cm³, 105 mmol) was added dropwise. The solution was stirred at room temperature for 2 h, diluted with water, and extracted with ether to yield an oil. Purification by flash column chromatography (silica; petrol-ether 9 : 1) gave first the starting dienone (0.54 g, 15%) and then the *trienone* (4) (1.24 g, 36%) as a pale yellow mobile oil, ν_{\max} 1 695 cm⁻¹; λ_{\max} (EtOH) 286.5 nm (log ϵ 3.95); δ 1.20 (3 H, Me-7a), 2.88 (2 H, m, 2 H-5), 5.87 (1 H, m, H-6), 5.98 (1 H, d, J 4.9 Hz, H-2), 6.05 (1 H, m, H-4), 6.17 (1 H, dd, H-7), and 7.68 (1 H, d, J 4.9 Hz, H-3) (decoupling gave $J_{6,7}$ 8.8 Hz); m/e 146 (M^+). The ketone was converted into its 2,4-dinitrophenylhydrazone (54%), m.p. 179.5–181.5 °C (from dichloromethane-petrol) (Found: C, 58.7; H, 4.0; N, 17.3. C₁₆H₁₄N₄O₄ requires C, 58.9; H, 4.3; N, 17.2%).

3-Methoxy-3-methyl-3aH-indene (1).—The trienone (4) (0.45 g, 3.1 mmol) in dry ether (4 cm³) was added dropwise to a suspension of oil-free potassium hydride (0.8 g, 4.0 mmol of 20% dispersion in oil) and 18-crown-6 (0.90 g, 3.4 mmol) in dry ether (5 cm³) at -18 °C under nitrogen. The purple mixture was maintained at -18 °C for 30 min and methyl fluorosulphonate (0.33 cm³, 4.05 mmol) was added. After 5 min the ether was removed in vacuo while the reaction flask was kept at -18 °C. The residue was suspended in cold ether-pentane (1 : 10) and the mixture applied to an alumina column maintained at -78 °C under nitrogen. The column was eluted under positive nitrogen pressure (applied by means of a flow controller¹⁰). About 100 cm³ of ether-pentane (1 : 10) was required to elute the yellow product. The solution contained 3-methoxy-3a-methyl-3aH-indene (0.03 g, 6%), λ_{\max} 219, 252, and 388 nm. The solution was rapidly evaporated and the residue was immediately redissolved in carbon tetrachloride to allow a n.m.r. spectrum to be recorded: δ (CCl₄) 1.26 (3 H, Me-3a), 3.71 (3 H, OMe), 4.88 (1 H, d, $J_{1,2}$ 2.2 Hz, H-2), 5.77 (2 H, 2 × dd, $J_{5,6}$ 5.0 Hz, H-5 + H-6), 5.98 (1 H, d, J 2.2 Hz, H-1), and 6.18 (2 H, dd, $J_{4,5}$ 8.9, $J_{6,7}$ 8.9 Hz, H-4 + H-7). The yellow colour was discharged when the solvent was removed from this sample at 0 °C.

In a second experiment, chromatography was performed at -10 °C with carbon tetrachloride as the eluant. This gave a slightly contaminated specimen of the enol ether. Chromatography at room temperature gave material which was substantially contaminated with a second component, subsequently identified as the ester (5) (see later).

Reactions of 3-Methoxy-3a-methyl-3aH-indene.—(a) *Cyclo-addition.* (i) *With 4-phenyltriazoline-3,5-dione.* The trienone (4) (0.545 g, 3.7 mmol) in dry dimethoxyethane (2 cm³) was added dropwise to a suspension of oil-free potassium hydride (1.0 g, 5.0 mmol of 20% dispersion in oil) and 18-crown-6 (1.1 g, 4.2 mmol) in dry dimethoxyethane (3 cm³) at -18 °C under nitrogen. After the deep purple mixture had been kept at -18 °C for 30 min, methyl

fluorosulphonate (0.35 cm³, 4.3 mmol) was added, followed after 5 min by a solution of 4-phenyltriazoline-3,5-dione (0.7 g, 4.0 mmol) in dimethoxyethane (5 cm³). This solution was added dropwise until a persistent pink colouration was observed. The mixture was then allowed to reach room temperature and filtered, and the filtrate was evaporated. Flash column chromatography (silica; ether-petrol 1 : 1) gave the *adduct* (10) [0.56 g, 45% from (3)] as colourless crystals, m.p. 101–102 °C (from ether-petrol) (Found: C, 67.8; H, 5.15; N, 12.8. C₁₉H₁₇N₃O₃ requires C, 68.1; H, 5.1; N, 12.5%); ν_{\max} (CHCl₃) 1 750 and 1 695 cm⁻¹; λ_{\max} (EtOH) 301 nm (log ϵ 4.08); δ 1.09 (3 H, Me-7b), 3.77 (3 H, OMe), 4.50 (1 H, d, $J_{7,7a}$ 5.8 Hz, H-7a), 6.04 (1 H, d, $J_{5,6}$ 5.55 Hz, H-5), 6.21 (1 H, dd, $J_{6,7}$ 8.9, $J_{7,7a}$ 5.8 Hz, H-7), 6.38 (1 H, dd, $J_{5,6}$ 5.55, $J_{6,7}$ 8.9 Hz, H-6), 6.52 (1 H, d, $J_{3,4}$ 5.55 Hz, H-4), 6.87 (1 H, d, $J_{3,4}$ 5.55 Hz, H-3), and 7.3–7.5 (5 H, m).

(ii) *With dimethyl acetylenedicarboxylate.* To a solution of the enol ether (1) in dimethoxyethane (50 cm³), prepared as before from the trienone (4) (2.06 g, 14.1 mmol) at -18 °C under nitrogen was added dimethyl acetylenedicarboxylate (2.1 cm³, 17.0 mmol) in dimethoxyethane (10 cm³). The solution was stirred at room temperature for 30 min, then filtered, and the filtrate was evaporated to leave an oil. Flash chromatography (silica; ether-petrol 1 : 2) gave *dimethyl 7a,7b-dihydro-2a-methoxy-7b-methyl-2aH-cyclopent[c,d]indene-1,2-dicarboxylate* (12) (2.55 g, 60%) as colourless crystals, m.p. 94–95 °C (from petrol) (Found: C, 67.5; H, 6.2. C₁₇H₁₈O₅ requires C, 67.55; H, 6.0%); ν_{\max} (KBr) 1 728 and 1 715 cm⁻¹; λ_{\max} (EtOH) 286.5 nm (log ϵ 4.06); δ_{H} 0.93 (3 H, Me-7b), 3.36 (3 H, OMe), 3.59 (1 H, dd, $J_{6,7a}$ 1.1, $J_{7,7a}$ 6.55 Hz, H-7a), 3.74 (3 H, CO₂Me), 3.76 (3 H, CO₂Me), 5.83 (1 H, dd, $J_{6,7}$ 9.05, $J_{7,7a}$ 6.55 Hz, H-7), 5.90 (1 H, d, $J_{5,6}$ 5.3 Hz, H-5), 6.15 (1 H, ddd, $J_{5,6}$ 5.3, $J_{6,7}$ 9.05, $J_{6,7a}$ 1.1 Hz, H-6), 6.40 (1 H, d, $J_{3,4}$ 5.82 Hz, H-4), and 6.49 (1 H, d, $J_{3,4}$ 5.82 Hz, H-3); δ_{C} 15.10 (CH₃-7b), 48.87 (C-7b), 49.78 (CO₂CH₃), 49.98 (CO₂CH₃), 52.05 (OCH₃), 54.06 (C-7a), 100.25 (C-2a), 113.96 (d), 120.21 (d), 125.98 (d), 134.04 (d), 136.84 (C-4a), 138.28 (d), 147.26 (C-1), 148.88 (C-2), 164.85 (CO₂Me) and 165.03 (CO₂Me); m/e 302 (M^+).

(iii) *With N-phenylmaleimide.* *N*-Phenylmaleimide (0.2 g, 1.16 mmol) in dimethoxyethane (2 cm³) was added to a solution of the tetraene (1) [from the trienone (4) (0.17 g, 1.16 mmol)] in dimethoxyethane (6 cm³) at -18 °C under nitrogen. After 15 min at -18 °C all the tetraene had been consumed (t.l.c.). The mixture was filtered and the filtrate was evaporated. Flash chromatography gave the *adduct* (13) (0.248 g, 64%) as colourless crystals, m.p. 91–93 °C (from cyclohexane) (Found: C, 75.5; H, 6.1; N, 4.25. C₂₁H₁₉NO₃ requires C, 75.65; H, 5.7; N, 4.2%); ν_{\max} (KBr) 1 767w and 1 705s cm⁻¹; δ 0.88 (3 H, Me-3a), 3.29 (1 H, d, J 7.9 Hz, H-8), 3.65 (1 H, d, J 7.9 Hz, H-9), 3.70 (3 H, OMe), 6.0 (1 H, dd, J 5.0 and 8.9 Hz, H-5), 6.1 (1 H, dd J 5.0 and 8.9 Hz, H-6), 6.18 (1 H, d, J 8.9 Hz, H-4), 6.19 (1 H, d, J 6.1 Hz, H-1), 6.23 (1 H, d, J 6.1 Hz, H-2), and 6.48 (1 H, d, J 8.9 Hz, H-7); m/e 333 (M^+).

(iv) *With other dienophiles.* Reaction with diethyl azodicformate in dimethoxyethane gave a 1 : 1 adduct as a yellow oil (24%) which was isolated by flash chromatography in an impure state. The n.m.r. spectrum of the compound was consistent with the structure (11): δ 1.05 (3 H, Me-7b), 1.1–1.5 (ca. 12 H, m), 3.1 (ca. 3 H, m), 3.51 (3 H, OMe), 4.0–4.4 (ca. 8 H, m), 5.9 (1 H, d, $J_{5,6}$ 5.55 Hz, H-5), 6.0 (1 H, m, H-7), 6.2 (1 H, dd, $J_{5,6}$ 5.55, $J_{6,7}$ 8.9 Hz,

H-6), 6.41 (1 H, d, $J_{3,4}$ 5.55 Hz, H-4), and 6.62 (1 H, m, H-3); m/e 334 (M^+). Attempts to purify the substance by p.l.c. were not successful.

Reaction with maleic anhydride gave, after flash chromatography, a 1:1 adduct (45%), m/e 258 (M^+), which was unstable and could not be characterised. Methyl propiolate gave a complex mixture of products. No reaction was observed with phenyl vinyl sulphoxide or with benzyne (from benzenediazonium-2-carboxylate).

(b) *Oxidation by air.* A solution of the enol ether (1) in dry ether, obtained from the trienone (4) (0.34 g, 2.3 mmol) was evaporated at -18°C and the residue was mixed with carbon tetrachloride. The slurry was filtered rapidly and the filtrate was applied, under pressure, to a short alumina column. The yellow eluate contained the enol ether (1) and a more polar compound in 2:1 ratio (by n.m.r.). After 4 h at 20°C the solution was nearly colourless. Evaporation gave (*Z*)-methyl 2-methylcinnamate (5) (0.14 g, 36%) as an oil; ν_{max} 1 718s and 1 630m cm^{-1} ; δ 2.28 (3 H, Me-2), 3.62 (3 H, CO_2Me), 6.05 (1 H, d, J 12 Hz), and 7.1—7.4 (5 H, m, $\text{ArH} + \text{ArCH}=\text{C}$). An authentic specimen was prepared from 2-methylphenylpropionic acid (0.3 g) * by conversion into the methyl ester with diazomethane (0.2 g, 62%) followed by hydrogenation over Lindlar's catalyst (0.05 g) in ethyl acetate containing quinoline; this gave the *Z*-cinnamic ester as an oil (0.16, 79%), b.p. $85\text{--}88^\circ\text{C}$ at 0.25 mmHg (Found: C, 75.0; H, 6.9. $\text{C}_{11}\text{H}_{12}\text{O}_2$ requires C, 75.0; H, 6.8%).

(c) *Thermal rearrangement in hexane.* A solution of the tetraene (1) was prepared in ether (5 cm^3) from the trienone (4) (0.26 g, 1.8 mmol). The ether was removed at -18°C and the residue was stirred with dry, degassed hexane (10 cm^3). The mixture was filtered at -15°C under nitrogen and the filtrate was heated under reflux under nitrogen for 2.5 h, after which time all the tetraene (1) had been consumed. A black tarry solid was removed by filtration and the filtrate was evaporated to leave a pale yellow oil (0.18 g). P.l.c. gave 1-methoxy-1-methyl-1H-indene (7) (9 mg, 3%) as a mobile oil, δ 1.50 (3 H, Me), 2.92 (3 H, OMe), 6.15 (1 H, d, J 6 Hz, H-3), 6.68 (1 H, d, J 6 Hz, H-2), and 7.1—7.4 (4 H, m); m/e 160 (M^+), 145, 130, 129, and 128. Hydrogenation (H_2 , Pd-C) gave 2,3-dihydro-1-methoxy-1-methyl-1H-indene (8) (83%), the structure of which was established by an independent synthesis (see later).

A second band isolated from the chromatography plate was an oil (31 mg), δ 0.95 (3 H, t), 1.04 and 1.31 (together, 6 H), 1.5 (2 H, m), 2.2—2.5 (2 H, m), 2.27 and 2.32 (together, 2 H), 5.35 (t) and 5.9 (t) (together, 1 H), 7.15 (3 H, m), and 7.35 (m) and 7.55 (d) (together, 1 H); m/e 200, 185, 172, and 171.

2,3-Dihydro-1-methoxy-1-methyl-1H-indene (8).—1-Methylindan-1-ol was prepared (66%) from indan-1-one and methylmagnesium iodide as yellow crystals, m.p. $53\text{--}55^\circ\text{C}$ (lit.⁷ $56\text{--}57^\circ\text{C}$). The alcohol (2.5 g, 16.9 mmol) in dry tetrahydrofuran (10 cm^3) was added to a suspension of sodium hydride (0.6 g, 25.3 mmol) in tetrahydrofuran (20 cm^3) at 0°C . After 1 h, iodomethane (3.5 g, 25 mmol) was added and the mixture was stirred at 0°C for a further 1 h. It was poured into water (100 cm^3) and the product was extracted with ether ($3 \times 10 \text{ cm}^3$). The ethereal solution was washed with brine, dried, and evaporated to give a dark oil. Flash chromatography (silica; petrol) gave compound (8) (0.88 g), a small specimen of which was

* This was prepared from (*E*)-2-methylcinnamic acid¹¹ by the general method described in ref. 12.

purified by p.l.c. 2,3-Dihydro-1-methoxy-1-methyl-1H-indene (8) showed δ 1.52 (3 H, Me), 1.9—3.0 (4 H, m), 3.08 (3 H, OMe), and 7.26 (4 H, m); m/e 162 (M^+), 147, and 130.

Thermal Reactions of Adducts.—(a) *The N-phenyltriazolinedione adduct (10).* The adduct (0.40 g, 1.2 mmol) was subjected to flash vacuum pyrolysis by sublimation at 100°C and 0.03 mmHg and passage of the vapour through a tube at 600°C on to a condenser held at -78°C . The product was a brown oil (0.12 g); starting material (0.19 g, 47%) was also recovered. P.l.c. gave a yellow oil which was tentatively identified as 2-methoxy-5-methylquinoline (16) (0.014 g, 13% based on starting material consumed); ν_{max} (film) 1 605, 1 400, 1 320, 1 270, and 1 245 cm^{-1} ; λ_{max} (EtOH) 207 (log ϵ 4.29), 224 (4.10), 228 (4.14), 237 (4.18), 268 (3.65), 274 (3.68), 284 (3.61), 298 (3.29), 306 (3.23), 312 (3.30), 319 (3.21), and 325 nm (3.29); δ 2.60 (3 H, Me), 4.05 (3 H, OMe), 6.90 (1 H, d, J 8.9 Hz, H-3), 7.20 (1 H, d, J 7.2 Hz, H-6), 7.50 (1 H, dd, J 7.2 and 7.8 Hz, H-7), 7.70 (1 H, d, J 7.8 Hz, H-8), and 8.15 (1 H, d, J 8.9 Hz, H-4); m/e 173, 172, 143, 142, and 141. These data were compared with those for a specimen of 2-methoxyquinoline;⁹ ν_{max} 1 610 and 1 605 cm^{-1} ; λ_{max} (EtOH) 210 (log ϵ 4.51), 221 (4.48), 225 (4.48), 232 (4.31), 236 (4.23), 258 (3.28), 266 (3.22), 277 (3.01), 297 (2.95), 303 (3.05), 309 (3.24), 315 (3.50), and 322 nm (3.30); δ 3.96 (3 H, OMe), 6.75 (1 H, d, J 8.9 Hz, H-3), 7.25 (1 H, td, J 7.2 and 1.1 Hz, H-5), 7.55 (2 H, m, H-6 and H-7), 7.75 (1 H, d, J 8.9 Hz, H-4), and 7.82 (1 H, dd, J 8.3 and 1.1 Hz, H-8).

(b) *The N-phenylmaleimide adduct (13).* The adduct (0.3 g, 0.9 mmol) was sublimed at $80\text{--}100^\circ\text{C}$ and 8×10^{-3} mmHg and the vapour was passed through a tube at 560°C on to a condenser at -78°C . The product was a mixture of 1-methoxy-1-methyl-1H-indene (5 mg, 3%) and *N*-phenylmaleimide (50 mg, 31%). The solid (0.189 g) which failed to sublime was separated by p.l.c. (silica; ether-hexane 1:1) into a mixture of two components. These were assigned the structures (14) and (15), respectively. The more polar component, the *endo*-adduct (14) (0.100 g, 33%) had a decomp. point of 180°C (Found: M^+ , 333.1376. $\text{C}_{21}\text{H}_{19}\text{NO}_3$ requires M , 333.1365); ν_{max} 1 715, 1 705, and 1 695 cm^{-1} ; δ 0.89 (3 H, Me-7b), 3.18 (1 H, dd, $J_{1,7a}$ 9.8, $J_{7,7a}$ 6.1 Hz, H-7a), 3.6 (5 H, m, OMe, H-1 and H-2), 5.88 (1 H, d, $J_{5,6}$ 5.0 Hz, H-5), 6.16 (1 H, dd, $J_{6,7}$ 9.4, $J_{7,7a}$ 6.1 Hz, H-7), 6.25 (1 H, dd, $J_{5,6}$ 5.0, $J_{6,7}$ 9.4 Hz, H-6), 6.38 (1 H, d, $J_{3,4}$ 5.6 Hz, H-4), 6.60 (1 H, d, $J_{3,4}$ 5.6 Hz, H-3), and 7.3—7.4 (5 H, m). The *exo*-adduct (15) (0.062 g, 21%), had m.p. $146\text{--}147^\circ\text{C}$ (from dichloromethane-pentane) (Found: M^+ , 333.1356. $\text{C}_{21}\text{H}_{19}\text{NO}_3$ requires M , 333.1365); ν_{max} 1 715, 1 705, and 1 695 cm^{-1} ; δ 0.88 (3 H, Me-7b), 2.60 (1 H, dd, $J_{1,2}$ 10, $J_{1,7a}$ 6.9 Hz, H-1), m, H-2 and H-7a), 3.54 (3 H, OMe), 6.00 (1 H, m, H-5), 6.15 (2 H, m, H-6 and H-7), 6.40 (1 H, d, $J_{3,4}$ 5.6 Hz, H-4), 6.83 (1 H, d, $J_{3,4}$ 5.6 Hz, H-3), and 7.25—7.50 (5 H, m). Irradiation at δ 6.15 caused the multiplet at δ 2.97 to collapse to a pair of doublets at δ 2.96 (1 H, d, $J_{1,2}$ 10 Hz, H-2), and 2.98 (1 H, d, $J_{1,7a}$ 6.9 Hz, H-7a). Irradiation at δ 2.97 caused the signal at δ 6.00 to appear as a poorly resolved dd, J 3.6 and 1.9 Hz, and it simplified the multiplet at δ 6.15.

Both adducts were recovered after being treated separately in xylene at 140°C for 5 h; no change or interconversion was detected by t.l.c.

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