Routes to 3a*H*-Indenes. Deprotonation and Methylation of some Indenones Bearing Ring Junction Substituents

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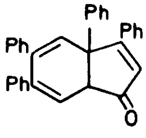
The trienones (1), (2), and (3) have been converted into the corresponding enolate anions by reaction with potassium hydride below −10 °C. Methyl fluorosulphonate was added to each solution: with the trienones (1) and (3), transient 3a*H*-indenes (4a) and (14) were detected and were intercepted by reaction with 4-phenyltriazolinedione. The tetraenol ether (4a) was also intercepted by *N*-phenylmaleimide. In all cases the products were the result of [8 + 2] rather than of [4 + 2] addition to the 3a*H*-indenes. The enolates and enol ethers derived from the trienones (1) and (2) were found to rearrange, by a [1,5] shift of the ring junction phenyl substituent, at or below room temperature.

We have described a preparation of a 3a*H*-indene derivative based on the introduction of a ring junction substituent into indan-1-one.[1] There were already a few compounds in the literature, which not only bore such a substituent but also were at the correct oxidation state for conversion directly into 3a*H*-indene derivatives by deprotonation and *O*-methylation. We identified three such compounds, the ketones (1),[2] (2),[3] and (3),[4] and undertook to repeat their preparation and to attempt their conversion into the corresponding methyl enol ethers.



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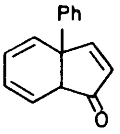

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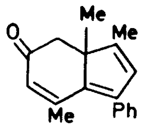

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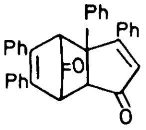
Generation and Reactions of the Enol Ether (4a).—The trienone (1) was prepared by the literature procedure,[2] in which the dimer (5) of 3,4-diphenylcyclopentanedione is thermally decarbonylated to give a mixture of the trienone and an isomeric indanone, (6). This mixture was more efficiently separated by column chromatography than by the literature procedure of fractional crystallisation.



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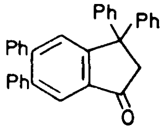

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The trienone was converted into the enolate anion (7) by reaction with sodium hydride or with potassium hydride in dimethoxyethane at −10 °C. With potassium hydride the deep blue-purple colour of the anion is produced almost instantaneously but with sodium hydride a longer period (10 min to 1 h) is required for complete reaction. The anion was also generated when lithium di-isopropylamide was used as the base, but subsequent reactions were much less clean. Freshly distilled methyl fluorosulphonate was added to the solution of the enolate anion (7) and the colour immediately changed to deep red. When the reaction mixture was allowed to remain at room temperature, the colour faded over a period of *ca.* 1.5 h. From the solution, the enol ether (8a) was isolated in yields of up to 88%.‡ The structure of the enol ether (8a) was established from its spectra: there was no carbonyl absorption in the i.r., and the ^{1}H n.m.r. contained signals at δ 3.98 for the *O*-methyl group and at 5.72 for the single vinylic hydrogen atom. The enol ether was converted into the indanone (6) when heated with potassium hydrogensulphate in aqueous dioxan.

The proposed reaction sequence is shown in the Scheme. *O*-Methylation gives the intermediate red 3a*H*-indene derivative (4a) which isomerises at room temperature to the enol ether (8a) by a [1,5] shift of the bridgehead phenyl substituent. Earlier work had established that the trienone (1) could be isomerised to the indanone (6) by heat,[2] by treatment with acid,[5] or by base.[6] These reactions were rationalised by proposing a [1,5] phenyl shift, analogous to that shown in the Scheme, in the enolate anion (7) or in the corresponding enol, but direct evidence for the presence of these intermediates was lacking.[6] We therefore sought to provide such evidence for the intermediacy of the enol ether (4a).

To the red solution obtained by methylation of the enolate anion (7), a solution of 4-phenyltriazoline-3,5-dione was added. The reaction was rapid, and a 1 : 1 adduct was isolated in 79% yield; none of the enol ether (8a) was detected. The structure (9) was assigned to the adduct on the basis of its ^{1}H and ^{13}C n.m.r. spectra. The ^{1}H n.m.r. spectrum shows three one-proton singlets at δ 5.33, 5.89, and 6.74 which were assigned to the hydrogen atoms attached to C-7a, C-3, and C-5 respectively. This spectrum does not completely exclude isomeric structures for the adduct, however. The ^{13}C n.m.r. spectrum contains signals at 57.76, 64.03, 65.09, and 81.47 p.p.m. which were assigned as shown in the diagram. These signals are not consistent with other possible structures for a 1 : 1 adduct: in particular, the two possible [4 + 2] cycloadducts of the tetraenol ether (4a) and 4-phenyltriazolinedione are excluded.

The intermediate (4a) was also intercepted with *N*-

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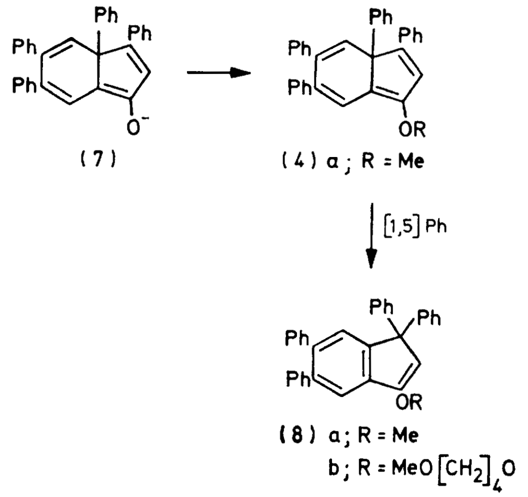
‡ When tetrahydrofuran was used as solvent the yield of the enol ether (8a) was much lower, and a second enol ether [8b; R = $(CH_2)_4OMe$] was also formed. It is likely that tetrahydrofuran is *O*-methylated by methyl fluorosulphonate, the oxonium cation being intercepted by the anion (7) to give the tetraenol ether [4b; R = $(CH_2)_4OMe$] and then, by rearrangement (8b).



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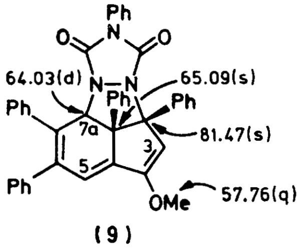
phenylmaleimide. The reaction took place slowly at room temperature and the major product was therefore the rearranged ether (8a), but a 1 : 1 adduct was also isolated in 18% yield. The ^{1}H n.m.r. spectrum of this adduct is consistent with structure (10), the key feature being the presence of three coupled one-proton signals at δ 4.05 (dd), 4.32 (d), and 4.78 (d), which were assigned as shown.

Although the 3a*H*-indene (4a) was too unstable to allow its isolation, these experiments establish its presence in solution. They also show that the system has a tendency to undergo [8 + 2] cycloaddition involving all of the peripheral π-electrons, rather than [4 + 2] addition. [8 + 2] Adducts have also been obtained from another 3a*H*-indene, 3-methoxy-3a-methyl-3a*H*-indene.[1]

Attempted O-*Methylation of the Trienone* (2).—The trienone (2) had previously been prepared from cyclooctatetraene di-anion by its reaction with methyl benzoate followed by treatment of the adduct with thionyl chloride, which gave the bicyclic chloride (11; X = Cl). This was hydrolysed to the alcohol (11; X = OH) which gave the ketone (2) on oxidation.[3] We repeated this sequence and attempted to carry out an *O*-methylation by a method similar to that successfully used for the analogous ketone (1). Potassium hydride alone was not a sufficiently strong base to produce the enolate anion of the ketone (2), but in the presence of an equivalent of 18-crown-6 the dark red anion was produced at −18 °C. Addition of methyl fluorosulphonate at −18 °C resulted in discharge of the red colour and the formation of a yellow solution. 4-Phenyltriazolinedione was added to the solution below −10 °C in an attempt to intercept the 3a*H*-indene, but in this case no adduct could be detected. The major product, which was isolated as a yellow oil in 25% yield, was identified as the indanone (12). Thus, no evidence was obtained for the intermediacy of a tetraenol ether corresponding to the tetraphenyl derivative (4a). It is probable that the indanone (12) is a hydrolysis product derived from a dimethylated compound, (13), since in an experiment involving the use of lithium di-isopropylamide as the base, a product was isolated in low yield which was tentatively identified as (13). The phenyl migration is clearly a process of low activation energy in this system: * indeed, the trienone (2) had previously been observed to rearrange readily to 3-phenylindan-1-one when heated with acid.[3]



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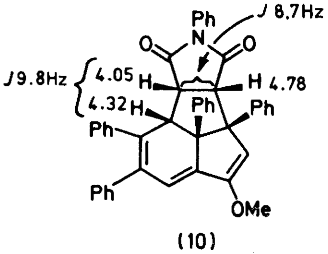

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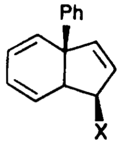

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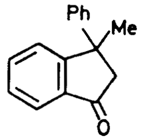

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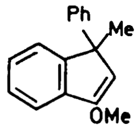

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Generation and Interception of the Enol Ether (14).—The preparation of the trienone (3) was carried out using the route described by Mellor and his co-workers.[4,7] By employing slightly modified reaction conditions for the last stage of the literature sequence, the reported yield for this stage was improved to 51%; compound (3) was then available in 5—7 g lots starting from 60 g of benzaldehyde.

It was again found necessary to use potassium hydride and a full equivalent of 18-crown-6 in order to produce the enolate anion of the ketone (3) efficiently. The deep purple solution of the anion was quenched with methyl fluorosulphonate, and the resulting solution was shown by t.l.c. to contain only one non-polar yellow component. When the solution was evaporated and the residue redissolved in carbon tetrachloride, only the starting ketone (3) was detected, and it could be recovered in high yield. It seems likely, therefore, that the transient yellow product is the enol ether (14), and that this is hydrolysed during the attempt at isolation. Significantly, no shift of the bridgehead methyl group was observed, in contrast to the ready phenyl shifts which took place in the corresponding experiments with ketones (1) and (2).

As before, 4-phenyltriazolinedione was added to the solution containing the transient yellow component in an attempt to intercept it. A single 1 : 1 adduct was isolated in 13% yield as an oil. On the basis of the ^{1}H n.m.r. spectrum the structure (15) was assigned to this adduct: the chemical shifts and coupling constants are

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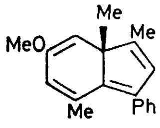
* Other attempts were made to generate 3a-phenyl-3a*H*-indene from related compounds (W. R. Jackson, F. D. King). Flash pyrolysis of the acetate (11; X = OAc) gave a mixture (1 : 10) of 1-phenyl- and 3-phenylindene in 86% yield, and treatment of the chloride (11; X = Cl) with lithium di-isopropylamide or lithium tetramethylpiperidide gave a mixture of dimers of phenylindenes, the structures of which were not elucidated.

shown. The isomeric structure (16) cannot be completely ruled out on the basis of this n.m.r. spectrum. The adduct shows a $\lambda_{max.}$ at 311 nm (log ε 4.90) in the u.v. spectrum, and this also supports the conjugated trienol ether structure (15) rather than (16). Hydrolysis of the adduct gave a mixture of two ketones: three ketones (showing different degrees of conjugation) are possible from (15), and one from (16). Structure (15) therefore appears to be the more likely.



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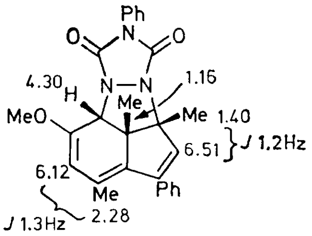

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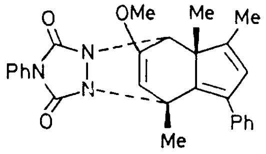

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Conclusions.—The results support our earlier assumption [1] that 3a*H*-indenes bearing a good migrating group at the bridgehead position were unlikely to be thermally stable: the instability of the enol ether (14) is evidently due to its ease of hydrolysis rather than to a tendency for the bridgehead group to migrate.

The three cycloadducts, (9), (10), and (15), which have been obtained from the reaction of the enol ether (4a) and (14), have all been assigned [8 + 2] structures. Taken in conjunction with the results described earlier,[1] this indicates that [8 + 2] addition appears to be a general feature of the chemistry of 3a*H*-indenes, and not the result of a particular pattern of substituents in the derivatives studied (for example, the methoxy-groups are at different positions in the three enol ethers which form adducts). It remains to be shown whether derivatives which lack an alkoxy-group will show the same propensity for [8 + 2] cycloaddition.

EXPERIMENTAL

For general points, see the preceding paper.

cis-3a,7a-*Dihydro*-3,3a,5,6-*tetraphenyl*-1H-*inden*-1-*one* (1).[8]—(a) 3,4-*Diphenyl*-4-*hydroxycyclopent*-2-*en*-1-*one*. Benzil (150 g, 0.71 mol) was suspended in acetone (120 cm^3, 1.6 mol) and aqueous potassium hydroxide (33%; 1.5 cm^3) was added. Once all the benzil had dissolved, more potassium hydroxide solution (37.5 cm^3) was added. The mixture was warmed at 70 °C for 0.5 h and then left to stand. The solid cake was broken up and was filtered off. It was washed with hot water and with ether and was then crystallised to give the cyclopentenone (104.5 g, 59%) as yellow crystals, m.p. 149—151 °C (from toluene) (lit.,[8] 147 °C).

(b) 3,4-*Diphenylcyclopenta*-2,4-*dien*-1-*one dimer* (5). The hydroxyenone (100 g, 0.4 mol) was stirred in a mixture of glacial acetic acid (120 cm^3) and concentrated sulphuric acid (20 cm^3) and the mixture was heated nearly to boiling for 10 min. It was then cooled and the fawn crystals which appeared were filtered off. Crystallisation gave the dimer (5) (83 g, 89%), m.p. 206—207 °C (from ethanol–toluene) (lit.,[2] 199—200 °C); $\nu_{max.}$ 1 760 and 1 680 cm^{-1}.

(c) *Thermolysis of the dimer* (5). The dimer (10 g, 22 mmol) was heated as a melt at 210 °C for 10 min. The cooled melt was subjected to column chromatography (silica, 250 g). Elution with ether–light petroleum (1 : 1) gave (i) 2,3-dihydro-3,3,5,6-tetraphenyl-1*H*-inden-1-one (6) (0.57 g, 6%), m.p. 172—174 °C (lit.,[2] 176 °C), $\nu_{max.}$ 1 700 cm^{-1}; δ 3.40 (2 H, H-2), 7.0—7.3 (20 H, m), 7.34 (1 H, H-7), and 7.76 (1 H, H-4); (ii) a mixture of (1) and (6) (3.5 g, 37%); and (iii) *cis*-3a,7a-dihydro-3,3a,5,6-tetraphenyl-1*H*-inden-1-one (1) (4.25 g, 45%), m.p. 165—166 °C (lit.,[2] 167 °C); $\nu_{max.}$ 1 690 cm^{-1}; δ 3.56 (1 H, d, H-7a), 5.98 (1 H, d, H-7), 6.20 (1 H, H-4), and 6.9—7.4 (21 H, m, ArH + H-2).

Generation and Interception of the Enol Ether (4a).—(a) The trienone (1) (0.4 g, 0.9 mmol) was dissolved in dry dimethoxyethane (8 cm^3) at −10 °C under nitrogen and sodium hydride (0.044 g, 1.8 mmol) was added to give a deep blue-purple solution. After 10 min, methyl fluorosulphonate (0.2 cm^3, 2.4 mmol) was added and the colour of the solution changed to a deep red. The reaction mixture was filtered and the filtrate was subjected to rapid chromatography on alumina (20 g). Elution with ether–hexane (1 : 1) was continued until all the red compound had been eluted. The u.v. spectrum of this solution showed maxima at λ 275, 321, and 345 nm. The red colour was discharged completely after 1.5 h; evaporation then gave 3-*methoxy*-1,1,5,6-*tetraphenyl*-1H-*indene* (8a) (0.253 g, 61%) as colourless crystals, m.p. 207—208 °C (from benzene–hexane) (Found: C, 90.5; H, 6.0. $C_{34}H_{26}O$ requires C, 90.6; H, 5.8%); $\nu_{max.}$ 1 615 and 1 595 cm^{-1}; δ 3.98 (3 H, OMe), 5.72 (1 H, H-2), and 7.1—7.5 (22 H, m); *m/e* 450 (M^+).

(b) A similar reaction in which potassium hydride was used as the base gave the enol ether (8a) in 88% yield.

(c) The enol ether (4a) was prepared from the trienone (1) (0.46 g, 1.1 mmol) and sodium hydride (0.04 g, 1.7 mmol) in tetrahydrofuran (10 cm^3) at −10 °C, followed by methylation with methyl fluorosulphonate (0.15 cm^{-3}, 1.8 mmol). After the red colour had faded the products were separated by layer chromatography [alumina; light petroleum–ether (3 : 1)]. This gave (i) the enol ether (8a) (0.032 g, 7%), (ii) 3-(4-*methoxybutoxy*)-1,1,5,6-*tetraphenyl*-1H-*indene* (8b) (0.03 g, 6%), m.p. 163—164 °C (from ether) (Found: C, 87.35; H, 6.8. $C_{38}H_{34}O_2$ requires C, 87.3; H, 6.6%); $\nu_{max.}$ (KBr) 1 615 and 1 595 cm^{-1}; δ 1.80 (4 H, m), 3.32 (3 H, OMe), 3.45 (2 H, t), 4.10 (2 H, t), 5.61 (1 H), and 7.05—7.45 (22 H, m), and (iii) unchanged trienone (1) (0.243 g, 53%).

(d) The trienone (1) (0.3 g, 0.7 mmol) in dimethoxyethane (8 cm^3) was treated with potassium hydride (0.2 g, 1.0 mmol) and methyl fluorosulphonate (0.1 cm^3, 1.2 mmol) as before. To the deep red reaction mixture was added freshly sublimed 4-phenyltriazoline-3,5-dione (0.13 g, 0.74 mmol) in dry dimethoxyethane (2 cm^3). The red colour of both solutions was discharged and the reaction mixture became yellow in colour. The reaction mixture was filtered and evaporated to leave a solid which was crystallised to give the *adduct* (9) (0.34 g, 79%) as colourless crystals, m.p. 247—249 °C (from benzene–hexane) (Found: C, 80.8; H, 5.05; N, 6.9. $C_{42}H_{31}N_3O_3$ requires C, 80.6; H, 5.0; N, 6.7%); $\nu_{max.}$ 1 710 and 1 594 cm^{-1}; δ_H 3.92 (3 H, OMe), 5.33

(1 H, H-7a), 5.89 (1 H, H-3), 6.73 (1 H, H-5), 6.8 (2 H, m), 7.0—7.25 (17 H, m), and 7.35—7.55 (6 H, m); δ_c 57.76 (1, OCH_3), 64.03 (d, C-7a), 65.09 (s, C-7b), 81.47 (s, C-2a), 108.54 (d, C-3), 120.76 (d, C-5), 125.35—140.47 (m, ArC), 149.14 (s, *C*O), 151.13 (s, *C*O), and 160.81 (s, Ar*C*, bonded to N).

(e) To a solution of the enol ether (4a), generated from the trienone (1) (0.50 g, 1.1 mmol) in dry dimethoxyethane (7 cm³) at -15 °C, was added *N*-phenylmaleimide (0.22 g, 1.2 mmol) in dimethoxyethane (3 cm³). The reaction mixture was stirred at -15 °C for 15 min then at room temperature until the red colour had been discharged (*ca.* 2 h). The reaction mixture was filtered and the filtrate was evaporated to leave a yellow oil (0.7 g). Chromatography on alumina (20 g) gave [with ether–light petroleum (1 : 2)] (i) a mixture (0.4 g) of the enol ether (8a) and the indanone (6) and (ii) the *adduct* (10) (0.13 g, 18%) as a yellow solid, m.p. 249—251 °C (from benzene–hexane) (Found: C, 84.2; H, 5.3; N, 2.4. $C_{44}H_{33}NO_3$ requires C, 84.7; H, 5.3; N, 2.25%); $\nu_{max.}$ 1 705, 1 595, and 1 365 cm⁻¹; δ 3.85 (3 H, OMe), 4.05 (1 H, dd, $J_{1,7a}$ 9.8, $J_{1,2}$ 8.7 Hz, H-1) 4.18 (1 H, d, $J_{1,2}$ 8.7 Hz, H-2), 4.32 (1 H, d, $J_{1,7a}$ 9.8 Hz, H-7a), 5.19 (1 H, H-3), 6.59 (1 H, H-5), and 6.85—7.50 (25 H, m).

cis-3a,7a-*Dihydro*-3a-*phenyl*-1H-*inden*-1-*one* (2).—(a) cis-1-exo-*Chloro*-3a,7a-*dihydro*-3a-*phenylindene* (11; X = Cl). To *syn*-9-hydroxy-9-phenylbicyclo[4.2.1]nona-2,4,7-triene [9] (9.0 g, 42.8 mmol) in dry ether (250 cm³) at 0 °C was added thionyl chloride (3.4 cm³, 47.3 mmol) in a mixture of pyridine (6.2 cm³, 77 mmol) and ether (40 cm³), dropwise during 40 min. The solution was stirred at room temperature for 1 h and the solvent was then removed. The residue was extracted with ether and the solution was washed with water, dried, and evaporated to give a brown oil (7.5 g). Distillation gave the chlorotriene (6.0 g, 61%), b.p. 75 °C at 0.03 mmHg, as a yellow oil which slowly solidified.

(b) cis-3a,7a-*Dihydro*-3a-*phenyl*-1H-*inden*-1-*ol* (11; X = OH). Aqueous potassium hydroxide (12 cm³; 1M) was added dropwise to a solution of the chlorotriene (2.0 g, 8.7 mmol) in tetrahydrofuran (25 cm³). After 24 h, the solution was poured into water (150 cm³). The product was extracted with ether (3 × 20 cm³). Column chromatography (silica; 60 g) gave [with ether–light petroleum (1 : 1)] the indenol (1.3 g, 71%), m.p. 69—71 °C (from light petroleum) (lit.,[3] 74 °C).

(c) The indenol (1.1 g, 5.2 mmol) in dry pyridine (4 cm³) was added in one portion with rapid stirring to a solution of chromium trioxide (1.55 g, 15.5 mmol) in dry pyridine (17.5 cm³). After 3 h the reaction mixture was poured into water. The product was extracted with ether and the ether solution was washed and dried. Distillation gave the indenone (2) (0.8 g, 74%), b.p. 90—95 °C at 0.015 mmHg.

Deprotonation of the Trienone (2).—A solution of the trienone (2) (0.30 g, 0.95 mmol) in dry dimethoxyethane (2 cm³) was added dropwise to a suspension of potassium hydride (0.48 g, 2.4 mmol of a 20% dispersion in oil) and 18-crown-6 (0.28 g, 1.1 mmol) in dimethoxyethane (1 cm³) at -18 °C under nitrogen. The solution rapidly became dark red. After 45 min methyl fluorosulphonate (0.2 cm³, 2.5 mmol) was added to give a yellow solution. T.l.c. [alumina; ether–light petroleum (1 : 19)] showed the presence of a non-polar product. After 10 min, 4-phenyltriazolinedione (0.185 g, 1.1 mmol) in dry dimethoxyethane (2 cm³) was added, and the solution was then kept at -10 °C for 30 min. The mixture was filtered and the filtrate was evaporated to give a brown oil. Layer chromatography [silica; ether–light petroleum (4 : 1)] gave one major product, identified as 2,3-*dihydro*-3-*methyl*-3-*phenyl*-1H-*inden*-1-*one* (12) (0.052 g, 25%) as a yellow oil (Found: *m/e* 222.1048. $C_{16}H_{14}O$ requires *m/e* 222.1046); $\nu_{max.}$ (film) 1 700 cm⁻¹; δ (60 MHz), 1.83 (3 H, Me-3), 2.94 (2 H, 2 × H-1), and 7.2—7.8 (9 H, m).

3a,4-*Dihydro*-3,3a,7-*trimethyl*-1-*phenyl*-5H-*inden*-5-*one* (3).—9-Hydroxy-4,8,9-trimethyl-6-phenylbicyclo[3.3.1]-nona-3,7-dien-2-one [7] (2.7 g, 10.0 mmol) was heated in benzene (350 cm³) containing toluene-4-sulphonic acid for 18 h. Column chromatography (silica) gave [with ether–benzene (1 : 4)] the trienone (4) (30—51%), m.p. 118—119 °C (lit.,[4] 118—119 °C).

General and Interception of the Tetraenol Ether (14).— (a) The trienone (4) (0.1 g, 0.4 mmol) in dimethoxyethane (2 cm³) was added dropwise to a suspension of potassium hydride (0.2 g, 1.0 mmol of 20% dispersion in oil) and 18-crown-6 (0.12 g, 0.45 mmol) at -18 °C. The dark purple reaction mixture was stirred at -18 °C for 3 h and methyl fluorosulphonate (0.1 cm³, 1.2 mmol) was added to give a pale red solution. T.l.c. (alumina) indicated that all the starting material had been consumed and that a non-polar yellow product had appeared. The reaction mixture was filtered and the filtrate was evaporated. The residue was dissolved in carbon tetrachloride. T.l.c. now showed that only the starting trienone was now present. Layer chromatography (silica) gave the trienone (4) (0.090 g, 90%).

(b) To a solution of the enol ether (14), prepared as above from the trienone (4) (0.2 g, 0.8 mmol) was added 4-phenyltriazolinedione (0.154 g, 0.88 mmol) in dimethoxyethane (2 cm³) at -18 °C. After 15 min the reaction mixture was filtered and the filtrate was evaporated. Layer chromatography of the residue [alumina; ether–light petroleum (3 : 17)] gave the *adduct* (15) (0.046 g, 13%) as a brown oil (Found: *m/e* 439.1928. $C_{27}H_{25}N_3O_3$ requires *m/e* 439.1896); $\nu_{max.}$ 1 700 cm⁻¹; $\lambda_{max.}$ (EtOH) 311 nm (log ε 4.90); δ 1.16 (3 H), 1.40 (3 H, d, *J* 1.2 Hz), 2.28 (3 H, d, *J* 1.3 Hz), 3.68 (3 H, 4.30 (1 H), 6.12 (1 H, q, *J* 1.3 Hz), 6.51 (1 H, q, *J* 1.2 Hz), 7.07 (2 H, m), 7.28 (4 H, m), and 7.40 (4 H, m). Decoupling experiments established the relationships between the resonances at δ 1.40 and 6.51 and at δ 2.28 and 6.12.

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